THE VOLATILE OILS

GILDEMEISTER AND HOFFMANN

SECOND EDITION
BY
E. GILDEMEISTER
TRANSLATED BY EDWARD KREMERS

VOL. II.

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THE
VOLATILE OILS

BY

E. GILDEMEISTER AND FR. HOFFMANN.

SECOND EDITION
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Written under the auspices of the firm of
SCHIMMEL & CO., MILTITZ NEAR LEIPZIG.

Authorized translation by
EDWARD KREMERS
MADISON, WIS.

SECOND VOLUME.

WITH FOUR MAPS, THREE TABLES AND NUMEROUS ILLUSTRATIONS.

JOHN WILEY AND SONS, Inc., 432, Fourth Avenue, NEW YORK.

1916.

PREFACE TO THE SECOND VOLUME.

In the preface to the first volume of the second edition it was pointed out that the individual essential oils would be dealt with in the second volume. As, however, in the course of compilation it was found that the matter had grown to more than twice its bulk, as compared with the first edition, and could not, therefore, be comprised in a single volume, it was deemed advisable to proceed to a further subdivision by allowing the manuscript, as far as it was ready, to appear as second volume. The inner arrangement remains unaltered. As was the case with the first edition, the essential oils are enumerated in the order in which the respective plants appear classified by A. Engler in his "Syllabus der Pflanzenfamilien". This second volume presents the oils up to and including those of the Zygophyllaceæ and of part of the Rutaceæ. A third volume will bring the work to its conclusion.

MILTITZ near Leipzig, June 1916.

E. GILDEMEISTER.

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Division: **Chlorophyceæ.**

Family: CHROOLEPIDACEÆ.

1. Oil of Trentepohlia Jolithus.

Trentepohlia Jolithus, (L.) Wallr. (*Chroolepus Jolithus,* Ag.), an alga belonging to the family *Chroolepidaceæ,* has a strong odor reminding of violets. Hence it is called, though not quite correctly, *Veilchenmoos.* In the fresh condition, the plant constitutes reddish-brown, when dry, grayish-green, thin felty coatings on rocks. Hence the name *Veilchenstein* applied to it *e. g.* in the German "Giant Mountains" or *Riesengebirge.* Upon distillation with water vapor, M. Bamberger and A. Landsiedl[1]) obtained a yellow volatile oil which possesses the characteristic odor of the plant.

Division: **Eumycetes.**

Family: POLYPORACEÆ.

2. Oil of Trametes suaveolens.

The *Weidenschwamm,* or bracket fungus growing on willow, *Trametes suaveolens,* Fr. (*Boletus suaveolens,* L.), formerly official as *Fungus suaveolens* or *Fungus salicis,* contains a substance characterized by a pleasant odor reminding of anise, which becomes particularly apparent when the cut fungi are being dried. The substance is destroyed when the fungus is

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[1]) Monatsh. f. Chem. **21** (1900), 571; Chem. Zentralbl. **1900**, II. 637.

distilled with water vapor. The aqueous distillate, which is rendered turbid by flocculi held in suspension, no longer has the odor of anise, but that of amanitol[1]) contained in fly agaric.

3. Oil of Boletus edulis.

The edible boletus, *Boletus edulis,* Bull., owes its pleasant odor to a volatile oil. Upon distillation of the dried fungus, H. Hænsel[2]) obtained 0,056 p. c. of a dark brown oil which melts at 34°, and which is readily soluble in ether but difficultly soluble in alcohol.

Family: AGARICACEÆ.

4. Oil of Amanita muscaria.

The petroleum ether extract of the comminuted fly agaric *Amanita muscaria,* L. (Fam. *Agaricaceæ*) contains, in addition to a fatty oil, a volatile oil characterized by a strong odor that is also peculiar to edible fungi[3]). Upon distillation of the dry fungus with water vapor Zellner[4]) obtained a small amount of camphor-like substance which he called *amanitol.* It constitutes fine white flocculi, which melt at 40°. It is neutral and has a peculiar odor reminding somewhat of parsley.

Family: PARMELIACEÆ.

5. Oil of Evernia prunastri.

Under the name of *Lichen quercinus viridis, Muscus arboreus, Muscus Acaciæ,* French *Mousse de chêne* or *Mousse odorante,* German *Eichenmoos,* the lichen *Evernia prunastri,* L. (Fam. *Parmeliaceæ*) is used in perfumery.

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[1]) J. Zellner, Monatsh. f. Chem. **29** (1908), 53; Chem. Zentralbl. **1908**, I. 1471. — Amanitol is also contained in the false *Feuerschwamm, Polyporus igniarius,* Fr., J. Zellner, Monatsh. f. Chem. **29** (1908), 1187.

[2]) Chem. Zentralbl. **1903**, I. 1137.

[3]) W. Heinisch and J. Zellner, Monatsh. f. Chem. **25** (1904), 537; Chem. Zentralbl. **1904**, II. 909.

[4]) Monatsh. f. Chem. **26** (1905), 742; Chem. Zentralbl. **1905**, II. 409.

The odoriferous constituents of this plant are used either in the form of an alcoholic tincture or as *Essence concrète*[1]) obtained by the extraction of the lichen with volatile solvents. It contains a volatile oil which can be obtained by treating the extract with acetone, which does not dissolve the resin and chlorophyll. Upon evaporation of the acetone there remains an oil which, after it has been distilled in vacuum, possesses a very pleasant odor. According to Gattefossé[2]) it consists almost entirely of a *phenol* (?), isomeric with carvacrol, which he has named lichenol. It is completely soluble in a 3 p. c. soda solution.

6. Oil of Iceland Moss.

The so called Iceland moss, a lichen, *Cetraria islandica,* L., yields upon distillation 0,051 p. c. of a brownish oil[3]) from which crystals separate upon standing. d_{15° 0,8765; A. V. 72; S. V. 98; α_D inactive to $+1^\circ 36'$.

Division: **Embryophyta Asiphonogama.**

Family: JUNGERMANNIACEÆ.

7. Oil of Mastigobryum trilobatum.

The oil of *Mastigobryum trilobatum,* L. (Fam. *Jungermanniaceæ* or liverworts) was first prepared by C. E. Lohmann[4]), later in somewhat larger amount by K. Mueller[5]). The latter examined it somewhat more carefully.

When air dried, the plant lost 90 p. c. of its weight. When correctly distilled with water vapor, the dry plant yielded 0,93 p.c.

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[1]) Seifensieder Ztg. **34** (1907), 393.

[2]) Parfum. moderne **4** (1911), 4.

[3]) H. Hænsel, Apotheker Ztg. **17** (1903), 744.

[4]) *Beitrag zur Chemie und Biologie der Lebermoose.* Dissertation. Jena 1903, 22; Report of Schimmel & Co. April **1904**, 107.

[5]) Zeitschr. f. physiol. Chem. **45** (1905), 299; Chem. Zentralbl. **1905**, II. 768; Report of Schimmel & Co. April **1906**, 108.

of an orange-yellow volatile oil, the odor of which reminded not only of that of sandal- and cedarwood, but also of pine needle oil. d_{15° 0,945 to 0,947 (a distillate with a poor yield showed d_{15° 0,975); $[\alpha]_D + 12{,}88^\circ$ (ascertained in connection with diluted oil); S. V. 5,4. Upon saponification a semi-solid mass of acids, melting at 16°, was obtained which yielded an ether-soluble lead salt. The bulk of the oil distilled between 260 to 270°. The distillate was bluish-green in color, d_{20° 0,946; $[\alpha]_D + 25{,}59^\circ$; it contained 87,06 p. c. C and 12,65 p. c. H. Upon oxidation of this principal fraction with chromic acid and glacial acetic acid, a substance $C_{10}H_{16}O$ (b. p. 260°) was obtained. Hence the formula $C_{10}H_{16}$ was assigned to the *hydrocarbon.* The higher fraction of the oil (b. p. 270 to 285°) contained 5,4 p. c. of oxygen and revealed the specific angle of rotation $[\alpha]_D + 42{,}21^\circ$ (in a 3,9 p. c. alcoholic solution).

8. Oil of Leioscyphus Taylori.

Dried at 100°, the powdered livermoss; *Leioscyphus Taylori,* Hook. (Fam. *Jungermanniaceæ*) yielded, upon distillation with water vapor, 1,6 p. c. of a viscid, bluish-green volatile oil[1]). This oil has an intensive, persistent, peculiar odor and a very disagreeable taste; d_{20° 0,978 and 0,986; $[\alpha]_D - 3{,}44^\circ$ (determined in a 9,03 p. c. alcoholic solution); S. V. 11,4. The analyses of fraction 260 to 265°, d 0,937, $[\alpha]_D - 22^\circ$, correspond with a sesquiterpene alcohol $C_{15}H_{26}O$. Fraction 265 to 278° appears to contain a *sesquiterpene* $C_{15}H_{24}$. Fraction 280 to 290° ($[\alpha]_{\text{white}} + 26{,}88^\circ$) contains a *sesquiterpene alcohol* $C_{15}H_{26}O$. Neither of the alcohols yielded solid benzoyl derivatives.

9. Oil of Madotheca lævigata.

The air-dried *Madotheca lævigata,* Schrad. (Fam. *Jungermanniaceæ*) yields 0,9 p. c. of a relatively limpid, orange-yellow oil[1]), which has a pleasant odor; d_{16° 0,856; $[\alpha]_D + 72{,}74^\circ$; S. V. 5,56. The peppermint-like taste of this liverwort is not due to the volatile oil. Fraction 150 — 160° (17 mm), d_{15° 0,968; $[\alpha]_D + 132{,}23^\circ$, boils with decomposition at 280° under atmospheric pressure and contains an *alcohol* $C_{10}H_{18}O$.

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[1]) K. Mueller, footnote 5 on p. 3.

10. Oil of Alicularia scalaris.

The oil[1]) of *Alicularia scalaris,* Corda (Fam. *Jungermanniaceæ*) is lemon-yellow in color. Its odor reminds of that of the forests; d_{15° 0,965; $[\alpha]_D - 33{,}49^\circ$[2]).

Family: POLYPODIACEÆ.

11. Oil of Malefern.

Origin. The rhizome of malefern, *Nephrodium filix mas,* Stremp. (*Aspidium filix mas,* L.) (Fam. *Polypodiaceæ*) owes its vermifuge properties in part to small amounts of a volatile oil. This was first prepared by Bock[3]) in 1851 by distillation with water vapor. The yield varies according to the season. From air-dried rhizomes, collected freshly in June, Ehrenberg[4]) obtained 0,025 p. c. of oil; from material, collected during the months September to November, 0,04 to 0,045 p. c.

Properties. The volatile oil of malefern is a light yellow liquid with an intensive malefern odor and an aromatic, finally pungent taste. It is readily soluble in ether and absolute alcohol. d 0,85 to 0,86. The bulk of the oil distills between 140 and 250°. Above this temperature decomposition sets in, dark colored products coming over as high as 350°.

Composition. In addition to free fatty acids (principally butyric acid), oil of male fern contains *hexyl and octyl esters of the fatty acid series,* from *butyric acid* to probably *pelargonic acid.*

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[1]) K. Mueller, footnote 5 on p. 3.

[2]) Volatile oils have also been prepared by C. E. Lohmann, footnote 4 p. 3, from the following liverworts: *Fimbriaria Blumeana, Pellia epiphylla, Metzgeria furcata, Fegatella conica, Marchantia polymorpha, Lunularia vulgaris, Targionia hypophylla, Aneura palmata, Madotheca platyphylla.* The yield varied between 0,01 and 0,9 p. c. of the dried material. The odor of the oils reminded of that of the respective liverworts. Small amounts of oil only were obtained, in several instances but a few drops. Hence very little could be ascertained about their chemical nature. Analyses revealed the ratio of carbon to hydrogen of 1 to from 1,51 to 1,61. This would seem to indicate that they belong to the terpene group.

[3]) Arch. der Pharm. **115** (1851), 262; Chem. Zentralbl. **1851**, 497.

[4]) Arch. der Pharm. **231** (1895), 345.

12. Oil of Polypodium phymatodes.

Polypodium phymatodes, L. (*Pleopeltis phymatodes*, F. Moore) (Fam. *Polypodiaceæ*) contains a volatile oil[1]) which is used by the South Sea Islanders for flavoring cocoanut oil.

Family: MARATTIACEÆ.

13. Oil of Angiopteris evecta.

The fern *Angiopteris evecta*, Hoffm. (Fam. *Marattiaceæ*) contains a volatile oil[2]) which is used by the South Sea Islanders for the same purpose for which they use that of *Polypodium phymatodes*.

Division: **Embryophyta Siphonogama.**

Family: TAXACEÆ.

14. Oil of Pherosphæra Fitzgeraldi.

Pherosphæra Fitzgeraldi, F. v. M.[3]) occurs in the mountains of New South Wales. The leaves, distilled in February, yielded 0,108 p. c. of oil. This had a lemon-yellow color and was characterized by the following constants: $d_{15°}^{22°}$ 0,8705; $\alpha_D + 15{,}1°$; $n_{D23°}$ 1,4841; S. V. 2,4 = 0,84 p. c. ester $CH_3COOC_{10}H_{17}$. With 10 vol. of 90 p. c. alcohol it does not yield a clear solution. Upon evaporation there remained a residue which congealed to a crystalline mass. Carefully fractionated, the oil was shown to consist principally of *terpenes*, of which d-*α-pinene* (nitrosochloride, m. p. 108°) was identified. In all probability traces of *limonene* and *dipentene* are also present. *Cadinene* was also identified (dichlorhydrate, m. p. 116°). The oil likewise contains an *aldehyde-like substance* which, however, could not be identified.

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[1]) Maiden, Useful native plants of Australia. London, Sydney 1889, p. 282.

[2]) Maiden, loc. cit., p. 253.

[3]) Baker and Smith, A research on the pines of Australia. Sydney 1910, p. 410.

15. Oil of Dacrydium Franklinii.

The conifer *Dacrydium Franklinii,* Hook.[1]) is restricted to Tasmania where it is known as Huon pine.

From the leaves 0,5 p. c. of volatile oil was obtained: $d_{15^\circ}^{17^\circ}$ 0,8667; $\alpha_D + 20{,}5^\circ$; n_{D25° 1,4815; soluble in an equal volume or more of absolute alcohol. In the carefully fractionated oil l-*α-pinene* (nitrosochloride, m. p. 110 to 111°) and d-*limonene* (tetrabromide, m. p. 104°) were identified. The principal constituent, however, is a new terpene named *dacrydene* by the authors. Dacrydene boils at 165 to 166° (corr.) (d_{22° 0,8524; $\alpha_D + 12{,}3^\circ$; n_{D22° 1,4749) and yields a nitrosochloride melting at 120 to 121°. The analysis agrees with the formula $C_{10}H_{16}$: found C 88,14 p. c.; H 11,65 p. c.; computed C 88,24 p. c., H 11,76 p. c. The addition of bromine was accompanied by the liberation of hydrogen bromide and resulted in the formation of a substance the analysis of which agreed with that of a tribromide. In addition there was indicated the presence of *methyleugenol,* which was identified by its oxidation to veratric acid (m. p. 178 to 179°).

The dry wood yielded 0,56 p. c. of oil: d_{18° 1,035; $\alpha_D + 1{,}4^\circ$; n_{D23° 1,5373; S. V. 3,1; also[2]) d_{15° 1,0443; $\alpha_D + 0^\circ\, 6'$; n_{D20° 1,53287; A. V. 0,9; E. V. 1,5. This oil consists largely (about 97,5 p. c.[2])) of *methyleugenol* (m. p. of the tribromide 77 to 78°; m. p. of the veratric acid 178 to 179°). Of *eugenol* (benzoyleugenol, m. p. 70°) only traces are present and at times it seems to be wanting completely[3]). The high boiling fractions yielded the color tests for *cadinene.*

16. Oil of Phyllocladus rhomboidalis.

The occurrence of the conifer, known as celery top pine *Phyllocladus rhomboidalis,* Rich.[4]) appears to be restricted to Tasmania. Distilled in July, the leaves, or, more correctly, the phyllocladia yielded 0,215 p. c. of volatile oil: d_{16} 0,8892; $\alpha_D - 12{,}3^\circ$; n_{D16° 1,4903; S. V. 1,5. It is difficultly soluble in diluted alcohol,

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[1]) Baker and Smith, A research on the pines of Australia. Sydney 1910, p. 397.

[2]) Report of Schimmel & Co. October **1910**, 145.

[3]) Baker and Smith., *loc. cit.*

[4]) The same, *loc. cit.* p. 416.

but yields a clear solution with 1 vol. of absolute alcohol. The oil contains 1 p.c. of alcohols to which possibly the aromatic odor of the oil must be attributed. The lower boiling fractions of the oil contain l-*α-pinene* (nitrosochloride, m. p. 108°; nitrosopinene, m. p. 132°). In addition, the oil probably contains a *sesquiterpene* (d_{24° 0,9209; $\alpha_D + 3,4^\circ$; n_{D23° 1,5065), the chloroformic solution of which is colored red by sulphuric acid. If bromine be added to the chloroformic solution of the sesquiterpene, a green color results, which darkens and finally changes to indigo blue. The distillation residue contains a colorless, crystalline substance of the following properties: m. p. 95°; $[\alpha]_D + 16,06^\circ$. Analysis revealed the formula $C_{20}H_{32}$, which was verified by a molecular weight determination. Its chloroformic solution is not colored by sulphuric acid.

Baker and Smith assume that the molecule has resulted from the union of two molecules of pinene and regard it as a diterpene which they have named *phyllocladene*. It is scarcely attacked by potassium permanganate, but by chromic acid in acetic acid solution. With concentrated nitric acid it yields a nitro compound which melts indistinctly between 115 to 120°. It is soluble in concentrated sulphuric acid. With neutral permanganate solution it does not react. In glacial acetic acid solution it first adds bromine, but soon substitution takes place. Hence phyllocladene appears to be a saturated compound.

Family: PINACEÆ.

17. Oil of Kauri Copal.

Kauri copal obtained from *Agathis australis*, Salisb. (*Dammara australis*, Lamb.) contains a volatile oil which can be obtained by distillation with water vapor, either directly or after having removed the resin acids with alkali[1]).

Upon destructive distillation O. Wallach[2]) obtained 22 p.c. of an oil. This consisted of *isoprene*, of an *oxygenated substance* boiling at 90°, of about 25 p.c. of d-*α-pinene* (nitroso-

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[1]) A. Tschirch and B. Niederstadt, Arch. der Pharm. **239** (1901), 308.

[2]) Liebig's Annalen **271** (1892), 308.

pinene, m. p. 129 to 130°; nitrolpiperidine, m. p. 119°), and dipentene (fraction 175°; tetrabromide m. p. 125°).

L. Schmölling¹) obtained, upon dry distillation, an oil that was light-yellow in color, mobile, and of a pleasant odor: d_{15° 0,8677; A.V. 3,0; S.V. 49; Iodine V. 288,9.

From oil that had been standing for a long period in a cool place fine crystalline needles had separated which, upon recrystallization from dilute alcohol, melted at 168°. Elementary analysis revealed the formula $C_9H_{16}O_2$²).

18. Oil of Manila Copal.

Manila copal, derived from *Agathis alba,* Lam.³) yields its volatile oil but difficultly to direct distillation with water vapor. A more complete separation can be accomplished by first neutralizing the resin acids with alkali, as was done by A. Tschirch and M. Koch⁴). From soft Manila copal these investigators obtained 6 p. c., from hard copal 5 p. c. of oil. From material of varying degrees of hardness, G. F. Richmond⁵) obtained yields that varied from 1,3 to 11,2 p. c. He obtained a lemon-yellow oil of a pleasant odor characterized by the following properties: $d_{4^\circ}^{15^\circ}$ 0,865; α_{D30° — 26,55°; n_{D30° 1,4648. The bulk of the oil boiled between 155 and 165° and contained *α-pinene* (hydrochloride, m. p. 124°).

Brooks⁵) has examined a copal oil which was not obtained by steam distillation but by dry distillation with a yield of about 6 p.c. The following constituents were identified: d-*limonene* (tetrabromide, m. p. 104°), d-*α-pinene* (nitrolbenzylamine, m. p. 122 to 123°), *β-pinene* (nopinic acid, m. p. 124 to 125°) and *camphene* (characterized by its conversion into *iso*borneol). From the low optical rotation of the limonene, the author infers the presence of *dipentene.*

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¹) Chem. Ztg. **29** (1905), 955.

²) A. Tschirch and M. Koch, Arch. der Pharm. **240** (1902), 228, footnote.

³) Philippine Journ. of Sc. **5** (1910), A, 185.

⁴) Arch. der Pharm. **240** (1902), 202.

⁵) Philippine Journ. of Sc. **5** (1910), A. 203. For the products resulting upon the dry distillation of Manila copal, compare also Tschirch and Koch *loc. cit.* also L. Schmölling, Chem. Ztg. **29** (1905), 955.

19. Oil of Agathis robusta.

The conifer *Agathis (Dammara) robusta,* C. Moore[1]), which is found along the coast of Queensland and which is known as "Queensland Kauri" or "Dundathu pine", yields an oleoresin from which 11,64 p. c. of volatile oil have been obtained. This oil has the following properties: $d_{15^\circ}^{16^\circ}$ 0,8629; $\alpha_D + 20,2^\circ$; n_{D16° 1,4766. Upon fractionation it yielded d-*α-pinene* almost exclusively (nitrosochloride, m. p. 108°; nitrolbenzylamine, m. p. 123 to 124°). The oil is practically identical with American turpentine oil and may hence be regarded as a valuable commercial article.

20. Oil of Araucaria Cunninghamii.

Araucaria Cunninghamii, Ait.[2]) grows along the Northern coast of Australia, in New South Wales and in Queensland, and is known as the Hoop, Colonial, or Moreton bay pine. The leaves distilled in November yielded 0,005 p. c. of oil which revealed the following constants: d_{21° 0,8974; n_{D21° 1,4977; S. V. 4,4 = 1,54 p.c. of ester $CH_3COOC_{10}H_{17}$; insoluble in 10 vol. of 90 p.c. alcohol. Apparently it consists of high boiling terpenes. The latex yielded upon distillation 3,8 p. c. of volatile oil, the odor of which reminded slightly of *menthene.* $d_{15^\circ}^{22^\circ}$ 0,8057; $\alpha_D + 31,2^\circ$; n_{D22° 1,457. After standing for ten months a resin had been deposited from which the oil was decanted. This boiled between 154 and 155° (corr.); d_{19° 0,7929; $\alpha_D \pm 0^\circ$; n_{D19° 1,4437. Analysis revealed the formula $C_{10}H_{20}$. Found: C 85,77 p. c.; H 14,15 p. c.; calculated for $C_{10}H_{20}$: C 85,71 p. c.; H 14,29 p. c. Hence the hydrocarbon is a *menthane.* Presumably the original oil contained a menthene from which the menthane resulted upon standing. The aqueous distillate also contained *acetic* and *butyric acids.*

21. Oil of Araucaria brasiliana.

When the older stems of *Araucaria brasiliana,* Lamb. are wounded, they yield a water-white gum resin[3]) which is known in Brasil as *Resina de pinhero.* It yields about 6. p. c. of oil, but nothing is known concerning its properties and composition.

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[1]) Baker and Smith, A research on the pines of Australia, Sydney 1910, p. 376.

[2]) *Ibidem* p. 318.

[3]) Th. Peckolt, Pharm. Rundsch. (New York) **11** (1893), 133.

The Oils of the Abietineæ.

Turpentine Oils, Pine Tar Oils, Wood Turpentine Oils, and Pine Needle Oils.

Turpentine oil, in the restricted sense, may be defined as the oil obtained by distilling turpentine with either water or steam that has not been superheated[1]). Pine tar oil, Ger. *Kienöl,* is obtained by the dry distillation of pine stumps rich in resin. Hence the application of the term turpentine oil to such an oil is not correct. A modification of the pine tar oil has recently been produced in the United States. The stumps of the pines that

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[1]) The definition for turpentine oil, proposed by M. Vèzes, Professor at the University at Bordeaux, and adopted by the International Congress for the Suppression of Adulterations, Paris 1909, reads as follows: —

"Turpentine oil is exclusively the product of the distillation (with water or non-superheated steam) of the resinous exudations of the several species of *Pinus.*

"It is a thin colorless liquid, occasionally slightly greenish or yellowish and possesses a characteristic odor.

"Under a pressure of 760 mm. of mercury, turpentine oil begins to boil at from 152 to 156°; at least 80 p. c. by weight should distil over below 164°.

"It should be neutral or slightly acid: The amount of acid in 1 kg. of oil should be neutralized by 1,5 g pure potassium hydroxide (KOH) (*i. e.* the acid number should not be larger than 1,5).

"Turpentine oil should not contain mineral oils or other products not resulting from the distillation of turpentine with water vapor. It may, however, contain small amounts, not to exceed ... p. c. of resin oil and colophony which result from the process of production (so-called normal adulterants, Fr. *adultérants normaux,* Ger. *normale Verunreinigungen*). (The amount has not been definitely established, probably 2,5 p. c. will be adopted.)

"The turpentine oil obtained from *Pinus maritima* (France, Spain, Portugal) is lævogyrate, α_D — 29 to — 33°. The density determined at + 25° should not be below 0,8575 (0,8655 at 15°).

"The oil obtained from *Pinus halepensis* (Greece, Algiers, Provence) is dextrogyrate, α_D + 38 to + 41°; $d_{25°}$ not below 0,8550 (0,8630 at 15°).

"The American oil, which is obtained indiscriminately from several species of pine *(P. palustris, P. heterophylla* etc.) is dextrogyrate as well as lævogyrate. The angle of rotation varies, but never exceeds the values given above for European oil; its density is not below 0,8560 at 25° (0,8640 at 15°)."

have been killed by boxing are distilled with steam, frequently with superheated steam. In the chapters which follow it is designated as wood turpentine oil. The aromatic distillates, obtained by steam distillation of the needles and cones of various coniferous plants, are grouped under the collective name pine needle oils, Ger. *Fichtennadelöle*.

As to their chemical composition, the distillates from the turpentine, the wood, the leaves and cones of the *Abietineæ* have, as a rule, the characteristic *pinene* in common. Most of the turpentine oils proper, also the pine tar oils, consist largely of this hydrocarbon or its isomers[1]). In the pine needle oils, however, pinene is frequently replaced by *camphene, limonene* and *oxygenated constituents,* notably *bornyl acetate.*

Turpentine Oils Proper.

Origin. For the commercial production of turpentine oil the representatives of the genus *Pinus* are used almost exclusively, rarely those of *Abies, Picea,* or *Larix.* The *Pinaceæ,* which come primarily under consideration in this industry, grow principally in dense forests in the temperate zones. In their schizogenous ducts they contain a resinous balsam known as turpentine. When the tree is wounded artificially, the turpentine begins to flow. This is a pathological phenomenon and yields the "healing balsam" in considerable quantities. When the bark is removed and the cambial layer is injured, the turpentine exudes as a clear or turbid, viscid liquid, consisting of a solution of resin in volatile oil. When exposed to the air, this resinous sap changes to a granular, crystalline, honey-like consistence or it dries to a brittle mass.

Upon distillation of turpentine, whether by itself or with water vapor, turpentine oil passes over and colophony remains. This is purified by re-melting and straining.

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[1]) The oil distilled from the turpentine of *Pinus serotina* consists chiefly of *limonene* (see p. 93); (other oils contain a large percentage of *phellandrene* or a hydrocarbon closely related to it; *P. Sabiniana* and *P. Jeffreyi* yield an oil consisting almost exclusively of n-*heptane*).

The principal countries of production, so far as the turpentine industry is concerned, are the United States of America, France, Spain, Russia, Austria, and Greece. In the world's commerce, American and French turpentine oil play the principal role at the present time. Not inconsiderable, however, are the amounts placed upon the market in recent years by Spain, whereas Greece supplies but little just at present. The turpentine oil produced in the other countries mentioned above is presumably consumed largely at home. The increased use of turpentine oil in many industries, in which it is indispensible, has given rise to the fear that the regions thus far opened up to production will not suffice in the long run. Hence attempts have been made to produce turpentine in other countries with large areas of pine forests, thus, *e. g.* in Algiers[1]), India[2]), Mexico[3]), Texas[4]) and San Domingo[5]). It is also reported that the Japanese intend to utilize the pine forests of Saghalien[6]) for the production of turpentine oil.

General Properties. Freshly distilled oil of turpentine is a colorless, mobile liquid, the peculiar odor of which varies somewhat according to its source. Thus the French oil reminds of juniper, and has a more pleasant and milder odor than the American oil, the odor of which reminds of rosin. The pungent odor of old oil of turpentine is said to be due to an aldehyde $C_{10}H_{16}O_3$, the origin of which is attributable to atmospheric oxygen[7]).

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[1]) Bull. de l'Office du Gouvern. de l'Algérie **14** (1908), 69 and **15** (1909), 50; Report of Schimmel & Co. October **1908**, 118 and April **1909**, 89.

[2]) Chemist and Druggist **65** (1904), 582, 831; Chem. Ztg. **33** (1909), 808; Report of Schimmel & Co. April **1905**, 78 and October **1909**, 118.

[3]) Oil, Paint and Drug Reporter **74** (1908), No. 9, p. 23; Report of Schimmel & Co. October **1908**, 118.

[4]) Nachrichten f. Handel u. Industrie **1908**, No. 102, p. 7; Report of Schimmel & Co. October **1908**, 119.

[5]) Chem. Ztg. **33** (1909), 659; Report of Schimmel & Co. October **1909**, 119.

[6]) Oil, Paint and Drug Reporter **77** (1910), No. 6, p. 9; Report of Schimmel & Co. April **1910**, 102.

[7]) If this aldehyde is removed by shaking with acid sodium sulphite solution, the oil, when distilled in a current of carbon dioxide, becomes almost odorless. Upon exposure to air, this peculiar odor, however, returns very soon. Schiff, Chem. Ztg. **20** (1896), 361.

Even at ordinary temperature turpentine oil is fairly volatile. Upon evaporation, a part of it is resinified, due to the absorption of oxygen. There remains a mass which at first is sticky and tough, but which on further exposure becomes brittle and like colophony in general.

On account of the free acids (resin acids, formic and acetic acids) which it contains, the crude oil of turpentine has a slightly acid reaction. Hence, for certain purposes it should be rectified with milk of lime before being used. Unless oxygen be excluded, oxydation products with an acid reaction are again soon formed.

PHARMACOLOGY. When turpentine oil is administered internally, or when its vapors are inhaled, it imparts a peculiar, violet-like odor to the urine. This interesting physiological property is possessed by all oils containing pinene. Other terpenes do not behave in like manner. Prolonged inhalation of turpentine oil vapors results in an unpleasant affection of the kidneys known as "painter's disease".

A case of poisoning due to the inhalation of turpentine oil vapors is reported by A. Drescher[1]). The workman who lost his life had been painting the inside of an iron boiler with a turpentine varnish.

According to Allen[2]) turpentine has been used successfully as an antidote in carbolic acid poisoning of horses. According to the same author, turpentine oil has been used very efficiently as antidote in accidental carbolic acid poisoning of a man.

In the case of phosphorus poisoning "ozonized" turpentine oil is administered as antidote. This results when turpentine oil is exposed to the action of light and air for some time. Under these conditions it takes up oxygen with the formation of peroxides which readily give off their oxygen again (compare p. 26). The nature of the action of turpentine oil as antidote in phosphorus poisoning is not known. Neither has it been proven that the so-called ozonized oil acts better than the fresh

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[1]) Concordia **13** (1906), 141; Report of Schimmel & Co. October **1906**, 79.

[2]) Am. Drug. and Pharm. Rec. **1904**, 269; Apotheker Ztg. **19** (1904), 447; Report of Schimmel & Co. October **1904**, 86.

oil[1]). The changes that have been observed by A. Colson[2]) when white phosphorus is dissolved in turpentine oil, may possibly aid in explaining the antidotal properties of the turpentine oil.

In Finland, turpentine oil is a universal popular remedy being used against catarrhal and rheumatic affections. As a remedy against intestinal worms, turpentine oil (a small tablespoonful) has there been employed with marked success. However, such large doses are not to be recommended, since they are mostly accompanied by serious after-effects, such as decided intoxication and irritation of the kidneys[3]).

Specific Gravity. At 15° the density of turpentine oil varies between 0,858 and 0,877. As a rule, it fluctuates between 0,865 and 0,870. However, this is true only of normal, freshly distilled commercial oils, or of such oils as have been kept in well stoppered, completely filled containers. In other words, it is true only of those oils that have not been subjected to undue oxydation under the influence of the air, which change is accompanied by an increase in the specific gravity. An increased specific gravity may also be due to faulty or careless distillation, thus causing the amounts of rosin oil and colophony ("normal adulterants"[4]), which are never wanting entirely in commercial oils, to be unduly high. A density lower than that recorded above would indicate adulteration, more particularly with petroleum hydrocarbons.

According to Vèzes[5]), the density of turpentine oil varies 0,0008 for each degree centigrade. (Compare vol. I. p. 559.)

Optical Rotation. The α_D or optical rotation of the turpentine oil of commerce fluctuates between wide limits, *viz.* between —33° and +41°. Although these figures are of no value in judging the purity of an oil, they are important in ascertaining

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[1]) Comp. R. Kobert, *Lehrbuch der Intoxikationen.* II. Ed. 1906. Vol. II. p. 293 ff.

[2]) Compt. rend. **146** (1908), 71, 401, 817; Report of Schimmel & Co. October **1908**, 125.

[3]) E. Sundvik, Pharm. Zentralh. **45** (1904), 859.

[4]) See p. 11, footnote, also p. 22.

[5]) Vèzes and Mouline, *Sur l'essai technique de l'essence de térébenthine des Landes. II. Série.* Bordeaux 1912. p. 5.

its source. French and Spanish turpentine oils are strongly lævogyrate, Greek and Algerian oils strongly dextrogyrate, whereas American turpentine oil is a mixture of several oils of varying angle of rotation. At times the commercial article is lævogyrate, at times dextrogyrate, but mostly the angle is not as large as that of the European oils. The limit numbers will be found under the descriptions of the several oils.

It is noteworthy that the angle of rotation decreases with age. Comp. p. 26, footnote 1.

Refraction. Concerning the index of refraction, or n_D, of turpentine oils only a few reliable data are available. At 15° the index of refraction is about 1,470. According to Coste[1]), the correction for every degree centigrade is 0,00037. Old, hence modified, turpentine oils have a higher refraction capacity than freshly distilled ones.

Abnormal refraction indicates adulteration: pine tar oil increases the refractive index, petroleum hydrocarbons lower it. The presence of the latter is verified by determining the index of refraction of the several fractions. Compare p. 46.

Solubility. In absolute alcohol turpentine oil is soluble in all proportions, but rather difficultly in dilute alcohol. In many instances this property makes relatively easy its detection as adulterant. However, the solubility of turpentine oil in alcohol undergoes decided changes upon aging. Whereas the solubility of most volatile oils diminishes with age, the case is reversed with turpentine oil[2]). In order to obtain a clear solution, more alcohol is required for freshly distilled or rectified turpentine oil, than for an old oil which has been in contact with the air for a long period. The explanation for this observation is based on the formation of oxygenated compounds which are more readily soluble.

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[1]) Analyst **33** (1908), 209 to 230; Chem. Zentralbl. **1908**, II. 731.

[2]) A normal American turpentine oil originally required 6 parts of 90 p. c. alcohol to effect solution. After standing seven weeks, only 3 parts were required to produce a clear solution. French oil, which had been standing 4 years in a flask not completely filled, was soluble to a clear solution in 1 part of 80 p. c. alcohol. Compare also the statements on p. 26, footnote 1.

Solubility of several turpentine oils in alcohol of various percentage strength, according to Ledermann and Godeffroy[1]).

Kind of terpentine oil	$d_{15°}$	Strength of alcohol expressed in percentage by volume				
		70	80	85	90	95
		The following number of parts are required				
1. French, crude	0,861	66	18	14	7	2
2. French, rect.	0,860	80	17	12	6,7—7	2—2,4
3. American, crude . . .	0,862	56	20	12	5	2
4. American, rect.	0,862	60—64	17—19	12—14	5—6	2,2
5. Austrian, crude	0,865	—	—	—	6	—
6. Austrian, rect.	0,862	—	—	13	8	3
7. Polish *(Kienöl)*	0,866	—	—	—	5	—
8. Russian *(Kienöl)* . . .	0,860	49	16	11	5,6	2

Because of this changeability, little reliance can be placed on solubility as a test for purity. As a rule, good turpentine oil is soluble to a clear solution in 5 to 8 parts of 90 p. c. alcohol.

As to the relative solubility of turpentine oil and alcohol, this subject has been investigated by M. Vèzes[2]) together with M. Mouline and R. Brédon. They determined the ratio of solubility of a large number of mixtures of turpentine oil and dilute alcohol of varying percentage strength. The results have been tabulated and represented graphically by curves. Turpentine oil and absolute alcohol are miscible in all proportions and do not separate when the temperature of the mixture is greatly decreased. However, the temperature of solutions of turpentine oil and dilute alcohol cannot be lowered *ad libitum* without bringing about separation. The temperature of separation depends on the strength of the alcohol, the ratio between alcohol and turpentine

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[1]) Zeitschr. d. allg. österr. Apoth. Ver. **15** (1876), 381; Jahresber. f. d. Pharm. **1877**, 394.

[2]) Bull. Soc. chim. III. **31** (1904), 1043. — Procès-verbaux des séances de la Société des Sciences physiques et naturelles de Bordeaux (séances du 16 juin 1904, du 28 juin 1906, du 13 juin et du 24 octobre 1907); Report of Schimmel & Co., April **1905**, 77; April **1907**, 99; April **1908**, 104.

oil, and upon the pressure to which the mixture is subjected. In these experiments the pressure was always the normal atmospheric pressure, hence negligible.

If a complete separation of the components of the turpentine oil-alcohol mixture is to be effected by means of water, sufficient water should be added to reduce the alcohol to 18,4 per cent. by volume. The upper layer then consists of pure oil, and the lower or aqueous-alcoholic layer contains only traces of oil, hence the separation may be regarded as complete.

Turpentine oil is soluble in all proportions in ether, chloroform, carbon disulphide, benzene, petroleum ether, aniline (compare also p. 34), glacial acetic acid[1]) (compare also p. 33), and the fatty oils. The ratio of solubility of turpentine oil and dimethyl sulphate has been studied by M. Dubroca[2]), that of turpentine oil and aniline by Queysanne[3]), also by Louïse[4]).

When turpentine oil is mixed with other volatile oils, turbidity occasionally is observed (compare vol. I, footnote 2 on p. 567). Oil of turpentine is itself an excellent solvent for fats, resins and most varieties of caoutchouc.

Boiling Temperature. Turpentine oil begins to boil somewhat below 155°. By far the largest part, namely 75 to 80 p. c., boils between 155 and 162°. Above 162° the thermometer rises rapidly and finally there remains in the flask a viscid, resinous mass the odor of which resembles that of colophony. According to Vèzes[5]), the requirements as to the boiling temperature of turpentine oil can be formulated in the following manner: Turpen-

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[1]) The mixture of equal volumes of glacial acetic acid and turpentine oil remains clear at 14,5 to 16,5°, provided the glacial acetic acid is 99,5 p. c. strong. The mixture is turbid or separates into two layers if the glacial acetic acid is 98,9 p. c. strong or weaker. P. W. Squire and C. M. Caines, Pharmaceutical Journ. **68** (1902), 512.

[2]) Journ. de Chim. phys. **5** (1907), 463; Report of Schimmel & Co. April **1908**, 104.

[3]) *Sur la solubilité réciproque de l'essence de térébenthine et de l'aniline.* Bordeaux 1909.

[4]) Compt. rend. **150** (1910), 526. Comp. also Vèzes, *ibidem* 698; P. E. Gallon, *Sur la solubilité réciproque de l'essence de térébenthine dextrogyre et de l'aniline.* Bordeaux 1911.

[5]) *Sur la définition de l'essence de térébenthine commercialement pure.* Bordeaux 1910, p. 7.

tine oil begins to boil between 152 and 156° (760 mm). At least 80 per cent. by weight should distill over below 164°[1]). So far as rectified American turpentine oil is concerned, detailed reports as to the amounts that distil over in the several fractions, also as to the optical rotation and the specific gravities of these fractions have been made by Kremers[2]).

A comparison of the course of careful fractionations of American and French turpentine oil, has been made readily possible by two tables published by B. Ahlström and O. Aschan[3]). These tables reveal not only the amounts that distil over for each degree, but also record the density and specific rotation of each fraction.

AMERICAN TURPENTINE OIL:

Fraction	$d_{4^\circ}^{15^\circ}$	$[\alpha]_D$	Approximate amount in grams
153 to 155°	0,8635	+ 14,61°	64
155 „ 156°	0,8643	+ 13,72°	323
156 „ 157°	0,8652	+ 10,67°	243
157 „ 158°	0,8663	+ 7,07°	92
158 „ 159°	0,8655	+ 3,58°	225
159 „ 160°	0,8686	— 0,36°	275
160 „ 161°	0,8700	— 4,60°	217
161 „ 162°	0,8707	—	lost
162 „ 163°	0,8715	— 10,58°	112
163 „ 164°	0,8722	— 13,38°	49
164 „ 175°	0,8745	— 13,17°	134

FRENCH TURPENTINE OIL:

Fraction	$d_{4^\circ}^{15^\circ}$	$[\alpha]_D$	Approximate amount in grams
153 to 155°	0,8637	— 42,30°	1005
155 „ 156°	0,8654	— 40,51°	983
156 „ 157°	0,8649	— 39,49°	757
157 „ 158°	0,8663	— 37,38°	284
158 „ 159°	0,8674	— 35,14°	297
159 „ 160°	0,8692	— 31,94°	280
160 „ 161°	0,8702	— 29,89°	180
161 „ 162°	0,8716	— 26,88°	123
162 „ 163°	0,8730	— 23,92°	58
163 „ 173°	0,8842	— 18,34°	197

Because of the oxygenated substances and polymerization products which they contain, the boiling temperature of old, resinified turpentine oils is considerably higher. In as much as the pine tar oils contain dipentene, sylvestrene and other sub-

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[1]) Coste [Analyst **33** (1908) 219 to 230; Chem. Zentralbl. **1908**, II. 731] demands that when 100 cc. are distilled from a 180 cc. Ladenburg fractioanting flask with a shortened Anschütz thermometer, nothing shall come over below 155°, 70 p. c. between 155 and 160°, and 95 p. c. between 155 and 180°.

[2]) Pharm. Review **15** (1897), 7.

[3]) Berl. Berichte **39** (1906), 1443, 1444.

stances, the percentage that distils over above 162° is greater with these oils.

Evaporation Residue. Upon evaporation turpentine oil is almost completely volatile. An abnormal, non-volatile residue not contained in the original oil, may, however, be encountered: on the one hand products of decomposition and polymerization may result where too high a temperature is used; on the other hand, slow evaporation due to too low a temperature may result in oxidation products.

If the evaporation residue is determined on a water bath in the ordinary manner, results that are too high are obtained, since the oil oxidizes most readily at water bath temperature and hence resinifies considerably. For this reason H. Herzfeld[1]) determines the evaporation residue at a temperature approximating that of the boiling temperature of the oil. Into a platinum dish, completely imbedded in a sand bath and heated to 155°, 5 cc. of oil are slowly transferred. After vapors cease to be given off, the dish is heated for 15 minutes longer. The results thus obtained vary but little. Considerable, however, are the differences in the results obtained by this method as compared with those obtained by the waterbath method.

In order to avoid ignition of the instantaneously formed turpentine vapors, Kollo[2]) has slightly modified the technique of the method. He places the platinum or nickel dish inside of a tin ring about as broad as a finger. The ring causes a more rapid evaporation at the point of contact, every drop evaporating as it is added, thus accomplishing the end sought more quickly and securely. The dish should project but slightly from the ring, is imbedded in sand up to the ring, and is heated to 155°. With the aid of a separating funnel, the tube of which is twice bent at right angles and drawn out to a point, the oil is added very slowly (100 drops per minute).

H. Wolff[3]), who has frequently observed a creeping of the last portion of the oil, avoids this evil by placing a cylinder over the evaporating dish. This cylinder, made of tin, should

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[1]) Chem. Revue Fett- u. Harzind. **1909**, 174; Pharm. Zentralh. **51** (1910), 72.

[2]) Pharm. Zentralh. **51** (1910), 154.

[3]) Farbenzeitung **16** (1911), 2746; Chem. Zentralbl. **1911**, II. 1181.

be about 5 cm. high and of a diameter exceeding that of the evaporating dish by about 1 cm. It is imbedded in the sand to the extent of about 1/2 cm.

In the case of a normal oil the residue thus determined does not exceed 1 p. c. However, in the case of an old oil, or of one adulterated with high boiling petroleum fractions, the residue is larger. As to how such an oil should be further investigated see p. 33.

Flash Point. The flash point of turpentine oil is recorded at 32°[1]) to 35°[2]) to 37,7°[3]). It must be remembered that the flash point will vary according to the apparatus used. Hence the statements as to the flash point that do not likewise record the apparatus employed in its determination are of little value. Apparently the above data pertain to a closed apparatus (Abels' petroleum tester, the apparatus of Pensky-Martens). The flash point of turpentine oil, when determined in an open apparatus, such as is employed in the examination of lubricating oils (Comp. Lunge-Berl, *Chemisch-technische Untersuchungsmethoden,* 6th ed. Berlin, vol. 3. p. 611), lies in the neighborhood of 41 to 42°. However, conclusions as to the purity of the turpentine oil are not warranted at present, for the observations are still too meagre. This much, however, seems apparent that the normal flash point is lowered by the addition of petroleum or low boiling hydrocarbons.

Acid Content. All crude oil distilled from turpentine contains normally small amounts of formic acid, acetic acid and resin oil. The last is due to the initial stages of pyrogenous decomposition, which sets in toward the end of the distillation when the colophony is heated to a certain point. The resin oil that passes over always contains some colophony[4]). These admixtures

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[1]) Long, Chem. Zentralbl. **1892**, II. 174. — Journ. analyt. and appl. Chemistry VI. No. 1; Journ. Parfum. et Savonn. **24** (1911), 113.

[2]) Vèzes, *Sur la définition de l'essence de térébenthine commercialement pure.* Bordeaux 1910, p. 2.

[3]) L. M. Nash, Analyst **36** (1911), 577; Chem. Zentralbl. **1912**, I. 448.

[4]) Comp. also Vèzes and Eustache, *Sur un mode simple de dosage de la colophane dans l'essence de térébenthine et dans l'huile de résine.* Bordeaux 1901.

(rosin oil and colophony) have been designated normal adulterants *("adultérants normaux")* by Vèzes[1]. The maximum in commercial oil should not exceed 2,5 p. c. and the acid value should not exceed 1,5[2]. Inasmuch as the average acid value of colophony is 170[3], an acid value of 1,5 corresponds to 0,0088 g. colophony in 1 g. of oil of turpentine, or 8,8 g. in 1 kg = 0,88 p. c.

The higher acid content observed in connection with old, resinified turpentine oils, is due to formic acid resulting as a product of oxydation.

Composition. The first elementary analysis of turpentine oil, referred to on p. 94 of vol. I, revealed that this oil consists of hydrocarbons $C_{10}H_{16}$. This conclusion was verified by later investigations. These, however, showed that the turpentine oils may differ physically in so far as some of them deviate the plane of polarized light to the left, others to the right. Berthelot[4] named the lævogyrate hydrocarbon *terebentene*, the dextrogyrate one *australene*. Wallach[5] suggested the name of *α-pinene* for both modifications and differentiated the two as l-*α-pinene* and d-*α-pinene*.

Among the constituents of turpentine oil the α-pinene predominates to such an extent, that this oil may be regarded as an α-pinene rendered impure by the presence of a few per cent. of other terpenes. The other terpene, the presence of which has been definitely established in turpentine oil, is β-pinene. In addition to pinonic acid, due to α-pinene, A. Bæyer[6] obtained upon the oxidation of French turpentine oil an isomeric acid, which melted at 125° and which he named nopinic acid. The formation of this acid he attributes to the hydrocarbon *nopinene*[7], which Wallach named *β-pinene* in order to distinguish it from

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[1] Vèzes, *Sur la définition de l'essence de térébenthine commercialement pure*, Bordeaux 1910, p. 8.

[2] *Ibidem* p. 9.

[3] *Ibidem* p. 10.

[4] Compt. rend. **55** (1862), 496 and 544. — Liebig's Annalen Suppl. II. (1862/63), 226.

[5] Liebig's Annalen **227** (1885), 300; **356** (1907), 227.

[6] Berl. Berichte **29** (1896), 25.

[7] Semmler's pseudopinene. Berl. Berichte **33** (1900), 1458.

α-pinene. However, it was not until Wallach[1]) had successfully accomplished the synthesis of β-pinene and after E. Gildemeister and H. Kœhler[2]) had isolated it in a fairly pure condition from hyssop oil, that it could be demonstrated conclusively that this new hydrocarbon is contained in fractions 163 to 166°[3]) of turpentine oil. For its properties see vol. I, p. 298.

Judging from experience thus far, American turpentine oil appears to be richer in β-pinene than the French oil. Nevertheless it contains only a few percent. It is noteworthy that both turpentine oils contain the same l-β-pinene.

In order to demonstrate the presence of β-pinene, it is oxidized to nopinic acid as described in vol. I, p. 299. For this purpose Schimmel & Co.[4]) utilized the last fractions obtained in the rectification of turpentine oil. 30 grams of a fraction, b. p. 161,5 to 162,5 under 753 mm. (d_{15° 0,8690; $\alpha_D - 0^\circ 14'$; n_{D20° 1,47322), when oxidized with permanganate in the presence of free sodium hydroxide, yielded upon concentration of the solutions 4,5 g (= 15 p. c.) of sodium nopinate. 30 g. of a fraction, b. p. 164 to 166° (d_{15° 0,8714; $\alpha_D - 8^\circ 23'$; n_{D20° 1,47558), yielded upon like treatment 7,5 g. (= 25 p. c.) of sodium nopinate. When the oxidation mixture was distilled with steam, an oil was recovered that possessed the following constants: d_{15° 0,8724; $\alpha_D - 10^\circ 59'$; n_{D20° 1,47714. Upon repetition of the oxidation this yielded additional amounts of the difficultly soluble sodium salt. It would seem, therefore, that fraction 164 to 166° consisted largely of β-pinene, although the specific gravity was rather high.

Inasmuch as α-pinene is one of the most labile terpenes, it is not surprising to find that some products of decomposition are introduced even during the process of preparation. As already mentioned, the oil contains traces of free acid, such as *formic acid, acetic acid* and the *resin acids*. At higher temperatures these act on the pinene with formation of dipentene and polymeric terpenes, both of which are found as companions of the pinene in turpentine oil.

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[1]) Liebig's Annalen **363** (1908), 1—19.

[2]) Wallach-Festschrift, Göttingen 1909, p. 414.

[3]) Comp. also Ahlström & Aschan, Berl. Berichte **39** (1906), 1445.

[4]) Report of Schimmel & Co. April **1908**, 103.

Certain observations and phenomena would seem to indicate that *camphene* and *fenchene* are among the normal constituents of turpentine oil. On account of the boiling points of these terpenes, which lie between those of the two pinenes an unobjectionable direct proof of their presence is impossible. However, as will be shown, the indirect proof of the presence of camphene may be considered as established.

In terebene, a product of the action of strong sulphuric acid on turpentine oil, Armstrong and Tilden[1]) found camphene. They assumed that the camphene had resulted in a manner analogous to its formation from pinene chlorhydrate, a possibility that could not be denied off hand. However, Power and Kleber[2]) regard it as probable that *camphene* is originally contained in the turpentine oil and that its presence becomes apparent after the destruction and removal of the pinene.

Bouchardat and Lafont[3]) heated French turpentine oil for 50 hrs. with benzoic acid anhydride and from the reaction product isolated camphene as well as esters of *iso*borneol and fenchyl alcohol.

By the action of sulphuric acid on French turpentine oil and subsequent treatment with alcoholic potassa, the same investigators[4]) obtained two potassium salts of the formula $C_{10}H_{17}OSO_2OK$. When heated with acids these yielded *l*-borneol and potassium acid sulphate, and *l*-fenchylalcohol and potassium acid sulfate respectively. While the formation of these two salts indicates the presence of camphene and fenchene, it does not necessarily follow that the formation of fenchylalcohol is due to fenchene originally present in the oil. It is more likely that the fenchyl alcohol may be attributed to β-pinene, which, as has been shown by Wallach[5]), is transformed into fenchene very readily. Of the same opinion are Barbier and Grignard[6]) who have isolated terpineol (obtained from α-pinene) and fenchyl alcohol by the action of glacial acetic acid and benzene sulphonic acid.

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[1]) Berl. Berichte **12** (1879), 1753.

[2]) Pharm. Rundsch. (New York) **12** (1894), 16.

[3]) Compt. rend. **113** (1891), 551.

[4]) Compt. rend. **125** (1897), 111.

[5]) Liebig's Annalen **363** (1908), 1 to 19.

[6]) Bull. Soc. chim. IV. **5** (1909), 512, 519.

Hence, while fenchene may not be regarded as one of the constituents of turpentine oil, the presence of camphene can be assumed with relative certainty. The presence of the lævogyrate modification of camphene has been demonstrated by Schimmel & Co[1]) in the following manner. By treating fraction 160 to 161° of American turpentine oil (sp. gr. 0,869; $\alpha_D + 1°16'$) with glacial acetic acid and sulphuric acid according to Bertram's method[2]) *iso*bornyl acetate was obtained. Upon saponification this yielded *iso*borneol (m. p. of phenylurethane, 138°). Inasmuch as special experiments demonstrated that neither α-pinene, regenerated from its nitrosochloride, nor β-pinene yield *iso*borneol when treated according to this method, its formation is attributable to camphene.

The occurrence of cymene supposed by Tilden[3]) has not yet been proven, neither the presence of limonene in the last fractions of turpentine oil[4]).

Whether *firpene,* found by Frankforter and Frary[5]) in the oil of the Western fir[6]), is to be regarded as a constituent of normal turpentine oil is doubtful. According to elementary analysis and molecular weight determination, firpene corresponds to the formula $C_{10}H_{16}$. It differs from pinene in its odor, also in its physical and chemical properties. Its constants are as follows: b.p. 152 to 153,5°; $d_{20°}$ 0,8598; $[\alpha]_D - 47,2°$; $n_{D20°}$ 1,47299. Firpene hydrochloride melts at 130 to 131°, hence has the same melting point as pinene hydrochloride. However it is more volatile and more readily soluble, also has a somewhat different odor. Its principal difference, however, lies in its totally different behavior toward chlorine. Whereas pinene hydrochloride shows no tendency to form a dichloride, firpene hydrochloride readily

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[1]) Report of Schimmel & Co. October **1897**, 62.

[2]) Journ. f. prakt. Chem. II. **49** (1894), 1.

[3]) Berl. Berichte **12** (1879), 1131.

[4]) Ahlström & Aschan, Berl. Berichte **39** (1906), 1446.

[5]) Journ. Americ. chem. Soc. **28** (1906), 1461.

[6]) What species is meant by this designation could not be ascertained. A. L. Brower refers to "western yellow pine" apparently as identical with "longleaf pine" [Oil, Paint and Drug Reporter **75** (1909), No. 18, p. 28 f.]. C. Mohr (The timber pines of the Southern U. S. Washington 1897) does not give this synonym.

yields such a compound. Firpene hydrobromide melts at 102°, pinene hydrobromide at 90°.

Toward nitrosyl chloride pinene and firpene behave differently. As is well known, the former yields a well crystallized nitrosochloride without difficultly. From firpene, however, no crystallizable nitrosochloride could be obtained.

Influence of Air and Light on Turpentine Oil. It is a well-known phenomenon that turpentine oil changes rapidly when allowed to stand in open vessels, more particularly in the presence of water. The oil becomes thick, an increase takes place in the specific gravity, index of refraction and boiling point, the optical rotation diminishes, the solubility in 90 p. c. alcohol increases, the originally neutral oil becomes acid and resinifies. Technically it is said to become "rancid"[1]). Formerly such an oil was designated as being ozonized because it acts strongly as an oxidizing agent.

All of these changes are attributable to slow oxidation by means of atmospheric oxygen. Schönbein[2]) assumed that the oil became charged with ozone by changing atmospheric oxygen to its active modification. Later it was demonstrated by Kingzett[3]),

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[1]) After having stood for 7 weeks in stoppered flask partly filled with air, the specific gravity of a normal American turpentine oil had changed from 0,867 to 0,897. It had become soluble in 3,5 vols. of 90 p. c. alcohol whereas originally it required 6 vols. to produce a clear solution.

The specific gravity of another sample of American oil, after prolonged standing, had increased to 0,913 and was soluble in 3 vols. of 90 p. c. alcohol.

After having stood four years in a well stoppered, but not completely filled flask, a French oil revealed the following changes: —

	Original normal oil.	The same after four years.
d	0,871	1,009
α_D	— 29° 55′	— 19° 18′

Whereas the original normal oil required 20 vols. of 80 p. c. alcohol to produce a clear solution, the oxidized oil was soluble in 1 vol. of 80 p. c. alcohol, and in all proportions in 90 p. c. alcohol. Compare p. 16, footnote 2.

[2]) Liebig's Annalen **102** (1857), 133.

[3]) Journ. chem. Soc. **27** (1874), 511. — Pharmaceutical Journ. III. **5** (1874), 84. — *Ibidem* **6** (1875), 225. — *Ibidem* **7** (1876), 261. — *Ibidem* **9** (1879), 772 and 811. — *Ibidem* **20** (1890), 868. — Chem. News **69** (1894), 143; comp. also Robbins, Pharmaceutical Journ. III. **9** (1879), 748, 792, 872.

Bardsky[1]) and Papasogli[2]) that such an oil contains no ozone[3]) but hydrogen peroxide.

As was first shown by Lœw[4]), other substances than hydrogen peroxide are contained in turpentine oil oxidized in the presence of moisture. Oxidized turpentine oil liberates iodine from potassium iodide, a property not revealed by hydrogen peroxide. As was already assumed by Kingzett[5]), this action is attributable to traces of organic peroxides. In the presence of water, these finally yield hydrogen peroxide, peroxide hydrates presumably being formed as intermediate products.

The situation has been cleared up by the work of C. Engler[6]). He showed that the action of atmospheric oxygen or pure oxygen on turpentine oil results in the formation of a peroxide-like oxidation product, $C_{10}H_{16}O_4$. This can give off one half of its oxygen, whereas the other half remains with the oil. He confirmed the observation previously made by Berthelot[7]), that 1 mol.

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[1]) Bardsky (Chem. Zentralbl. **1882**, 803) found hydrogen peroxide and, as he believes, nitric acid in water which had been shaken with oxidized turpentine oil.

[2]) According to Papasogli (Chem. Zentralbl. **1888**, 1548) water, that has stood in contact with turpentine oil for a longer period, contains hydrogen peroxide, camphoric acid (m. p. 176°), formic acid, acetic acid and an acid $C_{10}H_{18}O_2$ isomeric with campholic acid. In the oxidized turpentine oil itself hydroxysylvinic acid is supposed to be contained.

[3]) Although the correctness of these observations has nowhere been doubted, and the presence of hydrogen peroxide in turpentine oil may be regarded as settled, nevertheless numerous text books still contain the statement that ozone is contained in turpentine oil and in volatile oils in general. Inasmuch, however, as hydrogen peroxide and ozone destroy each other in accordance with the equation

$$O_3 + H_2O_2 = H_2O + 2O_2$$

(Schöne, Liebig's Annalen **196** [1879], 239), the presence of ozone is excluded. Comp. also C. Harries, Chem. Ztg. **31** (1907), 804.

[4]) Zeitschr. f. Chem. II. **6** (1870), 609; Chem. Zentralbl. **1870**, 821.

[5]) *Loc. cit.*

[6]) C. Engler and J. Weißberg, *Über Aktivierung des Sauerstoffs. Der aktive Sauerstoff des Terpentinöls.* Berl. Berichte **31** (1898), 3046. C. Engler, *Die Autoxydation des Terpentinöls. Ibidem* **33** (1900), 1090.

[7]) Annal. de Chim. et Phys. III. **58** (1860), 435; Jahresber. d. Chem. **12** (1859), 58.

of turpentine oil absorbs 4 atoms of oxygen, of which two are readily removed. Thus far, however, the isolation of either the compound $C_{10}H_{16}O_4$ or $C_{10}H_{16}O_2$ has not been successful.

When absolutely dry turpentine oil is activated, neither hydrogen peroxide nor ozone results. Turpentine oil activates oxygen most rapidly at 100°. Above this temperature no active oxygen is formed, but it is used up in the oxidation of the turpentine oil. 1 cc. of turpentine oil can activate 100 cc. of oxygen at 100°.

The turpentine oil charged with oxygen, whether moisture be present or not, is capable of transmitting oxygen to such substances which are not directly oxidizable by atmospheric oxygen. Thus, as has already been pointed out, iodine is liberated from potassium iodide. Indigo solution is bleached and arsenous acid is oxidized to arsenic acid. In the dark, activated turpentine oil retains its property for years.

These oxydation phemomena and the same changes in the turpentine oil take place more rapidly when warmed air saturated with moisture is passed through the oil¹).

As to the nature of the oxidation products, but little is known.

Definitely established is the presence of formic acid²), acetic acid and camphoric acid $C_{10}H_{16}O_4$ ³), whereas the presence of hydroxysylvinic acid is doubtful. Traces of an aldehyde⁴) have also been found, the composition of which agrees with that of the aldehyde of camphoric acid, *viz.* $C_{10}H_{16}O_3$. It possesses a benumbing odor and is probably the cause of the peculiar odor of the old "rancid" turpentine oil.

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¹) A turpentine oil, sp. gr. 0,864, when thus treated for 44 hrs. revealed a sp. gr. of 0,949. Kingzett observed in connection therewith an appreciable rise in the boiling temperature.

²) The exact proof of the presence of formic acid was first brought by Kingzett in 1910. Journ. Soc. chem. Industry **29** (1910), 791. — Comp. also *ibidem* **31** (1912), 265.

³) Papasogli, Chem. Zentralbl. **1888**, 1548.

⁴) Schiff, Chem. Ztg. **20** (1896), 361. This aldehyde appears to be most readily formed when turpentine oil is kept in partly filled and imperfectly stoppered flasks exposed to light. The amount of the unstable aldehyde formed does not exceed 1 p.c. As already mentioned, it can be removed by shaking the oil with sodium acid sulphite solution.

When exposed to the air on a watchglass for several days, the aldehyde resinifies, looses its toxic odor, and no longer reacts with rosaniline sulphate.

In a turpentine oil that had been completely resinified by exposure in shallow dishes, Tschirch and Brüning[1]) demonstrated the presence of a resin-like substance and of a small amount of a resinolic acid. They could not, however, find a peculiar resin acid, such as abietic acid, pimaric acid, &c. According to Tschirch[2]), the resenes are related to the terpenes and are probably to be regarded as hydroxypolyterpenes.

The action of direct sunlight on moist turpentine oil in the presence of air, or better still, of oxygen results in the formation of pinol hydrate (sobrerol), $C_{10}H_{18}O_2$. According to the solvent employed it crystallizes in laminæ or needles. The inactive modification melts at 131°, the active modifications at 150°[3]).

Detection of Adulterations of Turpentine Oil. If the determination of the specific gravity, solubility, boiling temperature and residue upon evaporation have revealed any abnormal qualities in an oil of turpentine, further examination is necessary to ascertain whether the oil is adulterated, also the nature of the adulterant. Inasmuch as the adulterants, as a rule, reveal a different additive capacity for halogens than does the oil of turpentine, the determination of iodine and bromine absorption should here be considered. Whereas both methods have been universally adopted in the analysis of fats, the opinions as to their applicability to turpentine oil are greatly divergent. For the sake of completeness, however, they should be mentioned, all the more since the German Customs Authorities demand the examination of turpentine oil as to its additive capacity for bromine.

IODINE ABSORPTION. The iodine value expresses the number of parts of iodine absorbed by 100 parts of turpentine oil. Hence an iodine value of 373 for turpentine oil implies that 100 g. of turpentine oil absorb 373 g. of iodine. For the method as well as for the preparation of the necessary solutions, reference should be had to treatises dealing with the analysis of fats,

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[1]) Arch. der Pharm. **238** (1900), 645.

[2]) *Grundlinien einer physiologischen Chemie der pflanzlichen Sekrete.* Arch. der Pharm. **245** (1907), 386.

[3]) Sobrero, Liebig's Annalen **80** (1851), 106. — Wallach, *ibidem* **259** (1890), 313. — Armstrong and Pope, Journ. chem. Soc. **59** (1891), 315; Chem. Zentralbl. **1891**, II. 168.

e.g. Lunge-Berl's *Chemisch-technische Untersuchungsmethoden*, 6th ed., vol. 3. p. 671.

Worstall[1]) sets aside 0,1 g. of oil with 40 ccm. of Hübl's iodine solution in a glass-stoppered flask over night and then titrates back the excess of iodine. The theoretical iodine value demanded by the change of $C_{10}H_{16}$ to $C_{10}H_{16}I_4$ is 373. The average found in the examination of 55 samples of pure turpentine oil is 384. Further investigation revealed the fact that the iodine absorption as indicated above is completed within 4 to 6 hrs. and that a large excess of iodine and prolonged action induces secondary reactions.

The iodine value of rosin spirit was found to be 185, that of rosin oil 97, of "refined wood turpentine" 212, and of "water white" 328, whereas the petroleum hydrocarbons of kerosene and naphtha add no iodine.

Hence even small additions of petroleum distillate may be detected by a reduction in the iodine value. According to Worstall, a turpentine oil with an iodine value below 370 is to be regarded as suspicious.

Mc. Gill[2]) corroborates Worstall's results and likewise places the lower limit for pure turpentine oil at 370.

It must be remembered, however, that comparable results are obtainable only when the conditions maintained are absolutely the same.

Thus Harvey[3]) who used Wijs' solution obtained iodine values ranging from 166 to 221, corresponding to the absorption of two atoms of iodine to one molecule of $C_{10}H_{16}$. According to Veitch and Donk[4]), genuine turpentine oil has an iodine value of 350 to 400 if Wijs' solution is employed.

A more detailed investigation, made because of the great discrepancy in the results, revealed the fact that the amount of halogen absorbed by the turpentine oil depends on the duration of the action and also on the excess of the Wijs' solution employed.

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[1]) Journ. Soc. chem. Industry **23** (1904), 302; Chem. Zentralbl. **1904**, I. 1676.

[2]) Journ. Soc. chem. Industry **26** (1907), 847; Chem. Zentralbl. **1907**, II. 1124.

[3]) Journ. Soc. chem. Industry **23** (1904), 413; Chem. Zentralbl. **1904**, II. 265. Comp. also F. W. Richardson and E. F. Whitaker, Journ. Soc. chem. Industry **30** (1911), 115; Chem. Zentralbl. **1911**, I. 1012.

[4]) U. S. Dept. of Agriculture, Bur. of Chemistry, Bull. No. **144**, 1911, p. 22.

BROMINE ABSORPTION. The value of this method is denied on the one hand as it is defended on the other[1]. Hence a final judgement cannot be passed thereon at present.

According to Vaubel[2] the bromination of turpentine oil is conducted in the following manner:

> "To a solution of 1 to 2 g. of turpentine oil in chloroform, about 100 cc. of water, 5 g. of potassium bromide and 10 cc. of hydrochloric acid or the equivalent amount of sulphuric acid are added. The mixture is then titrated with a standardized potassium bromate solution until a permanent bromine reaction is produced. The end reaction can be recognized either by the coloration of the chloroform or by transferring a drop of the aqueous solution to potassium oxide-starch test paper."

According to the equation $C_{10}H_{16} + 4\,Br = C_{10}H_{16}Br_4$, 100 g. of pinene should add 254 g. of bromine. For several pure turpentine oils Vaubel ascertained bromine values of from 220 to 240.

The directions issued by the German Customs Authorities for determining the bromine absorption[3] are as follows:

> "A mixture of 50 cc. of 98 per cent. (by weight) alcohol and 5 cc. of concentrated hydrochloric acid, sp. gr. 1,124 is introduced into a 150 cc. beaker. To this mixture 0,5 cc. of the oil to be examined are added, the amount being measured by means of a standardized pipette. The oil is completely dissolved by stirring the mixture with a glass rod.
>
> "By means of a burette of about 30 cc. capacity and calibrated into one-half cubic centimeters or less the bromine solution described below is added with constant stirring.
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> "At first the bromine set free by the action of the hydrochloric acid combines instantaneously with the turpentine oil. After about four-fifths of the requisite bromine solution

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[1] Comp. Evers, Chem. Ztg. **23** (1899), 312. — Schreiber and Zetzsche, *ibidem* **23** (1899), 686. — Böhme, Chem. Ztg. **30** (1906), 633. — Utz, Pharm. Zentralh. **49** (1908), 10. — Marcusson, Chem. Ztg. **33** (1909), 966, 978, 985. — Mansier, Annal. de la Chim. analyt. appl. **14** (1909), 417; Zeitschr. f. angew. Chem. **23** (1910), 46.

[2] Pharm. Ztg. **51** (1906), 257.

[3] *5. Nachtrag zu der Anleitung für die Zollabfertigung. Herausgegeben vom Reichsschatzamt.* Berlin 1910, p. 56.

have been added, the mixture is colored yellow. This color, however, disappears after a few seconds though it has been decidedly lemon-yellow. When, however, the disappearance of the bromine color lasts $^1/_2$ minute, only $^1/_2$ cc. of the solution is added at a time and the length of time required for the disappearance of the color is noted.

"If the period of decoloration lasts 1 minute or more, the reaction is regarded as being ended. In some of the less pure turpentine and pine tar oils a permanent yellow color is produced before the end of the reaction has been reached. In such a case, a few drops of the liquid, removed one minute after the last addition of the bromine salt solution, are added to a diluted zinc iodine-starch test solution. (See below.) If a deep blue color is produced at once, but not otherwise, the reaction may be regarded as ended.

"If 25 cc. or more of bromine salt solution have been used, the turpentine oil is free from mineral oils. If less than 25 cc. have been used it is doubtful. In this case the sample should be examined by a chemist according to method 2 (*i. e.* with fuming nitric acid)[1])."

The bromine salt solution required for the above test is prepared by dissolving 13,93 g. of pure potassium bromate and 50g. of potassium bromide in sufficient distilled water to make 1000 cc.

The zinc iodide-starch test solution is prepared by triturating 4 to 5 g. of starch with a little water to a milky liquid and adding this mixture in small amounts and while stirring to a boiling solution of 20 g. of pure zinc chloride in 100 cc. of water. The boiling is continued with the replacement of water lost by evaporation, until the starch is dissolved as completely as possible and the liquid has become clear. The solution is then diluted with water, 2 g. of pure, dry zinc iodide are added, the dilution completed to 1 liter and the solution filtered. Stored away in the dark, in well stoppered bottles, the clear solution can be kept. Previous to the test, one part of this solution is diluted with ten volumes of water. Of this diluted solution 3 to 4 cc. are transferred to test tubes in which the tests for bromine are made as indicated above.

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[1]) See p. 36.

DETECTION OF PETROLEUM. Ordinary kerosene as well as lighter and heavier fractions of petroleum are used for the adulteration of turpentine oil. The lower petroleum products are recognized by the lowering of the specific gravity, also by the depression of the inflammability test[1]). The heavier petroleum products are not volatile with water vapors. Hence, when turpentine oil is rectified with water vapor they remain behind as a fluorescing residue that is not acted upon by concentrated nitric acid and sulphuric acids.

The following fractions of American petroleum are mentioned by J. H. Long[2]) as suitable for adulteration. With their specific gravities they are here enumerated.

Gasolin	d_{15° 0,6508
Gasolin	„ 0,7001
Benzin	„ 0,7306
Standard White	„ 0,7999
Water White	„ 0,7918
Head Light	„ 0,7952
Mineral Seal	„ 0,8293
Paraffin Oil	„ 0,8906

As so-called patent turpentine oils, a number of products have made their appearance under a variety of fanciful names. They are mostly mixtures of petroleum with turpentine oil or camphor oil, or consist entirely of petroleum hydrocarbons. Some of the names applied to these products are[3]) "Canadian turpentine oil, patent turpentine, turpentyne, turpenteen, larixolin, paint oil."

According to Dunwody[4]) mixtures of turpentine oil and petroleum can be distinguished from pure turpentine oil by their solubility in 99 per cent. acetic acid (Comp. p. 18). Absolute acetic acid (99,5 to 100 p. c.) is miscible in all proportions with both petroleum and turpentine oil. An acetic acid made by adding 1 cc. of water to 99 cc. glacial acetic acid yields a clear solution with turpentine oil when mixed in the proportion of 1:1;

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[1]) Comp. p. 21.

[2]) Journ. anal. and appl. Chemistry **6**, No. 1; Journ. Parfum. et Savonn. **24** (1911), 112.

[3]) Pharm. Zentralh. **33** (1892), 131.

[4]) Americ. Journ. Pharm. **62** (1890), 288.

with petroleum, however, it does not. For the complete solution of turpentine oil-petroleum mixtures the following amounts of this acetic acid are required (99 + 1): —

Petroleum	1	2	3	4	5	7	8 cc.
Turpentine oil	9	8	7	6	5	3	2 „
Require for solution in acetic acid (99 + 1)	40	60	80	110	150	230	270 cc.

Conradson[1]) detects the presence of petroleum in turpentine oil according to the following method: On a water bath 50 cc. of oil are evaporated to 1 to 2 cc. If the oil is free from petroleum, the residue dissolves to form a clear solution in 5 to 10 cc. of glacial acetic acid. If 10 p. c. or more of petroleum are present, the mixture is turbid and upon standing separates into two layers.

Formerly the Prussian Customs Authorities directed the use of the different solubility of turpentine oil and mineral oils in aniline (comp. p. 18) as a means to detect patent turpentine oils.

> "To a measuring cylinder of 50 cc. capacity which is calibrated into cubic centimeters and which is provided with a glass stopper, 10 cc. of oil are transferred and then 10 cc. of aniline. The cylinder is then stoppered and thoroughly shaken. If after five minutes the liquid no longer appears uniform but reveals two layers, patent turpentine oil is present."

For the quantitative determination of petroleum in turpentine oil H. C. Frey[2]) uses somewhat different proportions. He recommends that 10 cc. of the oil be shaken with 30 cc. of aniline in a graduated tube for five minutes and that the mixture be then set aside. If petroleum be present it rises to the surface as a separate layer so that the amount can be read off. Care should be taken to have the aniline perfectly anhydrous. In order to test the utility of the method which, according to Frey, gives excellent results, Schimmel & Co.[3]) have tested turpentine oil to which varying amounts of petroleum had been added. With the above method the following results were obtained: —

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[1]) Journ. Soc. chem. Industry **16** (1897), 519; Chem. Zentralbl. **1897**, II. 449.

[2]) Journ. Americ. chem. Soc. **30** (1908), 420.

[3]) Report of Schimmel & Co. October **1908**, 123.

	d_{15°	Amount of oil separated	
		cc.	%
Turpentine oil + 5 % petroleum	—	—	—
„ + 10 % „	0,8641	0,8	8
„ + 15 % „	0,8605	2,2	22
„ + 20 % „	0,8564	2,8	28
„ + 30 % „	0,8493	4,2	42
„ + 50 % „	0,8356	5,9	59

The reading should be postponed for at least 24 hrs. since a turpentine oil to which petroleum up to 15 p. c. has been added yields, first of all, a clear solution. Later on this becomes turbid and the petroleum separates gradually. From the above table it becomes apparent that a petroleum content up to 5 p. c. cannot be detected according to Frey's method. A petroleum content between 5 and 10 p. c. is revealed but not in its entirety. In isolated cases even an oil to which 15 p. c. of petroleum had been added remained clear permanently so that even in such an instance the method was not reliable. Again, results that are too high are found when the petroleum content is greater, for then the aniline does not dissolve out all of the turpentine oil from its mixture with petroleum. Moreover, if as much as 15 p. c. be present, the adulteration is indicated by the specific gravity of the mixture, which for turpentine oil should not be below 0,864. These results scarcely render applicable the attribute "excellent" as applied to Frey's method. Nevertheless the method may prove useful provided the amount of petroleum added is not too small¹).

NITRIC ACID METHOD. For the quantitative determination of petroleum, the turpentine oil is oxidized with fuming nitric acid and the residual mineral oil is weighed. According to Burton²) 100 cc. of oil are transferred into a spacious flask connected with a reflux condenser. From a measuring funnel 300 cc.

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¹) According to H. S. Shrewsbury the method of Frey can only be used if the petroleum content varies between 30 and 70 p. c. Correct values within these limits can be had only by making the necessary corrections. Analyst **36** (1911), 137; Chem. Zentralbl. **1911**, I. 1560.

²) Americ. chem. Journ. **12** (1890), 102; Chem. Zentralbl. **1890**, I. 882.

of fuming nitric acid are allowed to drop slowly and the mixture kept well cooled. The residual oil is washed with hot water and weighed. Control experiments have revealed that the higher boiling petroleum fractions yield better results. The lower fractions are attacked somewhat by nitric acid. When a petroleum product boiling at 250° was used, 34,1 p. c. were found in place of 35 p. c. added; when a petroleum product boiling at 75° was used 17,9 p. c. were found in place of 20 p. c., and in an other experiment 28 p. c. in place of 30 p. c. A like method is described by Allen[1]), who, however, employs 400 cc. of fuming nitric acid in place of 300 cc. for the same amount of oil.

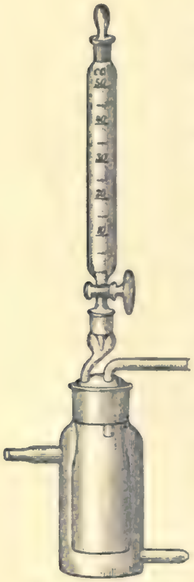

Fig. 1.

For this assay H. Herzfeld[2]) has constructed an apparatus (Fig. 1) which admits of the use of smaller amounts. To 10 cc. of turpentine oil contained in the lower vessel 15 cc. of fuming nitric acid, contained in the measuring cylinder, are added drop by drop. At the same time the mixture is well shaken and water is passed through the outer jacket of the apparatus. The operation being ended, the reaction mixture is transferred to the graduated cylinder and the volume of petroleum product read off. If the latter is to be weighed, it is washed several times with a few cc. of fuming nitric acid and finally with water.

Marcusson and Winterfeld[3]) regard it advantageous to reduce the temperature of the acid to — 10° and to use a special apparatus. This consists of a round bottomed flask with a long calibrated neck and a 10 cc. measuring funnel fitting into the ground glass neck. (fig. 2).

> "30 cc. of fuming nitric acid (sp. gr. 1,52) are transferred to the flask *a* and reduced to a temperature of — 10°. As a cooling medium a 15 p. c. solution of sodium

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[1]) Zeitschr. f. öff. Chem. 8 (1902), 446; Chem. Zentralbl. **1903**, I. 258.

[2]) Chem. Zentralbl. **1903**, I. 258. Later on the apparatus was supplied with a thermometer by Herzfeld.

[3]) Chem. Ztg. **33** (1909), 987.

chloride in a small tin jar is used. This jar is placed in a mixture of ice and coarse salt to bring about the proper reduction in temperature. The measuring funnel *b* is then inserted and filled up to the mark *d* (10 cc.) with turpentine oil which is added drop by drop to the nitric acid while the mixture is being shaken. The time required for the addition varies from ½ to 1 hour according to the benzin content. The larger the latter, the more rapidly the oil can be added.

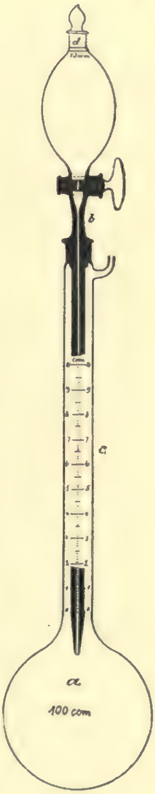

Fig. 2.

The reaction being ended the product is allowed to remain for another quarter of an hour in the cooling mixture. The measuring funnel having been removed, sufficient concentrated (but not fuming) nitric acid (d 1,4) cooled to — 10° is added with the aid of an ordinary glass funnel to force the insoluble oil into the calibrated neck *c*. After room temperature has been reached, the volume can be read off directly. Meanwhile, however, the bulk of the flask is allowed to remain in the salt solution in order to prevent side reactions by the nitric acid. If the specific gravity and boiling temperature of the portions insoluble in the nitric acid are to be determined, these can be withdrawn by means of a pipette. For this purpose a rather long rubber tube should be attached to the pipette. If but a small amount of benzin is present 20 cc. of oil can be added to 60 cc. of nitric acid"[1]).

If no oily layer separates on the acid, the sample in question may be regarded as free from benzin.

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[1]) The German Customs Authorities regard the oil as pure if the upper layer amounts to less than 0,2 cc. If, however, the index of refraction of the original turpentine oil exceeds 1,48 (at 17°), it is to be regarded as containing mineral oil if the layer exceeds 0,5 cc. (*Fünfter Nachtrag zu der Anleitung für die Zollabfertigung.* Published by the *Reichsschatzamt.* Berlin 1910, p. 57).

The acid is poured into 150 cc. of water and the mixture is heated for about $^1/_4$ hour on a steam bath in a hood. If the turpentine oil was pure no separation takes place. If, however, petroleum hydrocarbons are present, the separation of an oil is accompanied by turbidity and evolution of red vapors. After cooling, the oil is shaken out with ether. The ethereal solution is first washed with water, then with an approximately 8 p. c. potassium hydroxide solution (made from 50 g. potassium hydroxide, 500 g. water, 50 cc. alcohol), again with water, then dried with calcium chloride. After evaporation of the ether the residue is weighed. Note should, however, be taken of the fact that certain constituents of the benzin are attacked by the nitric acid and converted into water soluble compounds. Hence the amount of adulterant is not necessarily the same as the amount of the separated and weighed oil. Moreover, the different kinds of petroleum oils and benzin do not behave alike when treated as directed above. Inasmuch as analysts have not yet come to an agreement as to the correction which should be made, it becomes necessary to refer to the original literature¹).

For the examination of the nitric acid liquors for nitro compounds (from benzene hydrocarbons) see p. 50.

SULPHURIC ACID METHOD. It may be pointed out in advance that the differences of opinion regarding this method are as great as those concerning the nitric acid method. The idea to utilize the stability of the petroleum hydrocarbons toward strong sulphuric acid in order to detect their presence in turpentine oil, dates back to Armstrong²). Herzfeld³) improved the method by supplementing the treatment of concentrated sulphuric acid with a second treatment with fuming sulphuric acid. Eibner and Hue⁴) attribute the varying results obtained by analysts⁵) when

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¹) Marcusson, Chem. Ztg. **33** (1909), 966, 978, 985; **34** (1910), 285; **36** (1912), 413, 421. — Herzfeld, *ibidem* **33** (1909), 1081; **34** (1910), 885.

²) Journ. Soc. chem. Industry **1** (1882), 478; Chem. Zentralbl. **1883**, 206.

³) Zeitschr. f. öff. Chem. **9** (1903), 454; Chem. Zentralbl. **1904**, I. 548.

⁴) Chem. Ztg. **34** (1910), 643, 657.

⁵) Wilson, Zeitschr. f. angew. Chem. **1890**, 371. — Böhme, Chem. Ztg. **30** (1906), 633. — Mc. Candless, Journ. Americ. chem. Soc. **26** (1904), 981; Chem. Zentralbl. **1904**, II. 1074. — Marcusson, Chem. Ztg. Repert. **32** (1908), 325. — Coste, Analyst **33** (1908), 219; **34** (1909), 148; Chem. Zentralbl. **1908**, II. 731;

treating turpentine oil with sulphuric acid to the different strength of the fuming sulphuric acid employed and to variations in the conditions observed. The fuming sulphuric acid of commerce varies greatly and this variation is not sufficiently recognized by analysts. Hence they determined the conditions under which comparable results can be obtained provided the apparatus employed by them is used.

The burette adapted to shaking (fig. 3) used by Eibner and Hue consists of a lower narrow portion of about 10 cc. capacity. 7 cc. of this part are calibrated into $^1/_{10}$ cc. The wider, middle portion has a capacity of about 25 to 50 cc. It is provided with two projections of glass, by means of which the burette can be suspended from a clamp. The upper, narrow portion is likewise calibrated like the lower portion and is capped with a glass ground stopper provided with a small opening on the same side with the calibration, as illustrated in the cut. The object of the wider, middle portion is to enable a thorough mixing of the liquids. The upper calibration enables the reading off of the amount of residue six hours after the treatment with the concentrated sulphuric acid. The lower calibration enables a like reading of the amount of residue 40 to 50 minutes after the treatment with the fuming sulphuric acid.

> Directions: "By means of a burette, 15 cc. of concentrated sulphuric acid sp. gr. 1,84 are transferred to the shaking burette. From a 10 cc. burette $^1/_2$ cc. of the turpentine oil to be examined is added at a time. After each addition the stopper is inserted in such a manner that the small perforation is open. The burette is grasped about the middle, wider part and shaken thoroughly until the principle reaction ceases. The burette is then grasped about the upper portion, placed in as nearly a horizontal position as possible and shaken again so that all of the sulphuric acid comes in contact with the turpentine oil. This procedure is repeated until the 10 cc. of turpentine oil have been

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1909, I. 1614. — Marcusson, Chem. Ztg. **33** (1909), 966, 978, 985; **34** (1910), 285. — Herzfeld, *ibidem* **33** (1909), 1081; **34** (1910), 885. — Nicolardot u. Clément, Bull. Soc. chim. IV. **7** (1910), 173. — Morrell, Journ. Soc. chem. Industry **29** (1910), 241. — Coste, Analyst **35** (1910), 112; Chem. Zentralbl. **1910**, I. 1297.

added. Finally the stopper is turned so as to close the perforation and the mixture is once more thoroughly shaken. According to the amount of benzin present, the time of addition of the turpentine oil will vary from 15 to 50 minutes.

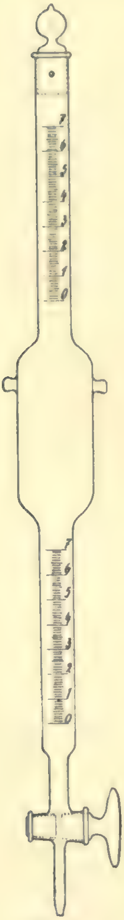

Fig. 3.

Concentrated sulphuric acid is then poured down the sides of the burette until the liquid has risen to about the 2 cc. mark of the upper calibration. After 6 hours the volume of the residue is read off. If this does not amount to more than 2 cc. the turpentine oil was probably pure. The polymerization products are then drawn off and, according to the volume, the residue is treated with varying amounts (see table) of fuming sulphuric acid containing 20 p. c. of anhydride. If the volume varies but little from the volumes recorded in the table, the nearest one is choosen. If the variation is greater interpolation is resorted to. 1 cc. of fuming sulphuric acid is added at a time. After each addition the stopper is placed in position so that the perforation is open. The liquid is allowed to flow into the middle portion of the burette, the lower portion is grasped with the left hand, the middle or wider portion with the right hand, the apparatus placed in as nearly a horizontal position as possible and the contents shaken thorougly.

After no more heat is produced, the burette is grasped at the upper end with the right hand and the contents are given another thorough shaking. Another cc. of acid is added going through the same procedure. After the required amount of sulphuric acid has been added the entire liquid is given a final thorough shaking and the burette suspended from a clamp. After 40 to 45 minutes the volume of the residue is read off. Pure oil yields a residue of from 0 to 3 p. c. (0 to 0,3 cc.). If the residue amounts to 4 p. c., adulteration is assumed. If it is larger, the amount of the adulteration can be directly computed; cc. × 10 = p. c."

Residue after treatment with 15 cc. conc. H_2SO_4		Quant. of fuming H_2SO_4 (abt. 20% SO_3)	Residue after treatment with 15 cc. conc. H_2SO_4		Quant. of fuming H_2SO_4 (abt. 20% SO_3)
%	cc.	cc.	%	cc.	cc.
5	2,04	7,0	40	4,65	2,2
10	2,41	5,8	45	5,03	1,8
15	2,78	5,2	50	5,40	1,5
20	3,16	4,6	55	5,78	1,2
25	3,53	4,0	60	6,16	0,7
30	3,90	3,4	65	6,50	—
35	4,28	2,8	70	7,00	—

P. van der Wielen[1]) suggests the following modification of the sulphuric acid method. To 80 cc. of sulphuric acid (d 1,698), contained in a flask of about 1 liter capacity, 20 cc. of the oil to be tested are added and the mixture set aside with frequent shaking. 300 cc. of water are added and the unchanged oil is distilled into a flask with a graduated neck. The oily distillate is dried and its index of refraction is determined, also the temperature at which its solution in aniline will separate. The refraction of the original oil should likewise be known. From these data, supplemented by the knowledge of the amount of oil that has not been polymerized by the sulphuric acid van der Wielen claims that reliable conclusions as to the addition of hydrocarbons[2]) can be drawn.

THE MERCUROUS ACETATE METHOD. This method of Nicolardot and Clément[3]) depends on the same principle on which the detection of petroleum or benzene by means of nitric acid or sulphuric acid depends. The natural constituents of turpentine oil are removed by oxidation, whereas the mineral oil constituents which are not attacked are determined quantitatively. For the purpose of carrying out this test, 70 g. of mercurous acetate are dissolved in 150 cc. of acetic acid, 50 cc. of the oil to be tested are added, and the mixture is heated in a flask, connected with a reflux condenser, on a water bath for 1/2 hr. The reaction mixture is distilled with steam and the volume of

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[1]) Pharm. Weekblad 8 (1911), No. 35.

[2]) By hydrocarbons the author here evidently means petroleum hydrocarbons.

[3]) Bull. Soc. chim. IV. 7 (1910), 173.

the distilled oil ascertained. Inasmuch as pure turpentine oil is thus completely oxidized without yielding a volatile residue, any distillate represents adulteration. "White spirit" is not volatilized quantitatively since it is partly attacked by the acetates of mercury. However, the deviation is small.

DETECTION OF ROSIN OIL AND ROSIN ESSENCES. The distillates obtained by the destructive distillation of colophony are used extensively for the adulteration of turpentine oil. According to the temperature employed during the distillation or the type of apparatus used (distillation over direct heat, with superheated steam, or vacuum) different products are obtained which upon fractionation can be resolved into distillates with greatly differing properties. Additional changes are produced by chemical treatment, such as that with alkalies and acids, bleaching, decoloration or aëration. The nomenclature of these products is not uniform. Hence, for this reason alone it is not surprising that the opinions of analysts concerning the detection of these products is at variance.

In general the lowest fractions of the colophony distillation are designated pinolin or resin spirit, rosin essence, turpentine essence and rosin spirit, whereas the higher boiling products are known as rosin oils. Of these distinction is made between light blue and green rosin oils, pitch oil, retinol, viscid rosin oil, &c. Inasmuch as the specific gravity of the rosin oils varies between 0,945 and 1,010¹) the lighter pinolin only comes into consideration as an adulterant for turpentine oil.

Thus far the following hydrocarbons have been found in rosin essence: cymene²), and the terpenes α-pinene, camphene and dipentene³).

The properties of these products actually vary as much as the concept "resin essence". A resin essence from Kahlbaum⁴) had the following properties: d_{15° 0,8656; n_{D15° 1,4826 (hence the index of refraction is higher than that of turpentine oil); 8 p. c.

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¹) Bottler, *Harze u. Harzindustrie.* Hannover 1907, p. 208.

²) Kelbe, Liebig's Annalen **210** (1881), 10.

³) Wallach and Rheindorff, Liebig's Annalen **271** (1892), 311. — Grimaldi, Chem. Ztg. **33** (1909), 1157.

⁴) R. Adan, Chem. Zentralbl. **1908**, II. 1749.

distilled over between 118 and 150°, 51 p.c. between 150 and 180°, 27 p.c. between 180 and 220°, 10 p.c. between 220 and 295°. The residue amounted to 10 p.c.

The examination of several rosin distillates in the laboratory of Schimmel & Co. yielded the following results: —

	Rosin oil, crude[1]	Rosin essence	Rosin essence after removal of the acids and phenols and rectification with water vapor.	Boiling temperature of the rosin essence freed from acids and phenols.
d_{15°	0,9789	0,8578	0,832	100 to 120° 6 %
α_D	$+39^\circ 10'$	$+3^\circ 30'$	$-0^\circ 5'$	120 „ 130° 18 %
n_{D20°	1,53771	1,46703	1,45991	130 „ 140° 15 %
A. V.	18,7	43,9	—	140 „ 150° 13 %
E. V.	5,2	7,3	—	150 „ 160° 10 %
Soluble	in 4,5 vols. and more of abs. alc.	in abt. 25 vols. of 80 % alcohol	in abt. 15 vols. of 80 % alcohol	160 „ 170° 14 % 170 „ 180° 10 % 180 „ 190° 6 %
	—	in abt. 7 vols. of 90 % alcohol	in abt. 3,5 vols. of 90 % alcohol	Residue 8 % 100 %

According to Aignan[2], the specific angle of rotation $[\alpha]_D$, of these varieties of rosin oil was as follows: —

1. *Huile blanche de choix rectifiée* — 36°
2. *Huile blanche fine rectifiée* . . — 16°
3. *Huile blanche rectifiée* . . . — 10°30.

According to Worstall[3] rosin essence has an iodine value of about 185, rosin oil one of about 97, whereas that of turpentine oil (see p. 30) is above 370.

According to Utz[4], the absorption of bromine diminishes with the degree of rectification.

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[1] With water vapor about 10 p.c. distil over: d_{15° 0,9237; $\alpha_D + 21^\circ 10'$.

[2] In the original [Compt. rend. **109** (1889), 944] the values are again as large. According to Vèzes und Mouline (*Sur l'essai technique de l'essence de térébenthine des Landes.* Bordeaux 1902, p. 2) these observations were made with a 200 mm. tube.

[3] Journ. Soc. chem. Industry **23** (1904), 302; Chem. Zentralbl. **1904**, I. 1676.

[4] Chem. Rev. Fett- u. Harzind. **13** (1906), 161; Chem. Zentralbl. **1906**, II. 636.

Inasmuch as resin essence usually contains portions that boil below 155° (see above) these should be isolated by fractional distillation. The identification of resin essence is brought about mostly by color reactions, which, however, do not always yield corresponding and unquestionable results when applied by different analysts to the several products used as adulterants. However, since better methods are wanting, the principal color reactions may here be mentioned.

According to Herzfeld, pinolin produces a yellowish-green color when shaken with an aqueous solution of sulphur dioxide. The same color reaction is also produced by *Kienöl,* a pine tar oil.

In order to demonstrate the presence of pinolin in turpentine oil, according to Valenta[1]) the oil is fractionated and fraction — 160° is utilized for the following reactions: With acetic acid anhydride and a drop of sulphuric acid it produces an intensively green color. Further, if 1 part of this fraction is carefully heated with 1 to 2 parts of a 6 p. c. solution of iodine in chloroform or carbon tetrachloride in a water bath or in the flame of a Bunsen burner, an intensively green or olive color is produced.

For the distinction of rosin essence (pinolin), more particularly of that fraction thereof boiling up to 170° *(Terpentinessenz)* and for distinguishing between it and similar oils, such as turpentine oil, pine tar oil, camphor oil and mineral oil, Grimaldi[2]) recommends a color reaction which depends on the characteristic green color produced by the action of tin and concentrated hydrochloric acid with the rosin essence. For the purpose of carrying out this test, 100 g. of the oil to be investigated are fractionated so that at first five fractions of 3 cc. each are collected, then fractions of 5° each up to 170°. To 3 cc. of each fraction an equal volume of concentrated hydrochloric acid is added without shaking and a piece of metallic tin as large as a grain of rice. The test tubes are heated for five minutes in a boiling water bath, shaken, and heated another five minutes. According to the amount of rosin essence or similar low-boiling substance present, an intensively emerald

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[1]) Chem. Ztg. **29** (1905), 807.

[2]) *Ibidem* **31** (1907), 1145.

green color is produced more or less readily. If the reaction is but faint, it is recommended to use 200 to 400 cc. for the test, to collect fractions of 30 cc. each and to re-fractionate these as recorded above. The other oils, *viz.* turpentine oil, pine tar oil, camphor oil and mineral oil yield a straw-yellow to brownish color with tin and concentrated hydrochloric acid. It is claimed that the presence of five per cent. of rosin essence in its mixtures with turpentine oil, and of 10 p. c. with pine tar oil can be detected.

Marcusson[1]) recommends the above reaction as serviceable.

According to Grimaldi[2]), Halphen's reaction can likewise be applied to the fractions of a questionable oil. It produces a yellowish-green color when bromine vapors are passed into a solution of the rosin essence in carbon tetrachloride in the presence of phenol. The fractionation is modified so as to collect at first six fractions of 1 cc. each (as above) and then fractions of 5° each. Fractions obtained from pinolin-containing oils show a coloration that varies between lemon yellow and an intense yellow which, after a few minutes changes to malachite green. The color is very intense and is produced with a single drop of oil. The presence of alcohol or water does not interfere with the reaction. With turpentine oil the reagent produces no coloration, with pine tar oil, rosin oil, camphor oil &c. a color intermediate between red and violet.

Grimaldi carries out the test in the following manner: Into a white porcelain dish, 4 cm. in diameter, there are placed a drop of the substance to be examined and 2 cc. of a mixture consisting of 1 cc. of molten, crystallized phenol and 2 cc. of carbon tetrachloride. By means of a special apparatus, provided with a rubber bulb and containing a solution of 3 cc. of bromine in 12 cc. of carbon tetrachloride, bromine vapors are spread above the dish. The uniform distribution of the bromine vapors is accomplished by means of a funnel-like attachment blown on to the spray and fitting closely to the rim of the dish. The action of the vapors is continued until a yellow coloration (ranging between lemon yellow and an intense

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[1]) Chem. Ztg. **33** (1909), 966.

[2]) *Ibidem* **31** (1907), 1145; **34** (1910), 721.

yellow) is observeable along the sides of the capsule and on the surface of the liquid. Rosin essence of the boiling temperature of 170° yields a yellow color which soon changes to malachite green. The time necessary for the appearance of the color varies according to the rosin essence content of the oil under examination. If the reaction is but faint, a larger amount of oil is needed as in the previous test. Fractions of 20 cc. are first collected and these are then refractionated into fractions of 1 cc. each.

As already pointed out under "Acid Content" on p. 22, traces of rosin oil almost invariably distill over with the turpentine oil. With the more primitive methods of distillation this cannot be avoided, hence a moderate rosin essence content must be tolerated.

According to Vèzes[1]), the presence of abnormal amounts of rosin oil can be detected refractometrically by testing the five equal fractions into which the turpentine oil has been resolved. This method likewise throws light on the presence of direct adulterants *("adultérants anormaux")*, such as petroleum hydrocarbons, carbon disulphide, &c.

> Test: 250 cc. of turpentine oil are resolved, by means of fractional distillation, into five parts of 50 cc. each, four of which are distillates, the residue constituting the fifth. Assuming that the boiling points of the adulterants vary from that of the turpentine oil, the middle fraction 3 may be regarded as pure turpentine oil and the adulterants looked for in the extreme fractions. Under like physical conditions the indices of refraction n_1, n_3 and n_5 of fractions 1, 3 and 5 respectively are determined. From the differences of the values found, *viz.* $n_3 - n_1 = \delta$ and $n_5 - n_3 = \Delta$, conclusions are drawn as to the purity of the oil. A systematic study of δ and Δ for mixtures of rectified turpentine oil with practically possible adulterants has established the fact that in the presence of exclusively normal impurities δ remains almost unchanged. (For rectified turpentine oil $0{,}0000 < \delta < 0{,}0010$). However, with the increase of the percentage of added substances, Δ increases. This increase corresponds to the formula $\Delta = 0{,}0032 + 0{,}0037 . X$ (X = p. c.

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[1]) Bull. Soc. chim. III. **29** (1903), 896.

rosin oil + colophony). The determination of the acid value A enables the computation of the percentage of colophony C according to the equation $C = \frac{A}{1,7}$, hence the difference X—C will yield the percentage of rosin oil. The addition of adulterant brings about a lowering of the boiling point and causes appreciable differences in the values for δ and Δ. Pure turpentine oil should reveal the following values.

δ should vary between 0,0000 and 0,0010,
$\Delta < 0{,}0125$ (corresponding to 2,5 p. c. of normal impurities),
$A < 1{,}5$[1]).

DETECTION OF PINE TAR OIL. The proof for the admixture of pine tar oil in turpentine oil is commonly afforded by demonstrating the presence of the byproducts of destructive distillation by means of color reactions. However, such a method yields no results if the malodorous byproducts have been carefully removed by means of chemicals. A considerable number of patents[2]) have been awarded to such processes. The detection of an adulteration with pine tar oil is possible only when the physical properties of the mixture have been greatly modified or if its chemical composition (comp. pine tar oils p. 102) differs materially from that of turpentine oil.

Inasmuch as higher boiling terpenes predominate in pine tar oils the addition of such an oil increases the boiling temperature of the adulterated turpentine oil. The specific gravity is but slightly increased by the addition of pine tar oil. The index

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[1]) In the paper referred to in footnote 1, p. 46 the statement occurs that $A < 1{,}0$. The permissible acid content A was later increased by Vèzes (*Sur la définition de l'essence de térébenthine commercialement pur.* Bordeaux 1910, p. 9) to 1,5.

[2]) The treatment of pine tar oil, with alkali and subsequently with acid, formerly in vogue, does not suffice completely to remove the undesirable constituents. According to the following patents, the oils thus treated are subsequently treated in a variety of ways: Ger. Pat. 170 543 (Kaas), Treatment with alcoholic potassa and then with sulphuric acid. — Ger. Pat. 170542 (Heber), Action of permanganate solution. — Ger. Pat. 180 499 (A. Hesse), Distillation over alkali or alkali earth metals. — Ger. Pat. 202 254 (Pellnitz), Treatment with ozonized air after the addition of acids, distillation with lime. — Ger. Pat. 204 392 (Ahlers), Action of zinc dust. — Ger. Pat. 239 546 and supplemental patents (Schindelmeiser), Heating with ammonia, with or without cyanides.

of refraction is also slightly increased. The optical rotation affords no clue.

So far as the color reactions are concerned, it should be noted that in many instances rosin essences and rosin oils behave like pine tar oil. This is not surprising since products of the dry distillation of turpentine are contained in pine tar oil as well as in the distillate of colophony.

The Herzfeld test[1]) with sulphurous acid is carried out in the following manner: In a test tube the oil to be examined is shaken with an equal volume of a solution of sulphurous acid. In the presence of pine tar oil the oily layer is colored yellowish green. It is claimed that the presence of 10 p. c. of pine tar oil in turpentine oil can thus be detected.

Another test is recommended by the same author. A small piece of potassium hydroxide is covered with the oil to be tested. The presence of pine tar oil is revealed by the brown coloration of the potassium hydroxide which soon results. H. Wolff[2]) has modified this test by shaking 0,5 to 1 cc. of potassa solution (d 1,3) with the oil, heating the mixture on a water bath for from 2 to 5 minutes and then adding 3 cc. of water to effect a separation of the emulsion. Pine tar oil colors the aqueous layer brown, turpentine oil produces only a slight coloration or none at all.

Wolff mentions two other pine tar oil tests:

5 cc. of oil are boiled with 5 drops of nitrobenzene and, after the addition of 2 cc. of 25 p. c. hydrochloric acid, are boiled for another 10 seconds. Pine tar oil is colored brown, the hydrochloric acid is colored brown to black (Lyon's reaction with concentrated hydrochloric acid). Turpentine oil produces a much lighter color.

If to a mixture of 4 cc. each of ferric chloride solution (1 : 2500) and of potassium ferricyanide solution (1 : 500) 2 or at most 10 drops of the oil to be tested are added and the mixture thoroughly shaken, pine tar oil rapidly produces a decided precipitation of Prussian blue, whereas turpentine oil produces a noticeable precipitate only after hours.

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[1]) Zeitschr. f. öff. Chem. **10** (1904), 382; Chem. Zentralbl. **1904**, II. 1770.

[2]) Farben Ztg. **17** (1911), 21, 78; Chem. Ztg. Repert. **36** (1912), 64.

For the like purpose C. Piest[1]) proposes the following reactions: 5 cc. of acetic acid anhydride are shaken with 5 cc. of turpentine oil in a test tube. While shaking and cooling, 10 drops of concentrated hydrochloric acid are added. After thorough cooling another 5 drops of concentrated hydrochloric acid are added. The liquid again becomes warmer and a clear solution results. When treated thus turpentine oil remains water white, pine tar oil turns black.

Old turpentine oils should in all cases be distilled before being tested.

The test suggested by Valenta[2]) is as follows: If equal volumes of a 1 p.c. gold chloride solution and turpentine oil are shaken in a test tube, heated in a waterbath for a minute then removed and again shaken, the turpentine oil reveals a separation of gold in the oily layer only. The solution itself is not decolorized. The pine tar oils, whether rectified or not, likewise pinolin, decolorize the gold solution completely. Pinolin decolorizes the solution most rapidly.

In order to distinguish between pine tar oil and turpentine oil, Utz[3]) employs the following test: Equal volumes of the oil and tin chloride solution, prepared according to the German Pharmacopœia, are mixed. Austrian turpentine oil colors the reagent yellow, but itself remains colorless; Greek oil imparts an orange color to the reagent, and is itself colored yellow; American turpentine oil also colors the reagent orange and itself turns yellow. All varieties of pine tar oil, however, colored the tin chloride solution a raspberry red, the oil itself mostly yellow. In some instances the oil was likewise colored raspberry red. In a few instances the well known brown to black coloration was produced. Positive results were also obtained with mixtures of pine tar oil and turpentine oil.

DETECTION OF VARIOUS HYDROCARBONS. Benzene and its homologues, "solvent naphtha", *"Schwerbenzol"*, all reduce the bromine value (normally 220 to 240) of the turpentine oil. According to Herzfeld)[4] these additions are recognized by

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[1]) Chem. Ztg. **36** (1912), 198.

[2]) *Ibidem* **29** (1905), 807.

[3]) Chem. Zentralbl. **1905**, I. 1673.

[4]) Zeitschr. f. öff. Chem. **9** (1903), 454; Chem. Zentralbl. **1909**, I. 549.

treating 10 cc. of oil with 30 cc. of concentrated sulphuric acid while cooling the mixture. Pure oils are thereby dissolved leaving not more than 1 cc. of residue. If a larger residue remains which can be brought into solution by subsequent shaking with fuming sulphuric acid, the presence of benzene hydrocarbons is probable. According to Marcusson[1]) this method is not reliable. While it is true that, in the cold, benzene and its immediate homologues are attacked but little by concentrated sulphuric acid, complete sulphonation results readily in the presence of large amounts of turpentine oil, so that the residue of adulterated oils is no greater than that of some pure oils. Herzfeld[2]), however is of the opinion that his method can be used if the mixture is well cooled and less sulphuric acid is used. Nevertheless[3]), Marcusson, after another test, adheres to his original opinion. The conflict of opinion concerning the utility of the sulphuric acid method may possibly be explained here, as on a previous occasion (comp. p. 39), in that the several analysts employed sulphuric acid of different strength in their tests.

The nitric acid method described on p. 37 is recommended by Marcusson[4]) as the best for the detection of benzene hydrocarbons. The nitric acid solution resulting is utilized for testing for benzene, toluene, xylene &c. their nitrocompounds being dissolved therein.

> "Into a $^1/_2$ l measuring flask, the neck of which is calibrated into $^1/_{10}$ cc. for 10 cc. and which contains 150 cc. of water, the nitric acid solution is poured. The mixture is heated for $^1/_4$ hour on a water bath in order to render the reaction products of the turpentine oil as water soluble as possible. After cooling, the solution is set aside for several hours, if necessary over night, in order that it may become clear. If reddish-brown oily drops (nitro compounds) have separated either on the bottom or at the surface, benzene hydrocarbons were present. If, however,

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[1]) Chem. Ztg. **33** (1909), 966.

[2]) *Ibidem* **33** (1909), 1081; **34** (1910), 885.

[3]) *Ibidem* **34** (1910), 285.

[4]) *Ibidem* **36** (1912), 413, 421.

only small amounts of resinous matter, usually floating on the surface, are observed, benzene hydrocarbons need not be suspected.

For the approximately quantitative determination of the benzene hydrocarbons, sulphuric acid of the specific gravity 1,6 is added to the reaction mixture. As a result of the increase of the specific gravity of the aqueous liquid, the oily nitro bodies rise to the surface and are brought into the graduated neck of the flask, when their volume can be measured. This volume is a direct indication of the benzene hydrocarbon content of the oil tested."

Marcusson[1]) has made a systematic investigation of the results produced by the addition of 10 p. c. of the several benzene hydrocarbons on the refraction of turpentine oil, also in how far this influence can be traced on the several fractions of such mixtures. Whereas with pure oils a slow increase in the refraction of the several fractions is observed, oils containing 10 p. c. of benzene compounds show a more or less marked drop. However, in the case of "solvent naptha" this is followed by a decided increase toward the end.

Carbon tetrachloride which, because of its high density, is added to conceal the addition of benzene, can, according to Marcusson be readily detected by means of the Beilstein copper test, also by the separation of potassium chloride when boiled with alcoholic potassa, and by fractionation. For its quantitative determination in the presence of turpentine oil and benzin, the chlorine content can be determined according to Carius' method. Pure carbon tetrachloride contains 92,2 p. c. Cl.

The adulteration of turpentine oil with copal oil has been observed by Vaubel[2]).

Production and commerce. So far as importance of production and the value of the product are concerned, the United States of America occupy the first position. This position is indicated by the following statistics:

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[1]) Chem. Ztg. **33** (1909), 967.

[2]) Zeitschr. f. angew. Chem. **23** (1910), 1165.

Production for 1910 expressed in bbls. of 50 gallons (= abt. 190 l. or 165 kg.):

Year[1]	1910	1909	1908	1907	1906	1905
Number	555 000	580 000	731 000	684 000	—	613 000
Value ($)	17 680 000	12 654 000	14 112 000	18 283 000	—	15 170 000

Export expressed in gallons:

Year[1]	1910	1909	1908	1907	1906	1905
Number	14 252 321	16 061 783	29 433 181	17 176 843	16 182 500	15 894 913
Value ($)	9 627 428	7 779 728	8 301 747	10 314 610	10 320 926	8 902 101

According to the Forestry Bureau of the United States Department of Agriculture 2,300 000 acres of pine forests were used in 1890 for turpentine orcharding.

So far as production and export of turpentine oil forty years ago were concerned, North and South Carolina only came into consideration. The exhaustion of the trees in these states caused the industry to move farther southward. Thus Charleston, S. C., formerly an important port for export, no longer exports turpentine oil. The commerce in this article has drifted to Savannah and Brunswick in Georgia. In the world's commerce Savannah is the principal market for turpentine oil. Here is collected all the information concerning production, shipments from the interior, export and consumption. Here also is regulated the world's price (in cents per gallon) for turpentine oil. But even Savannah no longer exports fully one-half of all the oil, as it did 12 years ago, but only one-third. The cause lies in the fact that the forests of Georgia, which were regarded inexhaustible only a short time ago, are no longer affording the same yield. Hence the industry has moved still farther south and has acquired considerable dimensions in Florida and Alabama. Naturally the seaports of these states have entered into sharp competition with Savannah[2]). In recent

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[1]) The fiscal year of the American turpentine industry begins April 1, and ends March 31.

[2]) According to the latest British consular reports, the export of turpentine products from Charleston has ceased completely since 1909. In Savannah, the amount of turpentine oil exported during the last three years has remained almost stationary, amounting to 5236774 gals. in 1909, with a

years attempts have been made to utilize the well-nigh untouched pine forests of the western states, especially of Arizona, the national Bureau of Forestry having taken the first steps in this direction. In Mexico, private companies have likewise taken up the production of turpentine (See p. 81), but the industry is still in its infancy.

The principal European markets for American turpentine oil are London and Hamburg. Antwerp likewise imports considerable quantities.

Imports of turpentine oil in London, in Engl. tons @ 1016 kg.

Year	Total	U. S.	France	Spain and Portugal	Russia and Scandin.	All other countries
1911	24 006	18 181	1183	260	4344	38
1910	23 612	18 264	1138	339	3777	94
1909	22 169	18 298	1020	69	2752	30
1908	28 684	25 184	1291	327	1849	33
1907	25 515	19 593	989	—	4910	23
1906	15 642	19 960	1535	—	4139	8

Expressed in percentages:

Year	U. S.	France	Russia	All other countries
1911	75,73	4,93	18,10	1,24
1910	77,35	4,82	16,00	1,83
1909	82,54	4,60	12,41	0,45
1908	87,79	4,50	6,45	1,26
1907	76,78	3,88	19,24	0,10
1906	77,84	5,99	16,14	0,03

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value of $ 2629464; 4355122 gals. in 1910, with a value of $ 2760193; and 5221316 gals. in 1911, with a value of $ 3039232. Brunswick exported 245950 gals. in 1911, with a value of $ 119725. The exports from Pensacola, Fla., however, increased very materially, *viz.* from 1920723 gals. in 1910, with a value of £ 253100 to 4629519 gals. in 1911, with a value of £ 424976. The exports in 1909 were valued at £ 167085.

Imports of turpentine oil in Hamburg, in barrels of 165 kg. (net)[1]).

Year	Total	American	French	Spanish
1911	49 323	42 102	5 618	1 603
1910	54 727	47 754	6 293	732
1909	70 896	60 727	8 119	2 050
1908	75 611	65 821	5 523	4 267
1907	66 938	58 025	5 406	3 507
1906	70 741	—	—	—
1905	65 224	—	—	—

Imports of Greek turpentine oil in Hamburg in iron drums with a net capacity of 400 to 600 kg.

1911	2021
1910	1734

German imports of American turpentine oil.

The figures represent gallons.

1910/11	1909/10	1908/09	1907/08	1906/07
2 124 544	2 732 203	3 199 332	3 487 411	2 481 103
1905/06	1904/05	1903/04	1902/03	1901/02
2 916 900	2 414 191	1 638 569	2 112 214	2 874 591

Inasmuch as Western Germany is supplied with turpentine oil via Antwerp, and since some of the turpentine oil imported by England, no doubt, later finds its way to Germany, the above figures do not represent the total German importations.

From the official German import statistics it does not become apparent how much turpentine oil enters the German customs district since turpentine is entered with pine needle oil and rosin spirit under number 353a of the revenue tariff.

The value of American turpentine oil is fixed not merely by supply and demand, but is frequently influenced by speculation, hence the price varies considerably. More particularly in recent years the news as to the threatened exhaustion of the present areas of production, also the quarrels between the several combinations has caused fluctuations such as have not been recorded since the civil war.

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[1]) Corresponds to about 50 gallons the capacity of the American barrels.

Expressed in cents per gallon, the market price in Savannah was as follows for the years indicated:

1911	1910	1909	1908	1907	1906
50¹/₄	77	56	38¹/₂	40¹/₂	67¹/₂

The highest price on record since the civil war was reached toward the end of March 1911 with 107, when the dreaded "dollar limit" was exceeded by 7 cents, only to drop toward the end of the year to one half of this amount.

Much less important for the world's market is the production of turpentine oil in France. Nevertheless it is sufficient to cover the demands of that country and to enable the exportation of a relatively large amount. The importation of American turpentine oils is rendered prohibitive by a duty of fr. 24.— and fr. 12.— respectively for each 100 kg.

The industry is located in the departments Landes and Gironde. The principal markets are Mont de Marsan, Dax, Bordeaux and Bayonne. The last two are export harbors of importance. Fifteen years ago the amount exported was relatively unimportant, amounting to 1938 metric tons in 1896 and to 1412 tons in 1897. In recent years the amount has increased materially, being recorded, in metric tons as follows:

1911[1])	1910	1909	1908	1907	1906	1905
9207	10 954	9220	9212	9754	12 922	12 214

Of these amounts about one-tenth was shipped to London.

As to quality, French turpentine oil is ranked highest among all commercial varieties. In the arts it is frequently preferred to the American oil. As a rule its market value is 5 p. c. higher than that of the American oil.

Of other countries which have produced considerable quantities of turpentine oil in recent years for the world's market, Spain should be mentioned. The industry is located on the northern coast in Bilbao and is in the hands of the *Union resinera española*. The following figures are taken from the commercial reports of this stock company:

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[1]) 11 Months of 1911.

Production of turpentine oil in kg.

Year	1909	1908	1907	1906
Distilled in Spain	4 209 583	4 357 408	3 825 461	3 982 527
Imported	343 011	327 304	785 295	221 815
	4 552 594	4 684 712	4 610 756	4 204 342

Sale of turpentine oil in kg.

Year	1909	1908	1907	1906
Foreign commerce	3 401 944	4 742 699	3 171 099	2 939 797
Domestic commerce	693 634	529 982	693 366	651 010

According to an English consular report, this company controls 54 037 hectares of pine forests. In 1910 the output amounted to 4728 metric tons, of which 4266 tons were exported and 705 tons were sold for domestic purposes. Via Irun 1838 tons were shipped by rail, 700 tons of which were exported to Switzerland.

Among the turpentine oils that enter commerce in relatively large amounts, that produced in Russia should be considered. However, it should be remembered that a considerable portion of the turpentine oil there produced is obtained by the destructive destillation of wood, hence should be regarded as pine tar oil. Russian statistics, not complete in other respects, do not differentiate between the two. Hence only a relative value can be attached to them.

The exports of "turpentine oil" from European Russia for

1910 were	12 243	English tons	valued at	246 753 £
1909 „	12 499	„ „	„ „	206 437 „

For the year 1904 the exports were

of "turpentine, crude"	278 000	poods	valued at	741 000 Rbl.
of "turpentine, distilled"	413 000	„	„ „	1 132 000 „

During the first seven months of the following years, the exports of "turpentine oil" were:

1910	279 000	poods	valued at	815 000 Rbl.
1909	223 000	„	„ „	618 000 „
1908	251 000	„	„ „	638 000 „

Exports of pine tar oil:

1906	500 000	poods	valued at	1 300 000 Rbl.

The North Russian product is regarded as the best, then the Siberian, and finally the Polish turpentine oil[1]).

In accordance with the quality, the commercial value of the Russian turpentine oil is considerably less than that of the varieties previously mentioned. It is indeed the poorest in quality of all commercial varieties. The Russian import duty of 1,08 Rbl. gold pro pood = ℳ 24.40 pro 100 kg. turpentine oil, is a duty for revenue only.

22. American Oil (Spirits) of Turpentine.

Oleum Terebinthinæ Americanum. — Amerikanisches Terpentinöl. — Essence de Térébenthine Américaine.

Origin. The turpentine forests of the southern states consist principally of three species of *Pinus* which are used in the production of turpentine, *viz. Pinus palustris,* Mill. (*Pinus australis,* Mchx.), the longleaf, long-leaved, or southern pitch pine, which is by far the most important American pine for the production of turpentine; the *Pinus heterophylla,* (Ell.) Sudw. (*Pinus cubensis,* Grisebach; *P. Tæda* var. *heterophylla,* Ell.) or Cuban pine, swamp pine, or slash pine, and the *Pinus echinata,* Mill. (*P. mitis,* Mchx.), or short-leaved yellow pine.

Because of the exhaustion of the pine forests along the coastlands of Virginia, North and South Carolina, the turpentine industry has almost completely disappeared from these regions so that they scarcely come into consideration as areas of production. The center of production has moved southward toward the mouth of the Mississippi. The principal producing states are Georgia, Florida and Alabama, followed by Mississippi and Louisiana. In Texas the owners of pine forests maintain a conservative attitude toward tapping because they fear a deterioration of the tree trunks as lumber[2]).

Production. At the beginning of the present century the unsparing exhaustion of the turpentine forests began to make itself felt and caused apprehension. It became apparent that the method of boxing then in use would ruin the forests in the

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[1]) Chem. Industrie **31** (1908), 179.

[2]) G. B. Sudworth, Oil, Paint and Drug Reporter **75** (1909), No. 11, p. 10.

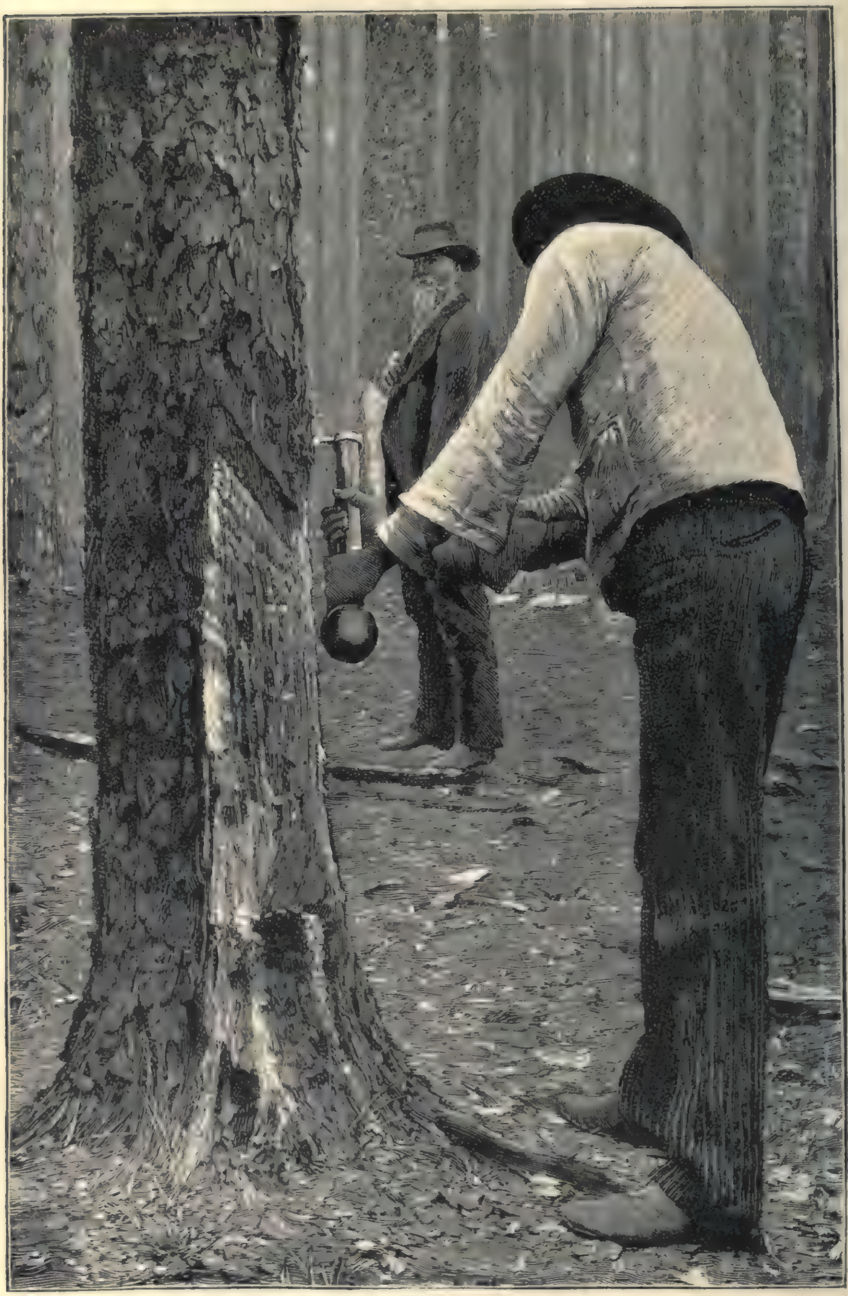

Fig. 4.

Boxing of trunks and removing of bark (Box-System).

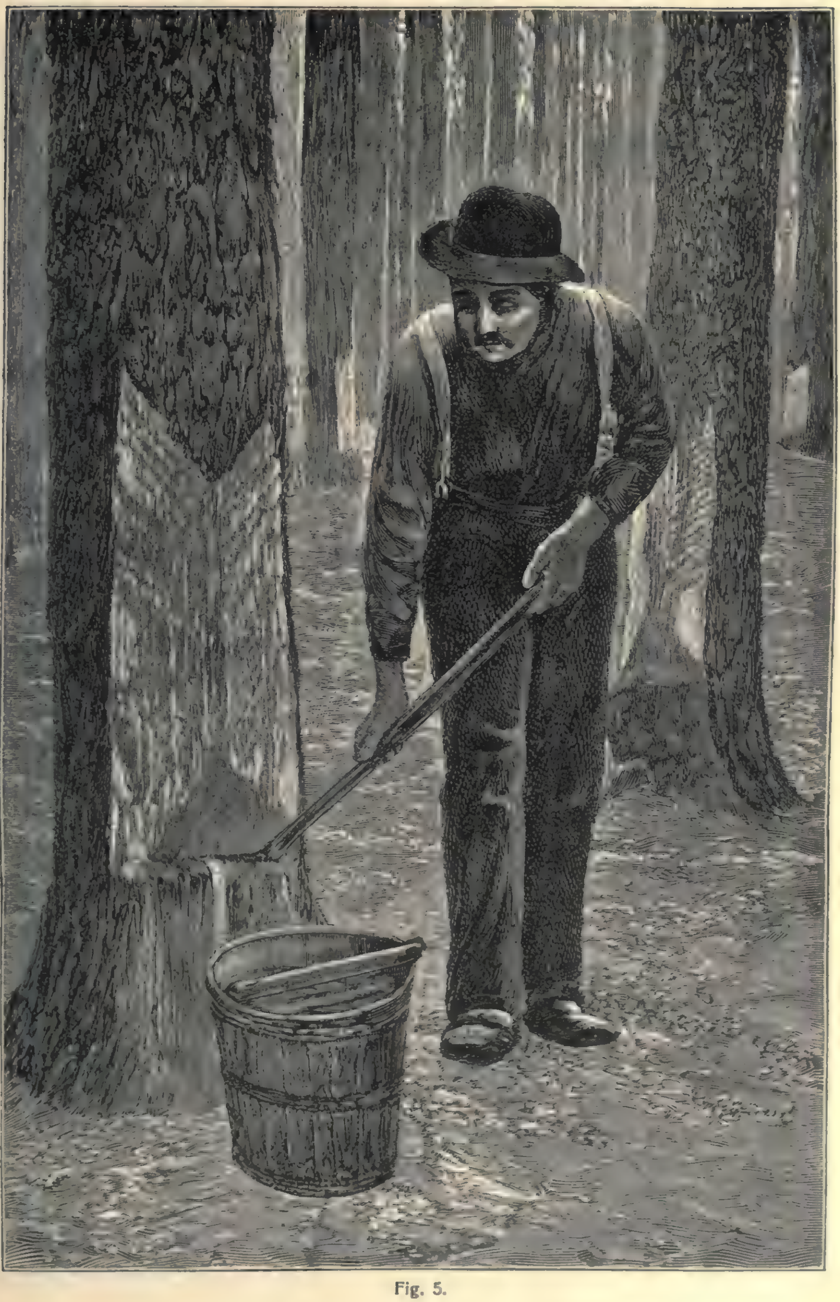

Fig. 5.

Removal of oleoresin from boxes (Box-System).

not distant future, hence it became necessary to look about for a remedy. A result of the boxing method, to be described later, was that after 5 to 6 years of tapping the trees yielded no more turpentine and died. When left to themselves, they were either blown down by the wind or destroyed by fire.

These circumstances induced Dr. Charles Herty[1]) to experiment with the French system of turpentining, which admits of greater protection to the tree[2]). The results were very satisfactory, more particularly after a few necessary improvements had been introduced. It is likely, therefore, that in the near future the change to the "cup and gutter system" will become quite general. According to G. B. Sudworth[3]), of the Bureau of Forestry of the U. S. Department of Agriculture, 1/8 of the orchards employed the new system in 1909, 7/8 still using the old system.

THE BOX SYSTEM.

The operations in the turpentine farms or orchards, which are mostly carried out by negroes, begin with the first dry days of spring, as a rule in April. With the aid of a heavy, sharp axe, a "box" is cut transversely across and into the trunk. The length of the box is about 17 inches, its greatest depth 6 to 7 inches, so that it has a capacity for at least a liter of turpentine. If the diameter of the trunk is great, a second box of equal size is hewn into the tree on the other side.

As soon as the sap flows in spring, a beginning is made with the wounding of the tree. On either side of the box a strip of bark two inches wide and about 8 inches high is removed ("cornering"). The bark of the area above the box thus indicated is then removed to the sap wood by means of an axe (hacking, chipping). According to the temperature, the exudation of oleoresin is stronger or weaker, the turpentine flowing into the reservoir beneath. The wounded surface is enlarged every week or two in accordance with the "bleeding", *i. e.* with the intensity of the formation and flow of the sap which, as stated, varies

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[1]) A new method of turpentine orcharding. Washington 1903.

[2]) At a much earlier date a method was patented in the U. S. by Schuler, which, like the French system, utilizes earthenware pots for the collection of turpentine. Ch. Mohr, The timber pines of the U. S. Washington 1897, p. 71.

[3]) *Loc. cit.*

with the temperature of the air. The wound is increased by exposing more sap wood by removing additional bark. (fig. 4.) This operation ("chipping") is continued to the end of October or as long as warm weather lasts.

In the beginning and so long as warm weather continues, the boxes fill every 2 to 4 weeks when the contents are removed to wooden pails by means of a flat trowel (fig. 5), whence the oleoresin is transferred to barrels. With the advent of the cooler season, the hardened oleoresin adhering to box and wound ("scrape") is removed. The wound is either allowed to heal, *i. e.* to cover with bark, or is worked anew the next spring. In the former instance, the tree is bled at a new place in the second or third season.

The average "turpentine farm" is organized in the following manner: The copper still has a capacity of about 800 gallons[1]) or 20 bbls. of turpentine. This requires an area of 4000 acres (= 1618 hectares) of forest in good condition. This area is sub-divided into 20 sections of about 10000 boxes each. This represents about 4000 to 5000 trees covering an area of about 200 acres, for, according to the size of the tree, each trunk is provided with more than one box: occasionally three and in exhaustive treatment even with four.

In rational operation, the 10000 boxes yield each time they are emptied 40 to 50 bbls. of turpentine of 280 lbs. each.

During the first year of operation and before the capacity of the tree is exhausted by excessive bleeding, the dip resin of such a turpentine farm amounts to 270 bbls. of 280 lbs. each and about 70 bbls. of scrape collected at the close of the campaign. It is figured that upon distillation each barrel of dip resin will yield 7 gallons and each barrel of scrape 3 gallons of turpentine oil. The total annual output, therefore, amounts to about 2200 gals. or 50 bbls. of turpentine oil and 260 bbls. colophony.

The turpentine collected during the first two or three months is almost colorless and is known as "virgin dip," the best commercial variety. It enters the market as "water white" (W. W.), the next best as "window glass" (W. G.). Less transparent and

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[1]) 1 Gallon = 3,785 liters.

more colored qualities of resin obtained later or from older turpentine are designated by letters of the alphabet from N to B.

During the second year of operation about 10 bbls. less of dip resin are obtained whereas the amount of scrape increases to 120 bbls. The amount of turpentine oil obtained during the second year amounts to about 40 bbls. of 50 gals. and about 200 bbls. of rosin. As to quality the oil of the second year is fully equal to that of the first, the colophony, however, is mostly somewhat darker. In the third year the amount of "dip" harvested is diminished.

With the continued use of the original boxes and the enlargement of the wound from year to year, the oleoresin suffers by prolonged exposure and consequent evaporation. The yield of oil diminishes and the quality of the colophony becomes inferior.

THE CUP AND GUTTER SYSTEM.

The new method may be regarded as a combination of the box system with the method commonly employed in France. The "box" made by chopping a hole into the tree is replaced by a "cup" fastened to the trunk by means of a nail. As in the box system the bark is removed to the sap wood and the wound increased upward with the advance of the operation. In order to conduct the oleoresin into the earthen cup suspended below (Fig. 6)[1]) two gutters made of strips of tin about 2 in. wide and from 6 to 12 in. long and bent at right angles, are utilized. These are fastened in incisions made by means of a broad axe in such a manner that each gutter is in a position of 60° to the main axis of the tree trunk. Hence the two form an open angle of 120° when viewed from above. However, the gutters are not of equal height, but one is fastened about 1 to 2 in. higher than the other, so that the turpentine flows from the upper gutter into the lower one and thence into the cup. With the enlargement of the wound upwards, the positions of gutters and cups are also raised. If the trees be thick and rich in oleoresin, several such cups can be fastened on several sides of the trunk. At first the wounds were enlarged by making

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[1]) For figures 6 to 8, I am endebted to the Forest Service of the U. S. Department of Agriculture, Washington, D. C.

Fig. 6.

Collection of Turpentine (Cup- and Gutter-System).

additional incisions 1 to $1^1/_2$ inches deep and $^1/_4$ to $^1/_2$ wide. Later, special axes were constructed whereby strips only $^3/_8$ to $^1/_2$ in. deep and $^1/_8$ to $^3/_{16}$ in. wide were removed, thereby sparing the tree still more.

The advantages of the cup and gutter system over the older box method lie in the fact that the trees remaining in the already thinned out pine forests are spared much more. Whereas the old method exhausted a forest in 4 to 5 years, the new method permits the trees to be operated from 15 to 20 years. Even at the end of this period the trees have a greater lumber value because of the lesser damage effected by the surface wounds.

The cup and gutter system admits of the tapping of young trees which formerly could not be used. The exhausted trees are less liable to destruction by fire. Whenever the dry grass burned, the readily combustible oleoresin in the boxes was apt to take fire, resulting in the destruction of the entire forest. Wind brakes were another danger, since the boxes weakened the trunks causing them to be blown over by storms.

According to the old system, the oleoresin had to traverse a much larger distance before reaching the container, *i. e.* the box. This distance amounted to 15 inches during the first year, to 30 in. during the second year, to 45 in. during the third and to 60 in., during the fourth year. As a result not only the loss from evaporation increased with each year, but the rosin deteriorated as well, becoming darker each year from prolonged exposure to the air. Whereas the old method yielded but 19 to 20 p. c. of oil upon distillation, the new method yields 22 to 25 p. c.

However, the new method likewise has its disadvantages[1]). The cups into which the balsam flows are frequently thrown to the ground by pigs and other animals feeding in the forests. Even when carefully handled many of the earthernware cups are broken. Finally, considerable loss of turpentine oil still results from evaporation. All of these disadvantages as well as the loss from fire can be removed, it is claimed, by certain modifications resulting in an air-tight connection between the tap of the tree and collecting vessel. A hole $2^3/_8$ in. in diameter and not too deep is bored into the sap wood. From the central

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[1]) Scientific American **105** (1911), 383.

axis of this hole two additional cavities, 3/4 in. in diameter, are bored in a direction slanting upward. By smoothing the bark around the central opening a flat cover can be fastened over it. This cover is connected by means of a tube with another cover at right angles to the first. To the latter a glass jar of about 1/2 l capacity can be screwed. The turpentine collects at first in the 3/4 in. bore holes, then in the wider opening and ultimately flows through the tube into the glass jar.

One disadvantage, at least in the beginning, lies in the higher cost of the glass jars and metal attachments as compared with the clay pots and strips of tin.

THE DISTILLATION OF TURPENTINE. As already stated, the distillation of the turpentine on the larger turpentine farms is carried out in large copper stills over direct flame. After the turpentine has been molten in the still, a thin stream of water from the upper part of the condensing vat is passed into the still without interruption to the end of the distillation of each charge. The distillation being ended, the liquid rosin is drawn off from the bottom of the still, strained by means of wire sieves, and filled into barrels for shipment.

The total output of a "turpentine farm", of the size given on p. 61, for the period of 4 years averaged 120000 gals. turpentine oil, 5200 bbls. of rosin of first quality, 4000 bbls. of second grade, and 2400 bbls. of common rosin, also 1200 bbls. of the poorest quality without market value[1]).

Properties. As a rule the specific gravity of American turpentine oil varies between 0,865 and 0,870. However, lighter oils (sp. gr. 0,858) and heavier oils (up to 0,877[2])) are observed occasionally. Freshly distilled or rectified oil is as a rule lighter than crude or old oil.

When distilled in a fractionating flask, about 85 p.c. passes[2]) over between 155 and 163°. For the properties of the individual fractions of a carefully fractionated American oil see p. 19.

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[1]) According to Dr. Carl Mohr's *"Verbreitung der Terpentin liefernden Pinus-Arten im Süden der Vereinigten Staaten und über die Gewinnung und Verarbeitung des Terpentins"*. Pharm. Rundsch. (New York) 2 (1884), 163, 187.

[2]) E. Kremers, Pharm. Review 15 (1897), 8.

As a rule, commercial American turpentine oil is dextrogyrate; not infrequently, however, lævogyrate. In 1884 Armstrong[1]) observed angles of rotation of $+13° 33'$ to $+14° 17'$ in connection with 28 samples of turpentine oil from Wilmington; and of $+9° 30'$ to $+12° 4'$ in connection with samples from Savannah. Two oils, obtained toward the close of the last century, from Savannah, were slightly lævogyrate: $\alpha_D - 0° 40'$ to $-2° 5'$. For oils obtained directly from this port, Dr. C. Kleber observed as high as $-22° 30'$[2]).

Fig. 7.

Turpentine distillery of the older type.

In a bulletin[3]) issued by the Department of Agriculture which deals primarily with wood turpentine oil and with pine tar oil (See later), the following properties of pure turpentine oil are recorded.

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[1]) Pharmaceutical Journ. III. **13** (1883), 584.

[2]) Private communication.

[3]) F. P. Veitch and M. G. Donk, Wood turpentine, its production, refining, properties and uses. U. S. Dept. of Agriculture, Bur. of Chemistry, Bulletin No. 144, 1911. p. 22.

Fig. 8.

Distillation of Turpentine in North America.

d_{20° 0,8617 to 0,8889; $\alpha_{D20^\circ} - 34{,}8^\circ$ to $+29{,}6^\circ$; n_{D20° 1,4684 to 1,4818; begins to boil (uncorr.) between 154 and 159°, 73 to 99 p. c. distilling over up to 170° and 88 to 99 p. c. up to 185°; iodine value, according to Wijs 350 to 400; A. V. 0,140 to 0,286; S. V. 2,44 to 8,60; colorimeter value (Lovibond) 0,7 to 2,5 for yellow and 0,0 to 0,5 for red.

The variation in the direction of the optical rotation is due to the fact that American turpentine oil is distilled from several species of *Pinus*. Long-leaved pine, *Pinus palustris*, yields dextrogyrate oil, Cuban or slash pine, *Pinus heterophylla*, lævogyrate oil. In the collection, the oleoresins of both are mixed indiscriminately resulting in variations of the optical rotation. Inasmuch as the oleoresin of *Pinus palustris* commonly predominates, the oil is mostly dextrogyrate.

C. H. Herty[1]) has made an interesting study of the optical rotation of the oils from the same tree for a prolonged period. Fourteen trees of a Florida turpentine farm were selected, half of which were *Pinus palustris*, the other half *Pinus heterophylla*. Three series of observations were made. For the first series three trees of each species were selected: a small, young tree, a medium tree, and an old large tree. For the second series two trees each of both species were selected which had yielded turpentine during the previous year, but which had been wounded only half as deep as customary. For the third series two trees of each species were selected that had been treated in the usual manner during the previous year.

The oils distilled from the oleoresins collected early in spring revealed great variation in their optical rotation. With two exceptions *Pinus palustris* yielded dextrogyrate oil, *Pinus heterophylla* lævogyrate oil. In the course of the campaign six more samples were collected from each tree. In most instances the angle of rotation remained constant throughout the year. Owing to unexplained biological conditions, variations of the optical rotation were observed in three instances. The tree that showed the greatest variations was the one from which one would have expected it least, since it was healthy and strong throughout. Difference in the direction of the rotation was like-

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[1]) Journ. Americ. chem. Soc. **30** (1908), 863.

wise observed in connection with trees of the same species. Inasmuch as they grew under the same conditions of climate, light and soil, no explanation has been found for this phenomenon. Inasmuch as the oils, consisting largely of pinene, revealed no differences in their boiling temperatures, the mixtures appear to consist of *d*- and *l*-pinene. The direction of rotation is influenced by the predominance of the one or other modification.

The oils of *Pinus Tæda,* L. (Loblolly pine) and *P. echinata,* Mill. (Shortleaf pine) are almost identical with the oils of *Pinus palustris,* Mill. and *P. heterophylla,* (Ell.) Sudworth. Their principal constituent is *α-pinene*[1]).

23. French Oil of Turpentine.

Oleum Terebinthinæ gallicum. — Französisches Terpentinöl. — Essence de Térébenthine Française.

Origin. The pine growing on the dunes ("Landes") of Southwestern France and used for the production of turpentine is *Pinus Pinaster,* Sol. (*Pinus maritima,* Poir.), the *Pin maritime* or *Pin de Bordeaux* of the French (Ger. *Seestrandkiefer* or *Igelföhre*). The country thus utilized constitutes a triangle outlined by the Atlantic ocean, the Garonne and Adour rivers. The pine forests cover an area of 200000 ha. in the Département de la Gironde, 500000 ha. in Lot-et-Garonne[2]). The principal markets for turpentine, turpentine oil, galipot and colophony are Mont de Marsan, Dax, Bordeaux and Bayonne.

The former production of turpentine in the Sologne ceased after the frosts of 1879/80 had largely killed the forests. However, the industry has recently been revived[3]).

THE PRODUCTION OF TURPENTINE[4]). The production of turpentine begins in spring with the flow of the sap. The bark

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[1]) Herty and Stem, Zeitschr. f. angew. Chem. 21 (1908), 1374.

[2]) Vèzes, *La gemme Landaise et son traitement.* Bordeaux 1905. — *La récolte et le traitement de la gemme du pin maritime.* Bordeaux 1910.

[3]) Corps gras industriels 34 (1908), 178.

[4]) Vèzes, *loc. cit.* — Oesterle, *Die Harzindustrie im Südwesten Frankreichs.* Berichte d. deutsch. pharm. Ges. 11 (1901), 217.

Fig. 9.

French Method for the Production of Turpentine.
According to the Reports of Roure-Bertrand Fils.

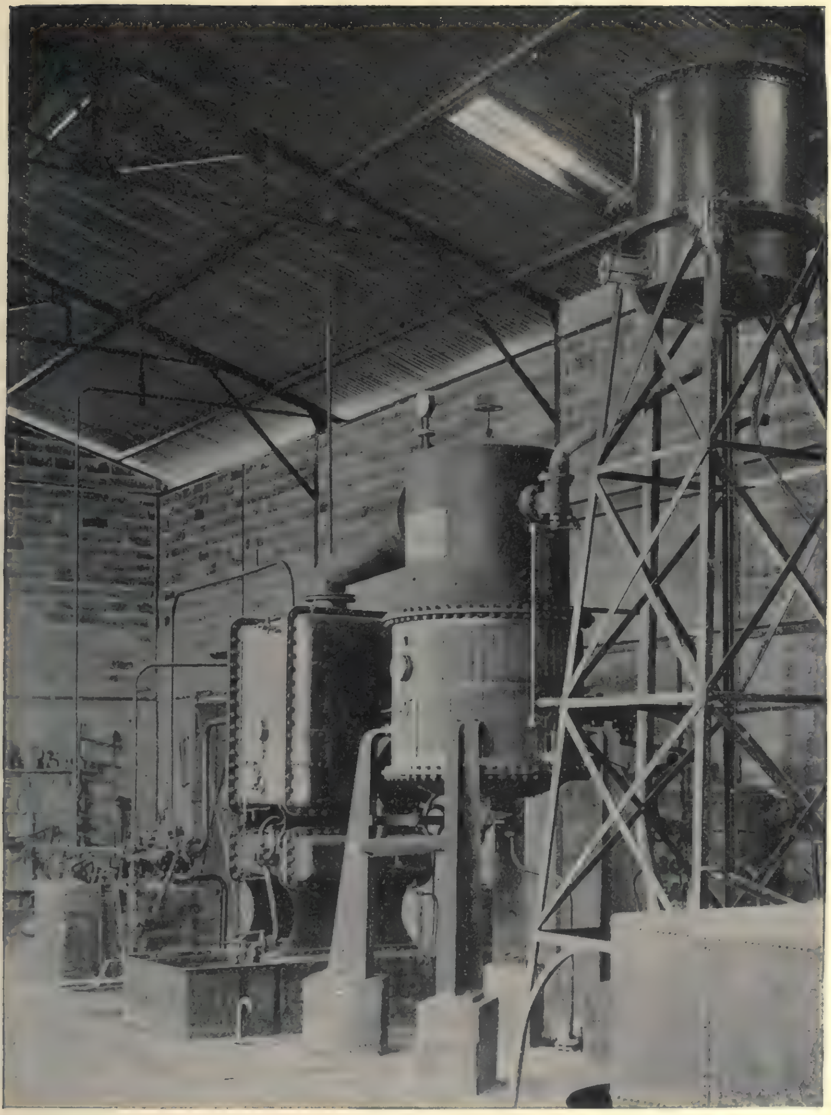

Fig. 10.

Modern French Turpentine Distillery.
According to the Reports of Roure-Bertrand Fils.

near the base of the tree is removed and a wound made *(carre)* 4 cm. long, 9 cm. wide and 1 cm. deep, *i. e.* to the sap wood. Beneath this wound a curved incision is made with a special instrument, and a strip of tin *(crampon)* inserted. Underneath it an earthern vessel is fastened by means of a nail so that the oleoresin will flow into it. In lengthening periods, varying according to the season, the wound is elongated upwards *(piquage),* the workman making incisions 1 to 2 cm. deep with his axe *(hachot).*

The oleoresin *(gemme)* flows slowly into the pot. A part of it, however, dries as it flows down and covers the ground with a yellowish white crust *(barras* or *galipot).* This is also collected and brought into commerce as such. The contents of the pots are emptied into larger collecting vessels *(escouarte)* or ditches *(barcous)* every 14 to 20 days. The galipot is collected twice during the campaign, *viz.,* in June and November.

During the second and subsequent years the wound is lengthened upwards to the extent of 75 cm. each year so that at the end of the fifth year the *carre* is almost 5 m long. Each year the pot is fastened at a higher point. When too high to be reached from the ground, a peculiarly constructed ladder (fig. 9 p. 70) is used.

The second *carre* is started to the right of the first and the third between the second and first so that they are separated by $^1/_3$ of the circumference of the tree. Not infrequently three other wounds are later inflicted between the first three.

A distinction is made between the *gemmage à vie,* which implies a protection of the tree, and the *gemmage à mort* which does not consider the life of the tree. The tapping of the trees begins with their 15th year and occasionally lasts 45 years so that trees may acquire the age of 60 years.

DISTILLATION OF THE TURPENTINE. The distilleries in the Landes are very numerous, there being one on almost every property. However, for the sake of avoiding fires, they are not in the forests. As a rule they are very primitive. There are probably 2 or 3 modern distilleries with modern equipment (fig. 10, p. 71) which belong to the large wood dealers[1]. The

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[1]) R. Lienhart, Bull. Sciences pharmacol. **17** (1911), 161.

common method is that of distillation over the free flame with the introduction of water. The bottom of the still is either flat or concave, the sides are 15 to 20 cm. high. On the sides there rests a conical section, the lower diameter of which is 1 m., the uppcr 75 cm., topped by a disc on which rests the helmet. The bottom is provided with an exit tube 10 cm. wide through which the colophony is drawn off at the end of the distillation. At about half the height, the still is provided with an inlet tube through which the turpentine, liquified by heat, is allowed to enter the still. The capacity of the still is about 300 l. At the highest point of the helmet, a funnel with stopcock is applied through which the water necessary for the distillation is allowed to enter. The distillation lasts somewhat more than an hour, hence from 8 to 10 distillations can be conducted in a day. The yield amounts to about 20 p.c. turpentine oil and 70 p.c. colophony, the loss of 10 p.c. being due to impurities and water contained in the turpentine.

The condenser consists of a copper spiral contained in a barrel through which water flows.

If the turpentine is not purified before distillation *(distillation à cru)* the yield is somewhat higher, but the residual colophony is not only impure but also dark in color so that it can be used only for the production of rosin oil. This oil is produced by distilling the rosin, to which some lime has been added, over direct flame. If a light colored, transparent colophony is desired, the turpentine is purified, previous to the distillation, by melting, decanting and filtration. *(Distillation à térébenthine.)*

The primitive method of distillation over direct flame has in many instances been replaced by the use of steam, either under pressure or superheated. The modified stills constructed for this purpose are protected by a series of patents[1]). Noteworthy is a recent patent by Castets (French patent No. 391835 of 1908). It admits of the continuous distillation of turpentine to turpentine oil and colophony under vacuum.

Properties[2]). d_{15° 0,865 to 0,875; α_D —29 to —23°. During storage, especially when carelessly stored, the angle of rotation

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[1]) Vèzes, *La gemme Landaise*, etc., p. 97.

[2]) Comp. also p. 11, footnote 1.

diminishes[1]). This explains some of the deviations recorded from the above figures.

When distilled, only a few drops pass over between 152 and 155°, about 85 to 90 p.c. boiling between 155 and 165°[2]).

24. Austrian ("Neustædter") Oil of Turpentine.

Origin and Production. The Austrian turpentine industry is located principally in Lower Austria, in the neighborhood of Wiener Neustadt. The area covered begins south of Vœslau, extends southward to Neunkirchen and northwestward to Hainfeld. The *Pinus Laricio,* Poir. (*P. Laricio* var. β *austriaca,* Endl.), Germ. *Schwarzkiefer, Schwarzfœhre* is used, it being tapped when it has reached an age of 50 years. The box system, the older American method, is employed.

Very near to the ground, a cavity is hewn into the trunk of the tree into which the oleoresin is caused to flow. Above this cavity *(Schrot* or *Grandel),* the bark and a part of the sap wood are removed from time to time by means of a curved axe *(Texel),* so that gradually a height of from 35 to 45 cm. is reached. Most of the turpentine thus produced flows into the cavity below. It is known as *Rinnpech* and is dipped out from time to time. That portion which remains on the trunk is removed at the end of the campaign and is known as *Scharrpech.* In order to prevent the healing of the wound, which extends $^2/_3$ around the tree, a small strip of bark is cut off twice each week during the season, *viz.* from the middle of March to the middle of September. In the course of 15 to 20 years $^2/_3$ of the circumference of the tree are deprived of their bark to a height of from 5 to 6 m. During the subsequent 5 to 10 years one-half of the remaining third is treated in like manner. At the end of 25 to 30 years all but $^1/_6$ of the stem is deprived of its bark to a height of 5 to 6 m. above the *Schrot,* when the tree is no longer useful for the production of

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[1]) See p. 26. Comp. Dubroca, Journ. de Chim. et Phys. 5 (1907), 468, also Polack, *Étude des mélanges doubles formés par l'oxalate d'éthyle avec l'essence de térébenthine.* Bordeaux 1910, p. 4.

[2]) For the detailed data of a fractional distillation of a French turpentine oil, see p. 19.

oleoresin. In order to prevent too slow a flow of oleoresin and consequent evaporation, it is directed to the *Schrot* by means of a channel of chips that are nailed to the tree. 100 trees yield about 300 kg. turpentine each year.

The distillation is quite commonly carried out in the most primitive manner in small copper stills over direct fire. Their average capacity is 75 kg. of crude oleoresin (commonly 2 parts *Rinnpech* and 1 part *Scharrpech*). The average yield of turpentine oil is 16,5 p.c., of colophony 64 p.c., the remainder consisting of resinous residues *(Pechgriefen),* water and impurities.

According to Stöger[1], the annual production of the area described above amounted to 5000 t. for 1880. The present output is estimated at 6000 t. The number of distilleries in this district are 16, one of which employs steam as well as direct heat.

Properties. Information concerning the properties of Austrian turpentine oil is very scant. Five samples examined by Schimmel & Co. revealed the following properties: d_{15° 0,863 to 0,870; α_D $-36^\circ 30'$ to $-39^\circ 10'$[2]; n_{D20° 1,46905 to 1,47033; soluble in 6 parts by volume or more of 90 p.c. alcohol; in a Ladenburg fractionating flask 48 p.c. distilled over between 156 and 158°, 32 p.c. between 158 and 160°, 14 p.c. between 160 and 165°, 8 p.c. between 165 and 175° (748 mm.), residue 10 p.c.

25. Spanish Oil of Turpentine.

For a number of years Spanish oil of turpentine has been a regular article of commerce. At the beginning of the present century the principal producers of turpentine in Spain united to form a corporation controlling 20 concerns with headquarters in Bilbao. The production of turpentine, which in 1898—99 had amounted to 1860000 kg., had risen to 3600000 kg. in 1905—6. Of the latter amount 67 p.c. were exported and 23 p.c. were

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[1] *Mitteil. a. d. forstl. Versuchswesen in Österreich* 1881, 408; A. Tschirch and G. Schmidt, Arch. der Pharm. 241 (1903), 570.

[2] A sample previously examined by Schimmel & Co. showed d_{15° 0,866 and α_D $+3^\circ 46'$. Inasmuch as Ledermann and Godeffroy (Jahresb. f. d. Pharm. 1877, 394) likewise record lævorotation in accordance with the angles given above, this oil apparently was not Austrian oil.

consumed in Spain[1]). The exported oil is shipped in tank cars to Antwerp from which point it is distributed.

Pinus Pinaster, Sol. is the principal species used in Spain for the production of turpentine. In harmony with this fact is the observation that the Spanish turpentine oil obtainable in Germany[2]) corresponds in its properties with those of the French oil, an observation which in itself would indicate the same source.

The oil of *Pinus halepensis,* Mill., the Spanish Aleppo pine has been examined by Fernandez[3]). Whereas other investigators had found the distillates of *Pinus halepensis,* Mill. to agree well in its properties with those of Spanish turpentine oil, Fernandez observed the unusual rotation of $[\alpha]_D - 8{,}73°$. Specific gravity $d_{20°}$ 0,859 and index of refraction (n_D 1,4654), however, were normal. Hence the oil examined was not identical with Aleppo pine oil, neither with the common Spanish turpentine oils.

26. Greek Oil of Turpentine.

Origin and Properties. Like the Spanish oil of turpentine, the Greek oil has acquired a certain commercial significance only in recent years[4]). Turpentine is produced in all of the provinces of Greece. It is obtained exclusively from the Aleppo pine (*Pinus halepensis,* Mill.), mostly by the Austrian method (see p. 74), though in recent years a beginning had been made with the French method. In 1907 the turpentine harvest amounted to approximately 7000 tons.

Only a part of the crude turpentine is used for the direct production of turpentine oil and colophony. Of oil 20 to 26 p. c. are obtained, of colophony 70 p. c., the balance consisting of water and mechanical impurities. The larger part of the oil, however, is not distilled directly from the turpentine. This is added to grape juice (in the case of red wines after the removal

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[1]) Chem. & Drugg. 71 (1907), 379. See also p. 55.

[2]) Judging from the properties of a sample of Portuguese oil of turpentine examined in the laboratory of Schimmel & Co. ($d_{15°}$ 0,8661; $\alpha_D - 32° 35'$) the oil is obtained from the same species as is the Spanish.

[3]) Paper read before the Spanish Society for Physics and Chemistry, Nov. 8. 1909; Chem. Ztg. 33 (1909), 1341.

[4]) Comp. p. 53.

of the skins), partly to increase the keeping qualities of the wine, partly to impart to it the desired resinous taste. From the oleoresin-containing yeast the turpentine oil is recovered by distillation, whereas the residue is worked up for colophony and calcium tartrate. This method of production accounts for the agreeable odor of the oil reminding of that of the wine[1]).

Properties. The oil frequently contains traces of alcohol which lowers the specific gravity and boiling temperature; d_{15° 0,8605 to 0,8660; $\alpha_D + 34$ to $+ 41^\circ$; n_{D20° 1,465 to 1,474; soluble in 7 and more vols. of 90 p. c. alcohol. When fractionally distilled[2]) (754 mm.) 6 p.c. passed over between 152 and 156°, 28 p.c. between 156 to 157°, 30 p.c. between 158 and 159°, 16 p. c. between 159 to 160°, residue 10 p. c.

Composition. Greek turpentine oil consists very largely of *d*-α-pinene with a high angle of rotation. Hence it is desirable as first material whenever a high optical rotation is wanted. E. Gildemeister and H. Köhler[3]) isolated from Greek turpentine oil *d*-α-pinene with the following properties: b. p. 156° (760 mm.); d_{15° 0,8642; $\alpha_D + 40^\circ 23'$; n_{D20° 1,46565.

27. Russian Oil of Turpentine.

Origin and Production[4]). In the governments Archangelsk and Wologda, forests of *Pinus silvestris,* L. cover an area of 1 000 000 ha. For the production of oleoresin, the forests are divided into sections in order to insure their permanence. The rotation demands a period of from 60 to 80 years. Trees, the diameter of which does not exceed 25 cm. at the height of a man and not 35 cm. at the base, are selected. With the exception of a strip 5 cm. wide (*Courroie,* Ger. *Riemen*), the bark is removed from the tree to the height of 1 m. This strip permits

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[1]) Utz, Apotheker Ztg. **19** (1904), 678. — Tschirch and Schulz, Arch. der Pharm. **245** (1907), 156.

[2]) Report of Schimmel & Co. October **1905**, 67. Comp. also J. Parry, Perfum. and Essent. Oil Record **2** (1911), 210.

[3]) *Wallach-Festschrift,* Göttingen 1909. p. 429.

[4]) According to M. Vèzes, *L'Industrie résinière en Russie.* Bordeaux 1902. A report based on the publications issued at the time of the Exposition of 1900 by the Regency of the Imperial Russian Dependencies.

the sap to pass upward and thus keeps the tree from dying. In subsequent years the bark is removed upward 1 m. each year until the fifth year. In the fifth year the "strip" is also removed whereupon the tree dries up and dies. On account of the cold climate, the turpentine does not flow down on the exposed surface of the trunc as it does in America, France and Austria. Hence it is not collected in special receptacles. The harvest is restricted to the scraping off of the galipot-like mass in fall. This is collected in bags held beneath the wound. The oleoresin thus collected contains up to 20 p. c. of chips. On the average a tree does not yield more than 50 g. galipot in a season. Compared with the production of other countries this is exceedingly small. At the beginning of the present century the annual output of galipot in the governments named above amounted to about 400 tons.

The distilleries for the production of the oil are erected in the forest. They are provided with one or two stills with a capacity of 2 to 3 tons containing a sieve bottom. The stills are heated over direct fire and the oil is distilled without the addition of water. Although the worst impurities are removed by means of the sieve bottom the colophony which is transferred to barrels while hot, is very impure. The pieces of wood and bark that collect on the sieve bottom *(croûtes)* are used in the manufacture of pitch.

The oil thus obtained is known as *Essence de térébenthine de résine,* Ger. *Harzterpentinöl,* to distinguish it from pine tar oil *(Essence de térébenthine de four)* obtained by the dry distillation of pine wood. It is brown in color and has an unpleasant odor that reminds but faintly of that of turpentine oil produced by steam distillation.

The distillation of galipot yields:

10 p. c. Resin turpentine oil
50 p. c. Colophony
40 p. c. Croûtes and loss.

The production of turpentine oil in the two governments mentioned above amounts to 40000 kg. annually. The dead trees are chopped down and the wood rich in resin is utilized in the production of pine tar oil.

Properties. Outside of Russia no distinction is made in commerce between Russian pine tar oil and Russian turpentine oil, hence it is impossible to distinguish between the properties of the former and the latter. Even the presence of empyreumatic substances cannot be used as a distinguishing means, since Russian turpentine, as already stated, is distilled over direct fire without the addition of water.

Composition. In Russian oil of turpentine distilled from oleoresin J. Schindelmeiser[1]) found β-pinene (m. p. of nopinic acid 126°), sylvestrene and dipentene. The presence of *d*-α-pinene may also be regarded as certain.

After repeated treatment with permanganate solution, Zelinski and Alexandroff[2]) obtained from the first fraction of Russian turpentine oil a hydrocarbon with high optical rotation, $[\alpha]_D - 70°45'$. Although it yielded no nitrosochloride, they regarded it as *l*-pinene. By exposing the first fraction of Siberian pine needle oil to a low temperature, Schindelmeiser[3]) isolated a strongly lævogyrate camphene, m. p. 40°, the molecular rotation of which was $-94°34'$ and the chlorhydrate of which melted at 150°. Schindelmeiser regards his camphene as identical with the not quite pure hydrocarbon of Zelinski and Alexandroff, hence *l*-camphene should, according to him, be regarded as a constituent of Russian turpentine oil.

Other *Pinaceæ* than *Pinus silvestris* are occasionally used in the production of turpentine in Russia. Since their oil probably is added to the common commercial article, the investigations of W. Schkatelow[4]) are of interest. He collected carefully the oleoresin of several conifers in different parts of Russia and distilled them. For the several oils he found the following properties.

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[1]) Chem. Ztg. **32** (1908), 8.

[2]) *Ibidem* **26** (1902), 1224.

[3]) Chem. Ztg. Repert. **27** (1903), 73; Chem. Zentralbl. **1903**, I. 835.

[4]) Moniteur scientifique IV. **22** (1908), I. 217; Chem. Zentralbl. **1908**, I. 2097.

Oleoresin from	Yield of oil	$[\alpha]_D$	d
Pinus silvestris[1]	from 15 to 16 %	+ 22° + 24° resp.	0,867 (15°)
Pinus Abies (Abies excelsa)	13,4 %	— 13,2°	0,873 (15°)
Larix sibirica	14,13 %	— 14,3°	0,870 (19°)
Pinus Cembra	6 %[2]	+ 14,04°	0,865 (15°)
Pinus taurica (Pinus Laricio Pallasiana)	20 %	— 75,9°	0,861 (19°)
Abies sibirica	28 %	— 35,6°	0,8751 (19°)

In a Russian publication that made its appearance while this book was in the press, J. Maisit[3]) points out that Russian turpentine oil, known there as *Schwefelterpentinöl,* contains the following constituents: traces of acetone, *d*-pinene, dipentene, *l*-limonene, *i*-sylvestrene (m. p. of dichlorhydrate 72 to 73°, optically inactive) and α-terpineol.

28. Algerian Oil of Turpentine.

Origin and Production. As in Greece, so in Algeria the Aleppo pine, *Pinus halepensis,* Mill. is used for the production of turpentine. Experiments made since 1905, have revealed that turpentine can be produced in Algeria as it is obtained in France from *Pinus Pinaster,* Sol. The number of Aleppo pines that can be used for this purpose is estimated at 20 or 30 millions, of which each can produce 1½ liters of turpentine annually[4]). In 1908 the government auctioned about 21 000 trees in the department Constantine[5]) for this purpose, and in 1909[6]) about 550 ha. of forest in the department of Oran.

Properties and Composition. Five samples of oil revealed the following constants[7]): d_{25° 0,8552 to 0,8568; $[\alpha]_D + 46,6$ to

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[1]) In the original the names of the botanical authors, of such great importance in connection with the *Abietinæ,* are missing.

[2]) Abt. 30 % of the oil passed over between 155 to 156°: $[\alpha]_D + 17°$.

[3]) *Die Harzungsversuche an der gemeinen Kiefer und der Fichte in Rußland und über das Terpentinöl aus dem Harze von Pinus silvestris,* L. Pharmaceutisches russisches Journ. **1912**, Nos. 1 to 6.

[4]) Bull. de l'Office du Gouvern. de l'Algérie **13** (1907), 100.

[5]) *Ibidem* **14** (1908), 69.

[6]) *Ibidem* **15** (1909), 50.

[7]) Vèzes, Bull. Soc. chim. IV. **5** (1909), 931.

$+ 47{,}6°$; n_D 1,4638 to 1,4652. When fractionated, 80 p.c. of the oil with the following properties distilled over between 155 and 156°: $d_{25°}$ 0,8541 to 0,8547; $[\alpha]_D + 47{,}4$ to 48,4°; n_D 1,4633 and 1,4639. With the exception of the density, these values agree well with those ascertained by Tsakalotos[1]) for Greek oil. As to density, they agree well with the values found by others for pure pinene. Hence about $^4/_5$ of the oil may be regarded as consisting of pure *d*-pinene.

29. Mexican Oil of Turpentine.

The threatened exhaustion of the turpentine forests in the United States has directed the attention of Americans to the large pine forests of Mexico. Experiments made in a turpentine orchard in Morelia, state of Oaxaca, with modern methods and tools yielded very satisfactory results. The outcome was an expansion of this industry which formerly had but slight dimensions.

For the production of turpentine in Mexico, it is characteristic that the trees prosper at an altitude of from 5000 to 9000 ft., whereas in the United States altitudes up to 1500 ft. only are considered. With the exception of a few regions, where the sap flows all year round, it is true that the higher altitudes in Mexico are unfavorable to the excretion of sap during the night. But the season in Mexico lasts longer, *viz.,* from the beginning of February to the beginning of November, whereas in the United States it lasts only from April to November. One of the principal difficulties in Mexico is found in the absence of railroads to the forests. One of the few exceptions is the three million acre forest of Col. W. C. Green and his associates which lies on a track to Madera, in the state Chihuahua. Their turpentine distilleries near Madera are operated with a profit. Eight of such distilleries are reported to exist in Mexico, *viz.* in the states Michoacan, Chihuahua, Oaxaca and Durango[2]).

According to G. Weigel[3]), Mexican turpentine is a crystalline mass of a slight lemon-yellow color and with a limonene-like

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[1]) Chem. Ztg. Repert. **32** (1908), 365.

[2]) Nachrichten f. Handel u. Industrie **1908**, No. 141, p. 4. — Oil, Paint and Drug Reporter **74** (1908), No. 9, p. 23 (August 31).

[3]) Pharm. Zentralh. **47** (1906), 866.

odor; A. V. 107,54; S. V. 115,12. Upon distillation with water vapor it yielded about 14 p.c. of oil with a pleasant odor: $\alpha_D + 33° 40'$.

30. Indian Oil of Turpentine.

Origin and Production. The constantly increasing consumption of turpentine oil induced the English Government as early as 1888 to try out in Dehra Dun[1]) (Northwest Provinces) the common *Pinus longifolia*, Roxb. for the production of turpentine. Since this place is too far removed from the railroad, the production at this point had to be abandoned[2]). Later two other distilleries were erected: one in Naini Tal in 1895 and the other in Nurpur in 1899, both in the district Kangra, Province of Punjab. Because of their more favorable location, both yield better returns. The production of turpentine extends over the extensive pine forests of the Himalaya in the north west province and in the Punjab[3]).

The total output of oil of but 50000 gals. has thus far been consumed at home[4]). The world market has not yet taken an interest in the product. A possible reason for this may lie in the sylvestrene content of the Indian oil of turpentine. Because of this variation in composition from other turpentine oils, it cannot be used equally well for all purposes.

According to a communication of the Forest Administration in the United Provinces[5]), the profits for the Naini-Tal district for 1911 amounted to 85195 Rs., as against 38705 Rs. for 1910. The production is to be increased greatly in the future. The trees, 250000 at a time, are tapped once in 15 years.

According to F. Rabak[6]), Indian turpentine is white, non-transparent, very sticky and granular, resulting from the crystallization of resin acid. The turpentine-like odor is peculiar, but pleasant, reminding somewhat of limonene; d 0,990; $[\alpha]_D - 7° 42'$; A. V. 129; E. V. 11. The yield of oil amounts to from 14 to 20 p.c.

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[1]) Chemist and Druggist **65** (1904), 831.

[2]) Chem. Ztg. **33** (1909), 808.

[3]) Comp. also G. Watt, The commercial products of India. London 1909, p. 889.

[4]) Chemist and Druggist **77** (1910), 625.

[5]) The Indian Trade Journal **25** (1912), No. 314, p. 25.

[6]) Pharm. Review **23** (1905), 229.

According to R. S. Pearson[1]) *Pinus excelsa,* Wall. and *P. Khasya,* Royle are used for the production of turpentine in India.

Properties. Indian oil of turpentine has a peculiar, pleasant, somewhat sweetish odor; $d_{15°}$ 0,866[2]) to 0,8734[3]); $\alpha_D + 0° 43'$ to $+ 3° 13'$ and $- 0° 45'$ to $- 2° 10'$[4]). Distilled from an ordinary fractionating flask, it begins to boil at 165°. The lowest fraction is lævogyrate, the higher fractions are dextrogyrate.

Composition. In addition to small amounts of α-pinene (m. p. of nitrolbenzylamin 121 to 122°) and β-pinene (m. p. of nopinic acid 125°), the oil contains appreciable amounts of *d*-sylvestrene (m. p. of chlorhydrate 71 to 72°). In the higher fractions a sesquiterpene of the following properties, has been found: $d_{15°}$ 0,9371; $\alpha_D + 37° 4'$; $n_{D20°}$ 1,50252. It yielded a chlorhydrate that crystallized in large needles and melted at 59,5 to 60,5°. The sesquiterpene could not be identified with any of the known ones[5]).

In addition to *l*-α-pinene and sylvestrene, H. H. Robinson[6]) found dipentene in the oil. According to Robinson, it is not impossible that the sylvestrene does not exist as such in the oil, but that the oil contains a hydrocarbon which, when treated with hydrogen chloride, yields a sylvestrene derivative, just as pinene, when acted upon with dry hydrogen chloride, yields a chlorhydrate which, upon the removal of hydrogen chloride, yields camphene.

31. Burma Turpentine Oil.

Origin and Production. The distillates of two pines that are indigenous to Burma and there widely distributed, *viz. Pinus Khasya,* Royle and *Pinus Merkusii,* Jungh. et de Vriese, have

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[1]) Commercial guide to the economic forest products of India. Calcutta 1912, p. 139. This contains an illustration of a tapped "Chir"-tree *(Pinus longifolia).*

[2]) Pharm. Review **23** (1905), 229.

[3]) Report of Schimmel & Co. April **1906**, 64.

[4]) Bull. Imp. Inst. **9** (1911), 8.

[5]) Report of Schimmel & Co. April **1911**, 117; October **1911**, 93.

[6]) Proceed. chem. Soc. **27** (1911), 247.

been examined by Armstrong[1]. Aside from their optical rotation, both are identical with French turpentine as to their properties. Armstrong is of the opinion that India can supply its entire demand of turpentine oil from Burma should it be possible there to create a turpentine industry.

The turpentine from *Pinus Merkusii* yielded almost 19 p.c. of oil with a specific gravity of 0,8610 and $[\alpha]_D + 31°45'$.

The turpentine from *Pinus Khasya* yielded upon distillation 13 p.c. of oil, sp. gr. 0,8627 and $[\alpha]_D + 36°28'$.

Under the directions of the Conservator of Forests for East Bengal and Assam, attempts on a smaller scale were made a few years ago to produce turpentine from *Pinus Khasya*[2]. However, the yield per tree did not amount to one ounce, hence the attempt had to be pronounced a failure. The failure was attributed principally to the season during which the trees were tapped.

Composition. Henderson and Eastburn[3] found d-α-pinene in Burma turpentine oil. It was identified by its oxidation to pinol hydrate (m. p. 131°) by means of mercuric acetate.

32. Japanese Turpentine Oil.

From Japanese turpentine, from *Pinus Thunbergii*, M. Burchardt[4] obtained 10 p.c. of a volatile oil. Upon fractionation the bulk of the oil distilled at 165°, the fractions coming over between the limits of 157 and 292°. Physical constants were not recorded[5].

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[1] Pharmaceutical Journ. III. **21** (1891), 1151; **56** (1896), 370.

[2] Chemist and Druggist **69** (1906), 961.

[3] Journ. chem. Soc. **95** (1909), 1465.

[4] Inaugural-Dissertation, Bern 1906, p. 22.

[5] In the island of Sachalin (Japan) there are large forests of *Abies sachalinensis*, Masters and *Larix dahurica*, Turcz. and of other conifers suitable to the production of turpentine. The Japanese Government plans to develop a turpentine industry on a large scale. (Oriental Druggist, Yokohama **3** (1909), Nos. 20 and 21, p. 2. — Oil, Paint and Drug Reporter **77** (1910), No. 6, p. 9. — Chem. Ztg. **34** (1910), 1326; **35** (1911), 468. — Chemist and Druggist **77** (1910), 638.)

33. East Indian Turpentine Oil.

An East Indian turpentine of unknown botanical origin has been examined by G. Weigel[1]). It was tenaceously viscid, brownish-yellow in color and had the characteristic odor of pinene: A. V. 145,45; S. V. 149,38. Upon distillation with water vapor it yielded about 14,5 p. c. of oil, $\alpha_D + 39°9'$.

34. Philippine Turpentine Oil.

In the north of Luzon, *Pinus insularis,* Endl. occurs in the Province of Benguet. It closely resembles the American *Pinus ponderosa,* Dougl. and the Indian *P. Khasya,* Royle. According to the observations of Richmond[2]) it yields an oleoresin that resembles crystallized honey in appearance and has a pleasant odor. Steam distillation yielded 23,4 p. c. of a water white turpentine oil. The constants of the oil are: $d_{30°}^{30°}$ 0,8593; $\alpha_{D30°} + 13$ to $+ 27°$; $n_{D30°}$ 1,4656; 96 p. c. of the oil distil over between 154 and 165,5°. The resin after filtration (leaving but 1 p. c. of impurities) was light in color and otherwise good. The oleoresin had been produced by the box system. It is supposed that the cup and gutter system would yield better results[3]).

The oil contains *d-α-pinene* (nitrosochloride, nitrolbenzylamine) and *β-pinene* (m. p. of nopinic acid, 121°)[4]).

35. Turpentine Oil from Picea excelsa.

The so-called Jura turpentine is obtained in the Swiss Jura from *Picea excelsa,* Lk. (*Pinus Picea,* Duroi, *Picea vulgaris,* Lk., Ger. *Rottanne* or *Rotfichte*)[5]). The fresh oleoresin yields readily upon distillation with water vapor 32 to 33 p. c. of oil, about the properties of which nothing is known.

From a turpentine obtained from the same species in the neighborhood of Naples, 18,3 p. c. of an oil were obtained. The

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[1]) Pharm. Zentralh. 47 (1906), 866.

[2]) Philippine Journ. of Sc. 4 (1909), A, 231.

[3]) See p. 62 under American turpentine oil.

[4]) B. T. Brooks, Philippine Journ. of Sc. 5 (1910), A, 229.

[5]) Flückiger, Schweiz. Wochenschr. f. Chem. u. Pharm. 13 (1875), 371. — A. Tschirch and E. Brüning, Arch. der Pharm. 238 (1900), 616.

sp. gr. was 0,866; $\alpha_D + 3°5'$ at 18°; S. V. 0. The oil possessed a delicate odor of pine needle oil[1]).

From a turpentine from Siebenbürgen (possibly a variety of this species), A. Tschirch and M. Koch[2]) obtained 30 p. c. of a volatile oil, the sp. gr. of which was 0,870 and which boiled between 175 and 180°.

The oil best examined is that from Finland. O. Aschan[3]) obtained a yield of 4,5 p.c. Fraction 155 to 160° (d 0,8657; $[\alpha]_D - 7,87°$) yielded a chlorhydrate that melted at 125 to 126° ($[\alpha]_D - 9,15°$), also a nitrosochloride (m. p. 113 to 114°), which was converted by the well-known method into nitrosopinene melting at 132 to 133°. Hence the fraction contains *l*-α-pinene. Fractions 168 to 173° ($\alpha_D - 19°20'$) and 173 to 178° ($\alpha_D - 23°28'$), when treated in ether solution with hydrogen chloride yielded dipentene dihydrochloride (m. p. 50°). Hence they contained *l*-limonene. Sylvestrene could not be detected.

Upon distillation with water vapor B. Kuriloff[4]) obtained 7,8 p.c. of oil. $d_{20°}$ 0,8635; $\alpha_D - 11,96°$. The fraction boiling up to 176,7° (772 mm) ($\alpha_D - 40,7°$) yielded a dichlorhydrate melting at 48,5°, hence contained *l*-limonene (l-*iso*terpene).

Although probable that this report pertains to *Picea excelsa,* it is not definitely established. The title reads: *"Untersuchung der Terpene des Öls aus dem Tannenharze (Pinus Abies)".* The author's name, which is of such importance especially in connection with this species, is wanting. *Pinus Abies,* Duroi is the *Edeltanne,* wheras *Pinus Abies,* L. is the *Rottanne.*

36. Turpentine Oil from Strassburg Turpentine.

Origin and Production. As is the case with *Abies balsamea,* Mill., the turpentine of *Abies alba,* Mill. *(Abies pectinata,* D. C., *Pinus Picea,* L., Ger. *Weisstanne* or *Edeltanne)* is secreted in small containers between the bark and sap wood. Outwardly they are visible as pustules. The oleoresin is collected by puncturing these pustules, or by opening them in some other

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[1]) Report of Schimmel & Co., October 1896, 72.

[2]) Arch. der Pharm. 240 (1902), 284.

[3]) Berl. Berichte 39 (1906), 1447.

[4]) Journ. f. prakt. Chem. II. 45 (1892), 123.

manner, *e. g.* by removing the bark. The dripping balsam is collected in small tin cans. The yield is always small and the collection of larger amounts requires time and labor. Up to the seventies of the last century Strassburg turpentine was collected near Mutzig and Barr in the Vosges mountains[1]). At present this aromatic turpentine possesses historical interest only.

Properties and composition. The lævogyrate turpentine has a sp. gr. of 1,120[2]) and yields 24 p. c. of a lævogyrate oil, the bulk of which distills over between 162 and 163°. Its sp. gr. is 0,860 to 0,861. Although no crystalline chlorhydrate was obtained with hydrogen chloride[3]) there can scarcely be any doubt but that this turpentine oil contains α-pinene.

37. Turpentine Oil from the Turpentine of Abies cephalonica.

Abies cephalonica, Lk., which occurs on mount Aenos in the Greek Island of Cephalonia, yields an oleoresin which, in that section, is used as a popular remedy: internally as cathartic and externally in skin diseases. From it E. J. Emmanuel[4]) obtained 17,4 p. c. of a colorless volatile oil. Under ordinary pressure it boiled between 89 (?) and 175° and at 15° had a sp. gr. of 0,9279. The optical rotation in a 200 mm tube was — 68°; $n_{D13,5°}$ 1,4745.

38. Turpentine oil from Venetian or Larch Turpentine.

Origin and Production. Venice turpentine is obtained from the larch, *Larix decidua,* Mill. (*Larix europæa,* DC., *Pinus Larix,* L.), which grows in the mountainous sections of central Europe. It is collected principally in the Southern Tirol, in the vicinity of Meran, Mals, Bozen, Kastelruth and Triest, also in Steiermark. Although schizogenous ducts occur in small numbers

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[1]) An exact communication as to the mode of collecting may be found in a paper by A. Tschirch and G. Weigel in the Arch. der Pharm. **238** (1900), 412.

[2]) Tschirch and Weigel, *loc. cit.,* p. 413.

[3]) Flückiger, Jahresber. f. Pharm. **1869**, 38; also Pharmacographia p. 615.

[4]) Arch. der Pharm. **250** (1912), 104.

in all parts of the wood and bark, experience as well as the botanical investigation by H. von Mohl in 1859[1]) have taught that they are more numerous and larger in the heart wood. Hence the production of larch turpentine has to be conducted differently from that of the other turpentines. The trees are not tapped in the region of the sap wood, but in spring one or several holes are bored to the center of the tree with bits 2,5 to 4 cm. in diameter. The openings are closed with wooden stoppers and are not opened until fall when the accumulated balsam is removed with an iron spoon. The opening is again closed for the accumulation of more balsam during the following summer.

If one or two holes are bored in the tree, the yield of balsam during the summer months amounts to but several hundred grams; this, however, remains constant for many years. If a larger number of holes are bored into a single trunk, and the balsam is induced to flow freely, several pounds of balsam may be obtained in a single summer. In this case, however, the tree is exhausted after a series of years and the wood becomes of inferior quality. Hence the mode of production that protects the tree is in the long run the more economic one[2]).

In the French Dauphiné and about Briançon, the balsam is obtained in a similar manner. However, the series of holes are bored in a straight line from below upwards, and each opening is provided with a short tube of tin or wood. When the first flow of balsam ceases the openings are closed with wooden stoppers, which are removed after two or three weeks to collect a second crop. The second flow is said to be greater than the first. The tapping is done each summer between March and September. Strong trees produce from 3 to 4 kg turpentine each year. After 40 to 50 years of such treatment the trees are exhausted[3]).

Inasmuch as there is no real demand for Venice turpentine oil, its distillation is not conducted on a large scale. The yield amounts to 13,5 to 15 p. c.

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[1]) Bot. Zeitung **17** (1859), 329, 377.

[2]) Wesseley, *Die österreichischen Alpenländer und ihre Forste.* 1853. P. 369. — A. Tschirch and G. Weigel, Arch. der Pharm. **238** (1900), 387.

[3]) G. Planchon and E. Collin, *Les drogues simples d'origine végétale.* Paris 1895. Tome 1, p. 70.

Properties[1]. d_{15° 0,865 to 0,878; $\alpha_D - 8^\circ 15'$ to -11°[2]; n_{D20° 1,46924; A. V. 0.; E. V. 5,9; soluble in 6 vol. and more of 90 p. c. alcohol. Distilled in a Ladenburg flask 60 p. c. come over between 157 and 161° (753 mm.), 20 p. c. between 161 and 164°, and 6 p. c. between 164 and 168°, residue 14 p. c.

Composition. Upon saturating the lower boiling fractions with hydrogen chloride, Flückiger[3] obtained a crystalline chlorhydrate $C_{10}H_{16}HCl$, from which the presence of α-pinene must be concluded.

Rabak[4] describes a larch turpentine which he obtained in the following manner from specimens of *Larix decidua* cultivated in North America: In April several holes, one inch in diameter, were bored to the center of the trunk. These holes were stoppered with corks. In October of the same year the turpentine was collected. It was light yellow in color and viscid: d_{22° 1,0004; α_D in 5 p.c. alcoholic solution $+ 2^\circ 20'$, hence $[\alpha]_D + 46^\circ 29'$; A.V. 60. Upon steam distillation it yielded 13,5 p.c. of a volatile oil with d_{22° 0,867 and $\alpha_D + 2^\circ 16'$. The principal constituent of the oil is α-pinene (m. p. of the nitrol benzylamine 121°).

39. Canada Balsam Oil.

Origin and Production. Canada balsam, known in North America as balsam of fir and as balsam of Gilead, is used principally for mounting microscopic sections. It is obtained from *Abies balsamea,* Mill. (*Pinus balsamea,* L.), which grows in British North America and in the northern and northwestern United States, but is collected principally in the Laurentine hills of the Province of Quebec. Some of the commercial balsam is said to be obtained from *Abies Fraseri,* Lindl., the double

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[1] Observations made in the laboratory of Schimmel & Co.

[2] The turpentine itself is dextrogyrate. Flückiger observed $\alpha_D + 9,5^\circ$, Schimmel & Co. $+ 29^\circ 20'$, hence the statement by Pereira (Pharmaceutical Journ. I. **5** (1845), 71), who says that the turpentine is lævogyrate, may be assumed as being erroneous.

[3] Neues Jahrb. f. Pharm. **31** (1869), 73; Jahresber. f. d. Pharm. **1869**, 37.

[4] Pharm. Review **23** (1905), 44.

balsam fir of the Northern Alleghanies, also from *Abies canadensis,* Mchx. (*Tsuga canadensis,* Carr.), the hemlock spruce, Ger. *Schierlingstanne*[1]). These conifers secrete a clear balsam in special receptacles between sap wood and bark. The laborious collection of the balsam is conducted from the middle of July to the middle of August and is performed mostly by descendants of the Indians who camp in the forests during the summer. For tapping the honey-like balsam they use small iron cans provided with a pointed lip. With this lip they penetrate the bark of the pustules that are visible on the larger branches. The oleoresin flows slowly into the cans which are emptied daily and then stuck into a new reservoir. One man can collect little more than $^1/_2$ gal. or $1^1/_2$ kg. daily; with the aid of children, however, double this amount. After a campaign the tapped trees must be allowed to rest 1 to 2 years, otherwise the secretion of oleoresin ceases or is too small. The commercial center for Canada balsam is Quebec. The annual production is quoted variously but in all probability does not exceed 20,000 kg.[2]).

Upon distillation, the balsam yields 16 to 24 p. c. of oil.

Properties. The odor of the oil is like that of turpentine oil; d_{15° 0,862 to 0,865. Though the balsam is dextrogyrate the oil is lævogyrate[3]) α_D — 26[4]) to —36°; n_{D20° 1,4730 to 1,4765; it boils between 160 and 167°.

Composition. *l*-α-pinene is the principal constituent of the oil. Upon saturating the oil with hydrogen chloride, Flückiger[5]) obtained a chlorhydrate $C_{10}H_{16}HCl$, and Emmerich[6]) prepared a nitrosochloride and from this pinene nitrolbenzylamine melting at 122°.

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[1]) The last-named tree occurs in large forests along the lower St. Lawrence and in Nova Scotia, New Brunswick and westward to Minnesota.

[2]) Fred. Stearns, Americ. Journ. Pharm. **31** (1859), 29. — Wm. Saunders, Proceed. Americ. pharm. Ass. **25** (1877), 337; Pharmaceutical Journ. III. **8** (1878), 813.

[3]) Rabak, Pharm. Review **23** (1905), 48.

[4]) E. Dowzard, Chemist and Druggist **64** (1904), 439.

[5]) Flückiger, Jahresber. f. Pharm. **1869**, 37 and Pharmacographia p. 613.

[6]) Americ. Journ. Pharm. **67** (1895), 135.

40. Oregon Balsam Oil.

Origin. The so-called Oregon balsam, which closely resembles the Canada balsam, was first mentioned in pharmaceutical literature in 1871[1]. It is obtained principally from the Douglas fir, *Pseudotsuga Douglasii,* Carr.[2] (*Pseudotsuga mucronata,* Sudworth; *Ps. taxifolia,* Carr., *Tsuga Douglasii,* Carr.), a conifer that is widely distributed in the Rocky Mountains and in the mountains of California and Oregon. With the exception of the darker color, Oregon balsam resembles Canada balsam in appearance. According to Rabak, the sp. gr. lies in the neighborhood of 1 (0,993 to 1,01). The balsam is slightly lævogyrate or dextrogyrate (—3° to +4°). Distilled with steam it yields 22 to 25 p. c. of volatile oil. According to G. B. Frankforter[3], the turpentine is liquid at 15° and solid at 0°; d_{20° 0,9821; $[\alpha]_D$ — 8,82°; n_{D20° 1,51745.

From the oleoresin of *Pseudotsuga taxifolia,* W. C. Blasdale[4] obtained 9 p. c. of oil; d 0,8583; α_D — 41° 21′; n_D 1,4754; which distilled principally between 157 and 160°.

The American firs *Abies concolor,* Lindl., *A. nobilis,* Lindl. and *A. amabilis,* Forb. yield similar oleoresins. According to Rabak[5] the properties of the balsam of *A. amabilis* are: d_{22° 0,969; color light yellow; optically inactive; yield of oil 40 p. c.

Properties. According to Rabak, Oregon balsam oil has a pleasant turpentine-like odor and distils over principally between 150 and 160°; d 0,822 to 0,882; α_D — 34 to — 40°. Frankforter observed the following constants: d_{20° 0,8621; $[\alpha]_D$ — 47,2°; n_D 1,47299.

The oil of *Abies amabilis* has a lemon-like odor and distils between 160 and 190°; d_{22° 0,85; α_D — 12° 17′.

Composition. According to Rabak, the bulk of the Oregon balsam oil consists of *l*-α-pinene (m. p. of nitrosochloride 106°; of nitrosopinene 125°).

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[1] Rabak, Pharm. Review **22** (1904), 293.

[2] The numerous synonyms of this tree are recorded by Rabak *loc. cit.*

[3] Journ. Americ. chem. Soc. **28** (1906), 1467.

[4] Journ. Americ. chem. Soc. **23** (1901), 162. — Pharm. Review **25** (1907), 363.

[5] Pharm. Review **23** (1905), 46.

According to the same investigator, the oil of *A. amabilis* consists of several terpenes: the lower boiling fraction of α-pinene (probably *l*-) (m. p. of nitrolbenzylamine 121°), the higher boiling fractions probably of *l*-limonene (m. p. of nitrolbenzylamine 97° in place of 93°).

If the distillate of the Douglas fir (*Pseudotsuga Douglasii,* Carr.) is distilled with low tension steam until all of the turpentine oil has passed over, there remains a viscid, yellow oil, "fir oil", which according to Benson and Darrin[1]) possesses the following constants: m. p. —40°; $[\alpha]_{D20^\circ}$ —37,6°; n_{D20° 1,4818; solubility in 70 p. c. alcohol 49:100; A. V. 1,55; S. V. 11,1; Iodine V. 185. From its composition, its behavior when fractionated, and from the ready formation of terpin hydrate when treated with 5 p. c. sulphuric acid, the authors conclude that at least one-third of the oil consists of terpineol.

41. Turpentine Oil from Pinus resinosa.

From the Norway pine, *Pinus resinosa,* (Torr.?) which occurs widely distributed through the northern and western United States G. B. Frankforter[2]) obtained a turpentine by the box method, also by extraction of the resinified stumps. Wood poor in resin yielded on the average 6,2 p. c., wood with a medium resin content 8,6 p. c. of turpentine. Stumps yielded 19,4 p. c., wood rich in resin 39,1 p. c., and very rich wood as much as 42 p. c. of turpentine. The constants are d_{20° 0,8137 (printer's error?); $[\alpha]_{D20^\circ} + 4^\circ$; n_D 1,47869. He obtained 22,1 p. c. of turpentine oil, 77,3 p. c. of colophony, and 0,6 p. c. water. According to its oil content the turpentine became semi-solid or solid after standing one or two months.

The turpentine oil had the following properties: d_{20° 0,8636; $[\alpha]_D + 17{,}39^\circ$; n_{D20° 1,47127; boiling temperature 153 to 154° (?). See also under wood turpentine oil p. 98.

According to Wenzell[3]) the oil of *Pinus ponderosa,* Laws. = *P. resinosa,* Torr. (*P. ponderosa,* Dougl.) contains a terpene (chlorhydrate).

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[1]) Journ. Ind. Eng. Chem. 3 (1911), 818; Journ. Soc. chem. Industry 30 (1911), 1407.

[2]) Journ. Americ. chem. Soc. 28 (1906), 1467.

[3]) Pharm. Review 18 (1900), 168.

42. Turpentine Oil from Pinus Murrayana.

From the turpentine collected from living trees of *Pinus Murrayana,* (Balf.) A. Murr., W. C. Blasdale[1]) obtained an oil with turpentine-like odor which distilled between 158 and 160°; d 0,8640; α_D — 15° 23′; n_D 1,4765.

43. Turpentine Oil from Abies concolor var. Lowiana.

The turpentine of *Abies concolor* var. *Lowiana* is light yellow in color and resembles Canada balsam. According to W. C. Blasdale[1]) it yields 20 p. c. oil; b. p. 155 to 160°; d 0,8578; α_D — 7° 9′; n_D 1,4738.

44. Turpentine Oil from Pinus serotina.

From the turpentine of the pond pine, *Pinus serotina,* Sudworth, Herty and W. S. Dickson[2]) obtained an oil by distillation. It is a clear liquid with a pleasant odor reminding of limonene, possessing the following constants: d_{20° 0,8478; α_{D20° — 105° 36′; n_{D20° 1,4734; A. V. 0; S. V. 1,54; Iodine V. 378; soluble in 1,35 parts of 95 p.c. alcohol at 22,5°, in 4,80 parts of 90 p. c. alcohol, in 8,10 parts 85 p. c. alcohol, 16,20 parts 80 p. c. alcohol and 56 parts of 70 p. c. alcohol. Upon distillation the oil was resolved into the following fractions: 27,4 p. c. with a b. p. of 172 to 175° (α_D — 87° 53′; n_{D20° 1,4716); 57,0 p. c. with a b. p. of 175 to 180° (α_D — 92° 21′; n_{D20° 1,4724); 8,4 p. c. with a b. p. of 180 to 185° (α_D — 92° 14′; n_{D20° 1,4744); and 7,2 p. c. above 185° (n_{D20° 1,5045). Fraction 175 to 176° (ordinary pressure) yielded upon bromination considerable portions of limonene tetrabromide, m. p. 103 to 104°. Hence the oil consisted largely of *l*-limonene.

45. Turpentine Oil from Pinus Sabiniana.

Origin. The turpentine of the Digger pine or nut pine, *Pinus Sabiniana,* Douglas[3]), which is indigenous to the western slopes

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[1]) Journ. Americ. chem. Soc. **23** (1901), 162; Pharm. Review **25** (1907), 363.

[2]) Journ. Americ. chem. Soc. **30** (1908), 872.

[3]) Synonyms and other botanical information are given by E. Kremers, Pharm. Review **18** (1900), 165.

of the Sierra Nevada in California, yields upon distillation an oil that is totally different in its composition and properties from the other turpentine oils.

The oleoresin consists of a tough, but slightly flowing, brownish-yellow mass with a greenish fluorescence and possesses a not unpleasant odor reminding of orange. It is soluble in alcohol, ether, benzene and partly soluble in petroleum ether. A. V. cold 156; S. V. hot 179,05. Upon distillation with steam Schimmel & Co.[1]) obtained 8,4 p. c. of an almost white volatile oil and 91,3 p. c. of a yellow, fragile resin.

Properties. Like the oil of *Pinus Jeffreyi,* this oil is characterized by possessing the lowest specific gravity of all volatile oils. Schimmel & Co.[2]) ascertained the following constants: d_{15° 0,6962; α_D — 0° 9′; 5 p. c. distil over between 97 and 98,5°; 87 p. c. between 98,5 and 99°, 8 p. c. above 99°. The principal fraction of 98,5 to 99° was optically inactive; d_{15° 0,6880; and corresponded otherwise in its properties with those recorded by Thorpe for heptane (see below).

The portion of the oil which boiled above 99° was resolved by fractionation in vacuum into 7 fractions. Their boiling points varied between 43 and 103° under 12 mm pressure. With the exception of the last fraction, which was dextrogyrate, all of the fractions were lævogyrate. That fraction, which in its boiling point corresponded to the terpene fractions, absorbed bromine freely with slight development of hydrogen bromide. A further investigation was not undertaken.

The oil was produced for the first time in California when during the War of Secession the production of turpentine had ceased in the Southern states[2]). In 1868 it was brought into the San Francisco market under the names abietene, butte-tine, erasine, aurantine and theoline as a substitute for benzin for the removal of stains.

Composition. The oil was first examined by W. T. Wenzell[3]). He found that the bulk of the crude oil, which boiled between

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[1]) Report of Schimmel & Co. October **1906**, 64.

[2]) W. T. Wenzell, Pharm. Review **22** (1904), 409.

[3]) Americ. Journ. Pharm. **44** (1872), 97; Chem. Zentralbl. **1872**, 712. — Pharmaceutical Journ. III. **2** (1872), 789.

101 and 105° consisted almost exclusively of a hydrocarbon sp. gr. 0,694 at 16,5° which he named abietene.

Abietene is not attacked by hydrochloric, sulphuric and nitric acids in the cold. According to Thorpe[1]) it is identical with heptane. This result was verified later by W. C. Blasdale[2]). The investigations of Venable[3]) upon heptane were not conducted, as was demonstrated later by Wenzell[1]), with the oil from *Pinus Sabiniana,* but with that of *Pinus Jeffreyi.*

46. Turpentine Oil from Pinus Jeffreyi.

Origin. Like *Pinus Sabiniana, P. Jeffreyi,* Murray occurs in the Sierra Nevada of California, but is found at higher altitudes. The turpentines of both pines resemble each other closely, and the oils appear to be identical. The abietene mentioned in connection with *Pinus Sabiniana* appears to be obtained indiscriminately from both species[4]).

From the excretions of recently felled trees, Blasdale[5]) obtained 3 p.c. of a colorless oil. After treatment with sulphuric acid, washing and drying, it boiled largely between 96 and 98°. d 0,6863; α_D 0; n_D 1,3905.

Composition. Like the oil of *Pinus Sabiniana,* this oil consists principally of n-heptane. The investigations of E. P. Venable[3]) were not conducted, as he supposed, with the hydrocarbon of *P. Sabiniana* but, as Wenzell later pointed out, with the abietene of *P. Jeffreyi.*

Wood Turpentine Oils.

As already pointed out on p. 57, the constantly increasing consumption of turpentine oil on the one hand and the disappearance of the pine forests suitable to the production of tur-

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[1]) Journ. chem. Soc. **35** (1878), 296; Chem. Zentralbl. **1879**, 565. — Liebig's Annalen **198** (1879), 364.

[2]) Journ. Americ. chem. Soc. **23** (1901), 162. — Chem. Zentralbl. **1901**, I. 1143.

[3]) Berl. Berichte **13** (1880), 1649.

[4]) E. Kremers, Pharm. Review **18** (1900), 165. — W. T. Wenzell, *ibidem* **22** (1904), 408.

[5]) Journ. Americ. chem. Soc. **23** (1901), 162; Pharm. Review **25** (1907), 363.

pentine on the other hand, have caused the United States of North America to improve the methods of production and thereby to increase the yield of turpentine. One source for the production of a technically valuable waste-product from pitchy pine stumps that occurred everywhere in large numbers, was for a long time practically neglected. It is true that in a few localities early attempts¹) were made to utilize resinous wood and the waste of saw mills by subjecting them to destructive distillation for the production of pine tar oil, tar, pyroligneous acid and pitch. However, because of the former low prices of turpentine oil, this industry does not appear to have been very remunerative at any time, hence did not expand. It is only in very recent times that the so-called wood turpentine oil has acquired a certain significance and has become the product of a flourishing industry.

Wood turpentine oil is neither a genuine turpentine oil, nor a pine tar oil (Ger. *Kienöl*). Like the latter, it is obtained from the resinous wood (Ger. *Kien*) of trunks and stumps, however, not by destructive, but by steam distillation. It has been introduced under such names as light wood oil, oil of fir, long-leaf pine oil, wood turpentine, steamed wood turpentine and stump turpentine. The lower boiling fractions have been designated wood spirits of turpentine²), the higher ones as white and yellow pine oil. Because of the method of preparation, those constituents produced at high temperature and characteristic of the pine tar oils, *viz.*, phenols, pyroligneous acid, furfurol, diacetyl etc., are wanting in the wood turpentine oils. But they also differ from genuine turpentine oils both physically and chemically. They contain a number of oxygenated substances that are entirely wanting in turpentine oil. Hence, the terpenes being less significant quantitatively, the specific gravity is higher and the viscosity greater. This difference in chemical composition is probably due to the process of resinification *(Verkienungsprozess)* which takes place in the stumps and roots,

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¹) C. Mohr, Pharm. Rundsch. (New York) 2 (1884), 163. — A description of modern plants for the utilization of the waste of saw mills is given by J. E. Teeple in his paper "Pine Products from Pine Woods." Seventh International Congress of Applied Chemistry, London 1909. Section IV A, 1, p. 54.

²) Report of Schimmel & Co. October 1911, 90.

resulting in the formation of alcohols (borneol, terpineol, fenchyl alcohol), ketones (camphor), oxides (cineol) and phenol ethers (methylchavicol) from the terpenes contained in the oleoresin. In part, this process of *Kienbildung* probably takes place in the living tree. As a result of the wound, a large number of resinous ducts are formed near the surface of the wound, which are gradually filled with oleoresin. This oleoresin differs from the ordinary turpentine merely by its lower terpene content. Due to repeated wounding, the part of the trunk beneath the wound becomes saturated with oleoresin. If for any reason (*e. g.* wind) the tree weakened by the boxes falls, the stump saturated with oleoresin and known as light wood remains often to a height of from 10 to 15 ft. the height of the tapped places. Its oleoresin content preserves it, whereas the portions rich in sap soon decay.

47. American Wood Turpentine Oil.

Production[1]. As early as 1841 attempts were made to utilize the "light wood", which name presumably owes its origin to the use made of it as torches[2], by subjecting it to destructive distillation. It was hoped that this wood might yield as much wood spirits, acetic acid, charcoal, gas and tar as did the foliage woods ("hard woods"). Experience, however, taught the error as to yield as well as to the application of the products. Modifications as to retorts, benches and mode of operation, however, did not yield results so long as the principle of destructive distillation was employed. More successful were the attempts first made in 1865 and recently renewed, to heat the wood in resin baths and to inject steam. This method, however, had the disadvantage of high cost as well as danger from fire. Moreover, the yields did not meet the expectations. Hull's method was next tried (1864). In upright stills the comminuted wood was distilled with superheated steam. Experience taught that the superheated steam at once carbonizes a part of the wood and thus results in destructive distillation, the products of which enter the turpentine oil as impurities. Moreover, insuffi-

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[1] E. J. Teeple, Journ. Soc. chem. Industry **26** (1907), 811.

[2] "Light wood" corresponds to the German *Kienholz.*

cient care was bestowed upon the uniformity of superheating. The use of non-superheated steam, employed as early as 1864 by Leffler, but forgotten and recently recommended by Krug, appears to be more promising. The wood is first exhausted withsteam and then subjected to destructive distillation or worked up in some other manner. Great care is bestowed upon the engineering aspects of the industry: the filling and emptying of the retorts, the proper distribution of steam, the stirring of the wood within the retort &c. According to Teeple, the yields according to this method amount to 25 gals. of oil per cord¹) and average 12 to 15 gals. An exhaustive account of the experiences relative to production, purification and uses of wood turpentine oil was compiled by the Department of Agriculture in 1911²). To enter upon further details of this interesting brochure would lead too far.

In 1910 there existed in the United States 30 factories that distilled soft woods. Yellow pine was principally distilled, also smaller amounts of Norway pine and Douglas fir. The factories worked up 192,442 cords of soft wood, against 115,310, 99,212 and 62,349 cords respectively for the years 1909 to 1907, thus revealing the increasing importance of the wood turpentine industry.

Properties. Under the designation wood turpentine oil a variety of oils with differing properties is found in the market. This is due to the practice that the colorless oils with lower boiling points consisting essentially of terpenes (wood spirits of turpentine) are collected by themselves and kept separate from the higher boiling oxygenated portions (white and yellow pine oils)³).

A "clear" oil obtained in a laboratory experiment by W. H. Walker, E. W. Wiggins and E. C. Smith⁴) had the sp. gr. 0,865 to 0,867. Eighty per cent. thereof distilled over below

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¹) 1 cord (Ger. *Klafter*) is a cubical measure 8 × 4 × 4 feet.

²) F. P. Veitch and M. G. Donk, Wood turpentine, its production, refining, properties, and uses. U. S. Dept. of Agriculture, Bur. of Chemistry, Bulletin No. 144, 1911; Report of Schimmel & Co. April **1912**, 126.

³) Similar products are also obtained upon the distillation of the waste of saw mills. Comp. Teeple, *loc. cit.*

⁴) Chemical Engineer (Philadelphia) **3** (1905), 78.

163°, a yellow oil boiled between 200 and 214°. According to Teeple¹), the sp. gr. of wood spirit of turpentine is about 0,865, that of pine oil between 0,935 and 0,947. The boiling temperature lies between 206 and 210°. 75 p. c. should distil over between 211 and 218°, and 50 p. c. between 213 and 217°. In connection with one sample the following constants were ascertained: $d_{15,5°}$ 0,945; $[\alpha]_D$ abt. — 11°; n_D 1,483. With the increased boiling point the density of the fractions increased, becoming constant at 217° (abt. 0,947). The samples of "yellow pine oil" examined by Schimmel & Co. varied in their properties from those recorded by Teeple. The density varied between 0,941 and 0,954 at 15°; the optical rotation between + 6 and — 5°. As an illustration, one of these oils had the following constants: $d_{15°}$ 0,946; α_D — 0°54′; $n_{D20°}$ 1,48393; A. V. 0,5; E. V. 0,9; E. V. after acetylation 186 (corresponding to 59,4 p. c. of alcohol $C_{10}H_{18}O$); soluble in 4 vol. of 60 p. c., in 2 vol. of 70 p. c. and 0,8 vol. of 80 p. c. alcohol. Another oil (for its constituents see "Composition") had the following constants: $d_{15°}$ 0,9536; α_D — 3°26′; $n_{D20°}$ 1,48537; A. V. 0; E. V. 14,2 (corresponding to 4,9 p. c. ester $C_{10}H_{17}OCOCH_3$): E. V. after acetylation 161,4 (corresponding to 50,5 p. c. alcohol $C_{10}H_{18}O$). By means of acetylation in xylene solution, the alcohol content was ascertained to be 58 p. c. The boiling temperature of the principal fraction lay between 190 and 220° (5 p. c. passed over between 160 and 190°).

In the brochure published by the Department of Agriculture and referred to on p. 98, footnote 2, the following constants are enumerated for wood turpentine oil distilled with steam: $d_{20°}$ 0,859 to 0,915; $\alpha_{D20°}$ + 16,5 to + 36,14°; $n_{D20°}$ 1,4673 to 1,4755; it begins to boil at from 153 to 177°, 0 to 95 p.c. passing over up to 170°, and from 20 to 98 p. c. up to 185°; iodine value according to Wijs 300 to 362; A. V. 0,080 to 0,312; S. V. 1,06 to 8,75; colorimetric value (Lovibond) for yellow 0,5 to 10,0 for red 0,2 to 1,4.

Composition. Walker, Wiggins and Smith²) were the first to examine wood turpentine oil. From the formation of a chlor-

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¹) Journ. Americ. chem. Soc. **30** (1908), 412 and Seventh International Congress of Applied Chemistry, London 1910. Section IV. A. 1, p. 54.

²) *Loc. cit.*

hydrate melting at 50°, which they obtained by passing hydrogen chloride into fraction 209 to 211°, they inferred the presence of terpineol. Teeple proved the presence of this alcohol by converting it into terpin hydrate (m. p. 118°), terpineol nitrosochloride (m. p. 101 to 103°) and terpineol nitrol piperide (m. p. 158 to 159°).

An examination in the laboratory of Schimmel & Co.[1] revealed that in addition to terpineol, the oil contains a number of other substances previously not observed in the oils of the *Abietineæ*.

The constants of the material used have already been recorded under "Properties." Upon fractionation *l*-α-terpineol separated as a solid (m. p. 35°; $[\alpha]_D - 4°40'$ in 25 p. c. alcoholic solution, m. p. of the phenyl urethane 111 to 113°).

In the first fraction b. p. 156 to 160° ($\alpha_D + 10°20'$) the presence of the following substances was demonstrated; α-pinene (m. p. of nitrosochloride 105 to 107°; m. p. of nitrolbenzylamine 123°), β-pinene (oxidation to nopinic acid) and camphene (the *iso*borneol obtained by hydration according to Bertram and Walbaum melted at 208 to 209°).

The fraction, b. p. 170 to 180° ($\alpha_D - 12°55'$) consisted principally of *l*-limonene and dipentene (m. p. of dipentene dihydrochloride 48°; m. p. of tetrabromide 122 to 123°). The tetrabromide obtained from fraction 175 to 177° was a mixture of limonene and dipentene tetrabromides. These were separated by fractional crystallization. The fraction that melted at 103 to 106° consisted of optically active tetrabromide (limonene tetrabromide), the more difficultly soluble fraction melted at 120 to 123° and was dipentene tetrabromide.

Fraction 174 to 180° also contained cineol which was converted into cineol resorcinol by shaking it with resorcinol solution. The cineol separated from this solution was identified by means of the iodol compound which melted at 110 to 112°.

Fraction 178 to 180° contained a small amount of γ-terpinene. The erythritol obtained by oxidation with permanganate melted at 232 to 235°.

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[1] Report of Schimmel & Co. April 1910, 103.

In the attempts to learn more about other constituents, the presence of α-terpineol interfered. Hence it was converted into terpin hydrate by shaking with dilute sulphuric acid. By means of steam distillation the other substances could be separated. The oil thus obtained was repeatedly fractionated. In this manner it was possible to isolate borneol, also methylchavicol, a substance previously not found in a Pinus oil.

The oil remaining after the hydrocarbon had been distilled off contained larger amounts of borneol (m. p. of borneol phthalic acid 164°). Fraction 210 to 215° was boiled with 100 p. c. formic acid for an hour for the purpose of removing terpineol. The bornyl formate, purified by fractionation, was saponified with potassium hydroxide. The solid borneol thus obtained, when recrystallized from petroleum ether, melted at 204° and was lævogyrate (m. p. of phenyl urethane, 137 to 139°; the semicarbazone of the camphor, obtained upon oxidation with chromic acid, melted at 237°).

The fractions in which the borneol was found also contained methylchavicol. After the borneol had been removed by means of its acid phthalic ester, the crude methylchavicol (d_{15° 0,9710; $\alpha_D - 0^\circ 27'$; n_{D20° 1,51726) boiled at 73 to 74° (4 to 5 mm.) and at 215° (758 mm.). Upon oxidation with permanganate, homoanisic acid (m. p. 83 to 84°) and anisic acid (m. p. 183 to 184°) resulted. When boiled with alcoholic potassa, anethol (b. p. 230 to 233°, m. p. above 15°) resulted.

The fractions following possessed a musty odor. They consisted largely of *i*-fenchyl alcohol. Fenchone could not be detected. However, from the fractions, from which fenchyl alcohol had been removed, a small amount of a semicarbazone, m. p. 233 to 235°, was obtained which was identical with camphor semicarbazone. Camphor, therefore, is present in traces only.

The identity of the *i*-fenchyl alcohol (b. p. 201 to 204°; m. p. 33 to 35°, when quickly heated 37 to 38°) was established by means of the acid phthalic ester (m. p. 142 to 143°). The ketone obtained by the oxidation of the alcohol with chromic acid (b. p. 192 to 193° and 193 to 194° respectively: d_{15° 0,9501; n_{D20° 1,47021), was *iso*fenchone (m. p. of oxime when quickly heated 159 to 160°).

This investigation therefore reveals that in addition to *l*-α-terpineol, "yellow pine oil" contains α- and β-pinene, camphene, *l*-limonene, dipentene, γ-terpinene, cineol, *i*-fenchyl alcohol, camphor, *l*-borneol, and methylchavicol. Thus the presence of cineol, fenchyl alcohol, camphor and methylchavicol in an oil of the *Abietineæ* has been demonstrated for the first time.

Pine Tar Oils.

Origin and Production. Since the middle ages, pine tar oil and wood vinegar are obtained as by-products in the production of tar and charcoal by means of destructive distillation of the wood rich in resin and of the roots of *Pinus silvestris,* L. In Russia, *Pinus Ledebourii,* Endl. (*Larix sibirica,* Ledebour) is said also to be used[1]). The industry is restricted to districts with large pine forests. In continental Europe most of the pine tar oil is produced in Eastern Germany, in Poland, in Finland and other parts of Northern Russia, also in Sweden.

The crude pine tar oil contains empyreumatic substances. Formerly it was purified merely by rectification with milk of lime or according to similar methods. Since more is known about these impurities, the oil is treated with dilute caustic soda solution which condenses diacetyl and its homologues to quinones of the benzene series, and which also destroys the unpleasant smelling substances of the lowest fractions. Subsequent treatment with moderately concentrated sulphuric acid resinifies furfurane, aldehydes and unsaturated compounds. Stronger sulphuric acid should be avoided, since it attacks the terpenes as well. These methods of purification, however, are not always sufficient, hence a number of patented[2]) processes are likewise employed.

But even the most carefully treated pine tar oil will never be identical with turpentine oil as to its properties since its chemical composition differs from that of the latter oil. For some uses this is of no consequence, for many purposes, *e. g.* for medicinal, turpentine oil can not be re-placed by pine tar oil.

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[1]) Tilden, Pharmaceutical Journ. III. 8 (1878), 539.

[2]) See footnote 2, p. 47.

Aside from its odor pine tar oil differs from turpentine oil by its very slight oxidation capacity, *i. e.* in its inability to absorb larger amounts of oxygen.

Properties. According to the character of the oil, as to whether it is crude, superficially purified, or completely freed from admixtures, pine tar oil differs materially as to its physical constants. Crude and poorly rectified oils possess a decided empyreumatic odor due to phenols that can be removed by shaking out the oil with soda lye. However, even carefully purified oil has an odor distinct from that of turpentine oil.

The sp. gr. of purified oil varies from 0,860 to 0,875, that of crude oil is lower; $\alpha_D + 4$ to $+ 16°$; $n_{D20°}$ 1,469 to 1,480; when distilled, only a small fraction, as a rule, distils over between 155 and 162°, whereas the bulk distils between 162 and 170° and higher.

Hence pine tar oil differs from turpentine oil in regard to its boiling temperature. This is due to the lower pinene content and to the predominance of higher-boiling terpenes, such as sylvestrene¹) and dipentene. The detection of pine tar oil can, therefore, be accomplished chemically by means of the isolation and identification of dipentene and sylvestrene, terpenes characteristic of pine tar oils²). In most instances, however, the color reactions of Herzfeld, Valenta and Utz described on p. 48 will suffice.

Composition. The several varieties of pine tar oils have, in general, the same composition. The constituents are: *d*-α-pinene, β-pinene, *d*-sylvestrene, limonene, cymene, and sesquiterpenes. In addition to these hydrocarbons, the crude oil contains oxygenated constituents, that are due to the heat employed in the destructive distillation, and are to be regarded

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¹) In order to ascertain whether sylvestrene and dipentene occur as original constituents in the wood of the pine or whether they are changed products produced during the process of distillation, Aschan and Hjelt (Chem. Ztg. 18 [1894], 1566) distilled the wood of the trunk with steam. Pinene and sylvestrene were found in the oil, but no dipentene. Hence sylvestrene appears to be a normal constituent of the pine, whereas the dipentene found in the pine tar oils appears to be an inversion product produced from the pinene under the influence of heat.

²) Sylvestrene also occurs in Russian as well as in Indian turpentine oil.

as decomposition products of the wood, the sap, and probably of the volatile oil. They are acetic acid, acetone, methyl alcohol[1]), furfurane, sylvane (α-methyl furfurane), α-α^1-dimethyl furfurane, benzene, toluene, m-xylene, furfurol, diacetyl, acetyl propionyl (probably), *iso*butyric acid methyl ester[2]), phenol (benzophenol), guaiacol and phlorol (not certain).

Adulterations. Pine tar oil is one of the cheapest volatile oils, and is frequently used as adulterant, but rarely adulterated itself. Occasionally admixtures of petroleum (Sundvik, *loc. cit.*) and of rosin essence have been observed.

48. German Pine Tar Oil.

Production. In Germany the distillation of tar is carried out only in the neighborhood of Torgau (Province of Saxony) and in the Lausitz. The production of charcoal, tar and pitch is the main object. Whereas the cut timber is worked up into boards and cord wood, the roots rich in resin are subjected to distillation after the splint, which is used as fuel, has first been removed. This operation is conducted[3]) in beehive-like ovens built of fire brick which are heated from the outside by means of a wood fire. The somewhat funnel-like floor of the ovens is provided with a wide exit-tube through which the total distillation products pass into a pit built of masonry. By means of a lateral branch of this tube the more volatile, aqueous and ethereal products of the distillation are passed through a condenser and collected in a Florentine flask in which the lighter oil is separated from the heavier wood vinegar.

The crude pine tar oil is purified by rectification over milk of lime and charcoal. Thus purified it is used in the preparation of iron varnishes, for cleansing type and electroplates, and in the preparation or dilution of cheaper grades of paint.

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[1]) E. Sundvik, *Über das durch trockne Destillation dargestellte Terpentinöl (Kienöl).* Festschrift für O. Hammarsten. Upsala 1906.

[2]) O. Aschan, *Über den Vorlauf des finländischen Terpentinöls (Kienöls).* Zeitschr. f. angew. Chem. **20** (1907), 1811.

[3]) According to personal observations made in connection with a large tar distillery in the neighborbood of Torgau.

Properties. German pine tar oil has a terebinthinate, empyreumatic odor, a light yellow color; sp. gr. 0,865 to 0,870; $\alpha_D + 9$ to $+ 22°$. A normal pine tar oil upon fractionation yielded 21,6 p. c. between 160 and 165°, 50,4 p. c. between 165 and 170°, 15,2 p. c. between 170 and 175°, 6,4 p. c. between 175 and 180°, residue 6,4 p. c.

Constituents. German pine tar oil contains d-*pinene,* d-*sylvestrene* and *dipentene* and does not differ in composition from the Russian, Polish and Swedish oils.

49. Russian or Polish Pine Tar Oil.

Origin and Production[1]. In Russia also pine tar oil is only a by-product in the charcoal and tar industry. This industry is widely distributed throughout Russia wherever there are large pine forests. The principal localities for the production of charcoal and tar are in Archangelsk, Wologda, Kostroma, Wjatka, Nishnij-Nowgorod and Twer[2].

In the first two mentioned governments the trees that have been used for the production of galipot, as described under Russian turpentine oil on p. 77, are allowed to die. The wood of the dead trees of *Pinus silvestris,* L. is cut into pieces which are subjected to destructive distillation in ovens that have a capacity of from 2 to 7 cbm. The vapors are passed by means of a copper tube through a condenser. According to this method 1 cbm. of wood yields 60 to 70 kg. tar and 6 to 8 kg. pine tar oil. The pyroligneous acid is discarded and the charcoal is used as a fuel for heating the apparatus.

The pine tar oil thus obtained, *Térébenthine de four (Essence jaune de four),* is of a brown color, and rendered impure by decomposition products, and has a very unpleasant odor. Hence it must be purified by rectification. This is accomplished by passing steam into a still containing the oil to which lime has been added. In this manner 75 to 78 p. c. of a

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[1] M. Vèzes, *L'Industrie résinière en Russie.* Bordeaux 1902. — Kowalewski, *Die Produktivkräfte Rußlands.* German translation. Leipzig 1898, p. 254, 255.

[2] Chem. Industrie 34 (1911), 158.

purified, light greenish oil is obtained, which, when rectified a second time over lime, yields a colorless oil *(Essence de térébenthine blanche rectifiée).*

Whereas in Archangelsk and Wologda the oleoresin secreted after wounding the pines is distilled for turpentine oil and rosin and the wood worked up for pine tar oils, in Kostroma the turpentine is allowed to remain on the trees and is distilled together with the wood. This operation is carried out in two successive steps in two apparatus, in the first with a gentle heat, in the second at a higher temperature. The first apparatus is an oven constructed of bricks with a capacity of 10 cbm. of wood. The products of distillation are carried off by means of wooden pipes which convey them to a copper worm condenser. The operation lasts 5 days. The pine tar oil is rendered impure by numerous decomposition products. The wood that remains after this operation is heated to a high temperature for the production of tar in iron retorts surrounded by a fire place of brick masonry. The distillate is collected in a chamber constructed of brick.

In Poland[1]) the production of pine tar oil has the character of a house industry and is conducted in a primitive manner in ovens constructed of clay.

The crude pine tar oil of the smaller producers in Poland is used locally. The larger factories which also buy up the output of the smaller producers, purify the oil by rectification over milk of lime and freshly burnt charcoal. The wood vinegar is largely worked over into calcium acetate.

Properties. The sp. gr. of Russian pine tar oil is 0,862 to 0,872; the angle of rotation $\alpha_D + 15°25'$ to $+24°$[2]). It boils from 155 to 180°[3]). Upon fractionating a normal Russian oil, Tilden[4]) obtained 10 p. c. between 160 and 171°, 63 p. c. between 171 and 172°, and 24 p. c. between 172 and 185°.

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[1]) According to a private communication by the late Prof. Dr. G. Wagner, of Warsaw, there were nearly 100 tar distilleries in Russian Poland in 1896, more particularly in the governments Lublin, Lomsha, and Suwalki. On the average each produced about 1500 to 2500 kilos of pine tar oil.

[2]) Comp. Armstrong, Pharmaceutical Journ. III. **13** (1883), 586.

[3]) Wallach, Liebig's Annalen **230** (1885), 245. — Tilden, Journ. chem. Soc. **33** (1878), 80 and Pharmaceutical Journ. III. **8** (1877), 447.

[4]) *Loc. cit.*, p. 102, footnote 1.

Composition. Polish pine tar oil was examined by Tilden in 1877 and by Flawitzky[1]) in 1887. They found d-*pinene;* a terpene boiling at 171 to 172°, which Tilden regarded as identical with *sylvestrene* although he did not succeed in obtaining the hydrochloride melting at 72°; also *cymene,* the presence of which was demonstrated by means of bromine and sulphuric acid[2]). Wallach later confirmed the presence of *α-pinene*[3]) and proved the presence of *sylvestrene* in fraction 170 to 180° by means of the hydrochloride melting at 72°. In the fraction about 180° he also found *dipentene* (dipentene tetrabromide) and a terpene which yielded a liquid bromo-addition product *(terpinene?).*

In the pinene fraction, J. Schindelmeiser[4]) demonstrated the presence of *β-pinene* (m. p. of nopinic acid 126°). According to the same investigator, Russian pine tar oil contains in addition to sylvestrene, *toluene, cymene,* a substance having a pungent quinone-like odor and saturated hydrocarbons of the methane series. One of these, boiling at 98 to 99° is presumably *heptane.* In the highest boiling fraction a *sesquiterpene* has been found, which, according to Schindelmeiser, is identical with the optically inactive hydrocarbon that accompanies cadinene in oil of cade.

50. Swedish Pine Tar Oil.

Properties. Swedish pine tar oil has the same properties as the other oils obtained by the destructive distillation of pine stumps. The constants obtained thus far from five samples only, are as follows: d_{15° 0,863 to 0,871; $\alpha_D + 6^\circ 30'$ to $+ 17^\circ 45'$. One of the samples examined contained about 1 p.c. of phenols.

Composition. According to an investigation made by Atterberg[5]) the oil contains d-*α-pinene* boiling between 156,5 and 157,5° (m. p. of pinene chlorhydrate 131°) and a terpene previously unknown, which boiled between 173 and 175°, which he charac-

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[1]) Berl. Berichte **20** (1887), 1956.

[2]) In the presence of terpenes this proof does not hold strictly true.

[3]) Liebig's Annalen **230** (1885), 246.

[4]) Chem. Ztg. **32** (1908), 8.

[5]) Berl. Berichte **10** (1877), 1202. Comp. Wallach, Liebig's Annalen **230** (1885), 240.

terized by means of a dichlorhydrate melting at 72 to 73° and which he named *sylvestrene*.

A communication concerning Swedish turpentine oil by J. Kondakow and J. Schindelmeiser¹) presumably pertains to pine tar oil since nothing is known concerning a turpentine industry in Sweden. In addition to sylvestrene and dipentene, these investigators found a hydrocarbon boiling between 174 and 176° ($\alpha_D \pm 0°$; $d_{19°}$ 0,854; n_D 1,49013) which did not react with hydrogen chloride and which upon oxidation with permanganate yielded hydroxy *iso*propyl benzoic acid (m. p. 155°). In addition the cymene sulphonic acid was identified by means of its barium salt, hence the hydrocarbon may be regarded as p-*cymene*. The same oil yielded upon fractionation a hydrocarbon that boiled at 145° which has not yet been identified.

51. Finland Pine Tar Oil.

Origin and Production. Inasmuch as the Finnish language makes no distinction between turpentine oil and pine tar oil, and since pine tar oil only is produced in that country, the latter is always implied when the former is mentioned. The pine tar oil is obtained from pine and spruce trunks²) as a by-product in the production of wood tar. The amounts produced are not inappreciable, more particularly since sealed iron tar ovens have been generally introduced.

Properties. For 13 samples of good commercial oil, E. Sundvik³) found the following properties: $d_{15°}$ 0,860 to 0,875; $\alpha_D + 8,45$ to 15,22°; n_D 1,4699 to 1,473.

Composition. The terpenes of two kinds of Finland pine tar oil have been examined by O. Aschan and E. Hjelt⁴).

1. Oil from southern Finland. After five successive fractionations the following principal fractions were obtained: 1) 155 to 160° 7,1 p.c., 2) 160 to 165° 30,2 p.c., 3) 165 to 170° 22,6 p.c., 4) 170 to 175° 20,1 p.c.

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¹) Chem. Ztg. **30** (1906), 722.

²) The forests of Finland consist of about 77 p.c. of pines and 12 p.c. of firs.

³) *Festschrift für* O. Hammarsten. Upsala 1906.

⁴) Chem. Ztg. **18** (1894), 1566, 1699, 1800.

The first fraction consisted of α-pinene (m. p. of chlorhydrate 123 to 124°; nitrosochloride; nitrosopinene). In fraction 170 to 174° sylvestrene (m. p. of dihydrochloride 72°) and dipentene (m. p. of dihydrochloride 49 to 50°) were shown to be present.

2. An oil from northern Finland differed from the former by the presence of a relatively larger amount of higher boiling fractions. Fractions 160 to 165° and 165 to 170° were insignificant whereas 32,2 p. c. were obtained between 170 and 174° and 21,2 p. c. between 174 and 178°. Pinene was found in the lower fractions, whereas the higher ones consisted chiefly of dipentene. Sylvestrene, although presumably present in small amounts, could not be detected.

Concerning the steam distillate of the wood rich in resin, which was prepared in order to ascertain whether sylvestrene and dipentene are normal constituents or reaction products due to heat, a statement will be found in footnote 1 on p. 103.

Our knowledge of the impurities or byproducts found in Finland pine tar oil will be found in the exhaustive reports of E. Sundvik and O. Aschan[1]). The substances found have already been enumerated on pp. 103 and 104.

52. American Pine Tar Oil.

Origin and Production[2]). The oldest method employed in the United States for the utilization of pine wood *viz.,* destructive distillation, is still employed to a considerable extent to-day. The cylindrical retorts employed are mounted horizontally. Their capacity varies from 3/4 to 5 cords and averages 1 to 2 cords[3]). A charge requires as a rule 24 to 48 hrs.; the largest charges demand as much time as five days. The pine tar oil that distils over first is rectified over alkali from a copper still. At first there distills over an unpleasant smelling liquid with a sp. gr. 0,840. This is followed by a fraction, sp. gr. 0,865 possessing

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[1]) Zeitschr. f. angew. Chem. **20** (1907), 1811.

[2]) J. E. Teeple, Pine products from pine woods. Seventh International Congress of Applied Chemistry. Section IV. A. 1, p. 60. — Journ. Soc. chem. Industry **26** (1907), 811.

[3]) 1 Cord = 8 × 4 × 4 feet.

the same properties as those of wood turpentine oil. Finally there distils over an oil which probably consists of dipentene and some sylvestrene. The specific gravity of the very last portions rises as high as 0,930. Apparently they contain terpineol. This is noteworthy since similar dense substances have not been observed in European pine tar oils from *Pinus silvestris*.

American pine tar oil is mostly used in the crude state as disinfectant or as a wood turpentine oil of inferior quality.

Properties. Two samples of American pine tar oil, presumably from Georgia, have been examined by E. Kremers[1]. They possessed a slightly empyreumatic odor. When shaken with 5 p.c. caustic soda solution their color darkened. d 0,856 and 0,860; $\alpha_D + 13°40'$ and $+13°42'$. Upon fractionation the bulk distilled over at the boiling point of pinene. The odor and rotation of the higher boiling fractions indicate dipentene.

For purified American pine tar oil, the Department of Agriculture records the following constants[2]: $d_{20°}$ 0,857 to 0,898; $\alpha_{D20°} + 34,4$ to $+77,6°$; $n_{D20°}$ 1,4666 to 1,4810; it begins to boil at 150 to 166° (uncorr.), up to 170° 0 to 93 p.c. distill over, up to 185° 61 to 97 p.c.; iodine value according to Wijs 300 to 398; A.V. 0,028 to 0,246; S.V. 0,65 to 4,32; colorimeter value (Lovibond) for yellow 0,4 to 4,5, for red 0,0 to 0,8.

Pine Needle Oils.

(Distillates from needles and cones of the *Abietineæ*.)

The fragrant oils distilled from the young leaves and twigs, also the one-year-old cones of pines, firs and larches are commonly designated, though not quite correctly, as pine needle oils (Ger. *Fichtennadelöle*).

Commonly the names assigned to the commercial distillates of this group in the price lists of manufacturers and dealers are no more correct. Hence it is not always possible to infer the correct botanical source from the commercial name. Inasmuch

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[1] Pharm. Review **22** (1904), 150.

[2] F. P. Veitch and M. G. Donk, Wood turpentine, its production, refining, properties, and uses. U. S. Dept. of Agriculture, Bur. of Chemistry, Bulletin No. 144, 1911; Report of Schimmel & Co. April **1912**, 126.

as well established names, though wrong, are difficult to eradicate, it is likely that they will be continued for some time. It may scarcely be necessary to point out that in the following accounts the correct names only are applied.

This condition is partly due to the confusion that exists both in the scientific as well as the common nomenclature of the conifers. For this reason the statements found in older literature must be accepted cautiously.

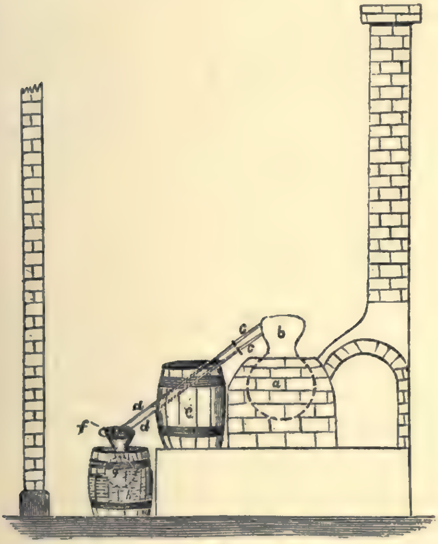

Fig. 11.

Old Thuringian still for pine needle oils.

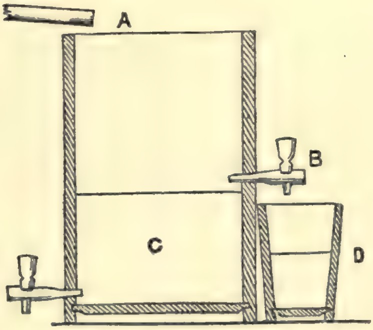

Fig. 12.

Receptacle for the collection of the distillate and the separation of the oil from the water.

On account of their balsamic and refreshing pine-woods odor, these oils have been used extensively in the preparation of various pine essences for spraying of dwelling and sick rooms, in the preparation of aromatic baths, in perfumery and in the finer soap industry. Hence in recent years they have become common articles of commerce.

The pine needle oils, more particularly the cheaper ones, are frequently adulterated with turpentine oil. Inasmuch as pinene is likewise a normal constituent of these oils, its presence is not indicative of adulteration. The presence of an appreciable addition of turpentine oil can be ascertained by means of fractional distillation. The amounts distilling over between certain temperature limits are compared with those of a genuine oil. In case of oils adulterated with turpentine oil, the amounts distilling over at 160° or below 170° are much larger than with pure oils.

As clues for such examinations, the results of quantitative fractionations are recorded in connection with the principal oils to be discussed hereafter. In the examination of these oils, the optical rotation is of much greater importance than the specific gravity, for the latter shows but unappreciable differences. On the other hand, the saponification value of those oils to which turpentine oil has been added is always lower. Hence, in general this constant affords a good clue as to the normal character of the pine needle oils.

53. Needle Oil from Abies alba.

The *Edeltannennadelöl* is obtained by distillation of the needles and twigs of *Abies alba,* Mill. *(Abies pectinata,* DC., *Abies excelsa,* Lk., Ger. *Edeltanne, Weißtanne* or *Silbertanne)* principally in Switzerland, the Tirol (in the Puster valley), Lower Austria and Steiermark, occasionally also in Thuringia and the Black Forest. The whole material yields 0,2 to 0,3 p. c. oil. From comminuted needles Schimmel & Co.[1]) obtained 0,56 p. c. of oil.

Properties[2]). This oil is a colorless liquid possessing a very pleasant, balsamic odor. The specific gravity varies according to its origin. With Tirolese and Swiss oils d_{15° lies between 0,867 and 0,875, whereas those of Lower and Upper Austria are frequently heavier, up to 0,886; α_D — 34 to — 60°. In a few exceptional cases — 64° has been observed, these oils possibly containing cone oil. n_{D20° 1,473 to 1,474, and for oils with a high specific gravity up to 1,476. A. V. mostly absent or up to 2,0. Bornyl acetate 4,5 to 11 p. c. Soluble in 4 to 7 vol. and more of 90 p. c. alcohol, occasionally with slight tur-

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[1]) Report of Schimmel & Co., April **1906**, 56.

[2]) Report of Schimmel & Co. October **1892**, 34; April **1893**, 56.

bidity. Upon distillation 8 p. c. pass over below 170°, and 55 p. c. between 170 and 185°. Above this temperature partial decomposition of the bornyl acetate sets in with the formation of acetic acid.

Composition. Bertram and Walbaum[1]) ascertained the presence of the following constituents: *l*-α-pinene (m. p. of pinene nitrolbenzylamine 122 to 123°), *l*-limonene (m. p. of tetrabromide 104°), *l*-bornyl acetate[2]) and a sesquiterpene not yet identified. Of the greatest importance, so far as the odor of the oil is concerned, is the presence of small amounts of lauric aldehyde determined by Schimmel & Co.[3]) (m. p. of semicarbazone 101,5 to 102,5°). In addition there appears to be present traces of decylic aldehyde[3]).

According to O. Aschan[4]), the lowest boiling fractions contain santene, C_9H_{14} (blue coloration on addition of nitrosylchloride).

54. Cone Oil from Abies alba.

Origin and Production. The oil from the cones of *Abies alba,* Ger. *Templinöl* is distilled in Switzerland, *e. g.* in the Emmental, and in several regions of the Oberland, also in the Thuringian forest. The one-year-old cones collected in August and September are subjected to steam distillation.

In Switzerland[5]) the cones, picked in September, are smashed with a wooden mallet in order to free the seeds for the purpose of increasing the yield of oil, which is distilled from a common copper still with water. The still is heated directly by a wood fire. The condenser consists of a serpentine tube in a wooden tub. The distillate is collected in the old-fashioned *Scheidgläsern.* These are a sort of glass separating funnel of 3 to 4 liters capacity with a large body. The opening in the bottom is closed by means of a stick fitted more tightly into the orifice by means of a piece of cloth. From time to time the stopper is raised to draw off the water in order to separate it from the

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[1]) Arch. der Pharm. **231** (1893), 291.

[2]) Comp. also Hirschsohn, Pharm. Zeitschr. f. Russland **31** (1892), 593.

[3]) Report of Schimmel & Co. April **1904**, 78.

[4]) Berl. Berichte **40** (1907), 4919.

[5]) Lüdy, Schweiz. Wochenschr. f. Chem. u. Pharm. **45** (1907), 818.

Fig. 13.

Collection of Cones: Picker *(Brecher)* and gatherers *(Leser)*.

Fig. 14.

Larger distilling apparatus.

Distillation of *Edeltannenzapfen* in Switzerland.

Fig. 15.
Distilling apparatus.

Fig. 16.
Interior of a distillery *(Brennhütte)*.

Distillation of *Edeltannenzapfen* in Switzerland.

oil floating on the surface. From a charge of 60 kg of cones about 400 g oil are obtained, however, the yield varies according to locality and climatic conditions. Unless care is taken to regulate the water supply, the addition of not enough water or by distilling too long, the oil acquires an inferior empyreumatic odor.

Properties. This oil is colorless with a pleasant balsamic odor reminding somewhat of lemons and oranges. Specific gravity 0,851 to 0,870; $\alpha_D - 60$ to $- 84°$. Thuringian oils occasionally have a lower optical rotation due possibly to the presence of the oil from the cones of *Picea excelsa,* Lk. The ester content, computed as bornyl acetate, varies from 0 to 6 p. c. With 5 to 8 vols. of 90 p. c. alcohol the oil yields a clear solution, rarely a turbid one. It is characterized by a high content of *l*-limonene. The higher the lævorotation and the lower the specific gravity, the richer the oil is in limonene.

When distilled, 11 p. c. pass over between 150 and 170° and 37 p. c. between 170 and 185°. Above this temperature partial decomposition sets in with liberation of acetic acid.

Composition. Of the older investigations of *Templinöl* those of Flückiger[1]) and Berthelot[2]) should be mentioned. These investigators studied the action of strong acids on the oil and obtained terpin hydrate, a terpene monochlorhydrate and a terpene dichlorhydrate. The formation of these substances is attributable to the presence of pinene and limonene found later.

Later Wallach[3]) examined a *Templinöl* that had been labeled *Fichtennadelöl* and found pinene and limonene to be the principal constituents. Bertram and Walbaum[4]) showed that the pinene is also lævogyrate and that *Templinöl* consists largely of *l*-α-pinene and *l*-limonene. In addition they found only small amounts of ester the nature of which was not sufficiently determined.

Later Schimmel & Co.[5]) showed that borneol occurs as ester (presumably as bornyl acetate) in the oil (m. p. of the acid

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[1]) Vierteljahresschrift f. prakt. Pharm. **5** (1865), 1; Jahresber. d. Chem. **1855**, 642.

[2]) Journ. de Pharm. et Chim. III. **29** (1856), 38; Chem. Zentralbl. **1856**, 139.

[3]) Liebig's Annalen **227** (1885), 287.

[4]) Arch. der Pharm. **231** (1893), 293.

[5]) Report of Schimmel & Co. April **1909**, 80.

phthalic acid ester 164°). In addition there appear to be present another alcohol (b. p. 190 to 197°, d_{15° 0,9013) and a sesquiterpene.

On account of its high *l*-limonene content, the *Edeltannenzapfenöl* is the best source for the production of this hydrocarbon.

55. Seed Oil from Abies alba.

Whereas the seeds of this conifer are as a rule distilled with the cones, Schimmel & Co.[1]) on one occasion, distilled them by themselves. Inasmuch as the cones owe their oil principally to the seeds which they contain, it was to be assumed that the yield would prove high and that the oil would correspond to that distilled ordinarily from the cones. Both assumptions proved correct. However, the seeds had to be crushed before being distilled otherwise they yielded but $^1/_5$ of the oil which they contained. Whereas the entire seeds yielded but 2,3 p. c. oil, the crushed seeds yielded 12 and 13 p. c. The constants were the same as those of the cone oil and fluctuated between the following limits: d_{15° 0,8629 to 0,8668; $\alpha_D - 68° 14'$ to $-76° 38'$; n_{D20° 1,47636 to 1,47812; A. V. 0,5 to 1,8; E. V. 0,9 to 3,7, corresponding to 0,3 to 1,3 p. c. of bornyl acetate; soluble in 5 to 7 vol. and more of 90 p. c. alcohol. The oil of the seeds is located between the shell and the kernel.

56. Needle Oil from Picea excelsa.

Origin. The German *Fichtennadelöl* proper is distilled from the fresh needles and shoots of the Norway spruce, *Picea excelsa,* Lk. *(Picea vulgaris,* Lk., Ger. *Fichte* or *Rottanne).* So far as is known, however, it is nowhere produced for commercial purposes. The yield amounts to from 0,15[2]) to 0,25 p.c.

Properties. The odor of this oil is just as agreeably aromatic as that of the oils distilled from the needles and cones of *Abies alba.* Sp. gr. 0,880 to 0,888; $\alpha_D - 21° 40'$ to $-37°$.

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[1]) Report of Schimmel & Co. October 1912, 94.

[2]) Bertram and Walbaum, Arch. der Pharm. **231** (1893), 295.

Upon fractional distillation of the oil Bertram and Walbaum[1]) obtained 20 p. c. between 160 and 170° and 50 p. c. between 170 and 185°. Above this temperature decomposition set in. Umney[2]) obtained 41 p.c. between 163 and 173°, 16 p.c. between 173 and 176°, 13 p.c. between 176 and 185°, 14 p.c. between 185 and 220°, and a residue of 16 p. c.

The bornyl acetate content amounts to 8,3 to 9,8 p. c.

Composition. Fraction 160 to 170° of this oil contains *l*-α-pinene (m. p. of nitrolbenzylamine 122 to 123°, of nitrosopinene 132°). Fraction 170 to 175° consists of a mixture of *l*-phellandrene (m. p. of nitrite 101°) and dipentene (m. p. of dichlorhydrate 50°). In the higher boiling fractions *l*-bornylacetate and cadinene (m. p. of dichlorhydrate 118°) have been found[3]).

According to O. Aschan[4]) the lowest boiling fractions of the German and Swedish *Fichtennadelöl* contain santene, C_9H_{14} (blue coloration with nitrosylchloride).

From the buds of this spruce, H. Hænsel[5]) obtained 0,288 p. c. of an oil, sp. gr. 0,9338 at 15°.

57. Cone Oil from Picea excelsa.

From the one-year-old fruit cones of *Picea excelsa*, Lk. (Ger. *Fichte* or *Rottanne*) obtained from Thuringia, Schimmel & Co.[6]) distilled an oil which, when rectified, possessed the following properties: d_{15° 0,8743; $\alpha_D - 19^\circ 15'$; A. V. 1,8; E. V. 3,9 = 1,4 p. c. of ester computed as bornyl acetate; soluble in 7 vols. and more of 90 p. c. alcohol. The oil was of a greenish-yellow color and, compared with other coniferous oils, had a somewhat flat and musty odor.

58. Needle Oil from Pinus montana.

Origin and Production. The so-called *Latschenkieferöl* or *Krummholzöl* is obtained by steam distillation from the fresh

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[1]) Bertram and Walbaum, Arch. der Pharm. **231** (1893), 296.

[2]) Pharmaceutical Journ. **55** (1895), 162.

[3]) Bertram and Walbaum, *loc. cit.* 296.

[4]) Berl. Berichte **40** (1907), 4919.

[5]) Pharm. Ztg. **48** (1903), 574.

[6]) Report of Schimmel & Co. April **1907**, 84.

Fig. 17.

Distillation of *Latschenkiefer* oil in the southern Tirol.

Fig. 18.

Interior of a *Latschenkieferöl*distillery.

needles, twigs and younger branches of *Pinus montana,* Mill. *(Pinus Pumilio,* Hænke, *Pinus Mughus,* Scop., Ger. *Latschenkiefer, Zwergkiefer, Legföhre, Krummholz).* The industry is located principally in the Austrian Alps, especially Tirol (Pustertal, Imst, Fernpaß, Kalkbachtal, Ampezzotal, Val Popena), in the southern parts of Lower Austria and along the northern border of Steiermark, also in the Tatra mountains in the neighborhood of the Green Lake. The yield is reported as 0,4 to 0,45 p. c. However, lower results are frequently obtained because of irrational methods of distillation. An experimental distillation conducted in Leipzig yielded 0,26 p. c.[1]) from fresh twigs obtained from Siebenbürgen, and 0,68 to 0,71 p. c.[2]) from like material obtained from Hungary. The young wood without the needles yielded 0,27 p. c. of oil[2]). Finely cut material from Steiermark yielded 0,41 p. c.[3]). The distillation by Schimmel & Co. in Miltitz of twigs obtained from Innsbruck yielded 0,58 p. c.

Properties. This oil has an agreeable balsamic odor. It is colorless and its sp. gr. varies between 0,863 to 0,875, that of Tirolese oils drops as low as 0,860. A specific gravity higher than 0,871 is frequently the result of oxygen absorption (resinification). The oils distilled experimentally at Leipzig cannot be regarded as normal, since the crude material must have dried out somewhat during the prolonged transportation. Hence their higher specific gravity, up to 0,892. The angle of rotation of normal oils fluctuates between —4° 30′ and —9°, that of Tirolese oils occasionally rises as high as —15° 20′; $n_{D20°}$ 1,475 to 1,480; A. V. up to 1,0; ester content (bornyl acetate) 3 to 8 p. c.; soluble in 4,5 to 8 vol. and more of 90 p. c. alcohol, occasionally with slight turbidity.

When distilled fractionally nothing passed over below or between 160 and 170°, 70 p. c. between 170 and 185°[4]). An oil distilled by Umney[5]) yielded 2 p. c. between 155 and 165°, 59 p. c. between 165 and 180°, 21 p. c. between 180 and 200°, 18 p. c. above 200°.

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[1]) Report of Schimmel & Co. October **1893**, 33.

[2]) *Ibidem* October **1896**, 72.

[3]) *Ibidem* April **1906**, 56.

[4]) Bertram and Walbaum, Arch. der Pharm. **231** (1893), 297.

[5]) Pharmaceutical Journ. **55** (1895), 163.

Composition[1]. The lowest fraction contains but very little *l*-α-pinene[2] (m. p. of pinene nitrolbenzylamine 122 to 123°). The succeeding fractions contain *l*-phellandrene (m. p. of nitrite 102°), sylvestrene[3] (m. p. of dichlorhydrate 72°) and bornylacetate. The highest fractions contain cadinene (m. p. of dichlorhydrate 118°).

Several new oxygenated constituents were found in the oil by E. Böcker and A. Hahn[4]. They examined an oil that had been freed from terpenes and sesquiterpenes (b. p. 85 to 178° under 13 mm.), which they resolved into several fractions. From fraction 148 to 160° ($\alpha_D - 14° 15'$; S. V. 53) a solid bisulphite compound was obtained. From this a liquid having a faint balsamic odor and the elementary composition $C_{15}H_{26}O$ was regenerated. With fuchsine in sulphurous acid solution it produces a red color. Presumably this substance is an aldehyde. From its behavior toward a glacial acetic acid solution of bromine the inference is drawn that it probably contains one double bond.

From fraction 127 to 148° (13 mm.) the same investigators obtained a bisulphite compound which was decomposed with difficulty. There resulted a lævogyrate compound $C_{15}H_{24}O$ with 2 double bonds, which appears to be a ketone.

Finally fraction 87 to 95° (14 mm.; $d_{15°}$ 0,9288; $\alpha_D - 18° 15'$; S. V. 65) was treated with sodium acid sulphite. A readily volatile oil was isolated that possessed the peculiar aroma of the *Latschenkieferöl*. This interesting body possesses the following properties: b. p. 216 to 217° (754 mm.); $d_{15°}$ 0,9314; $d_{20°}$ 0,9288; $\alpha_D - 15° 0'$; n_D 1,46459. It has the composition $C_8H_{14}O$. On account of its high density and high boiling point Böcker and Hahn regard pumilone, the name given to this new substance, as a cyclic compound. It does not react with either sulphurous acid solution of fuchsine or ammoniacal silver solution. With potassium permanganate a mixture of two acids was obtained thus indicating the ketone character of the compound. Pumilone is a saturated compound and yields a semicarbazone melting at

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[1] Bertram and Walbaum, *loc. cit.* 297. — See also Buchner, Liebig's Annalen **116** (1860), 323.

[2] First found by Atterberg and described by him as terebentene. Berl. Berichte **14** (1881), 2531.

[3] The presence of sylvestrene in this oil was suspected by Atterberg.

[4] Journ. f. prakt. Chem. II. **83** (1911), 489.

116 to 117°. It is contained to the extent of but 1 to 2 p. c. in the original oil.

Adulteration. A *Latschenkieferöl* that attracted attention because of its low price was examined in the laboratory of Schimmel & Co.[1]). It was found to have been diluted with American turpentine oil as became apparent from the following results: $d_{15°}$ 0,8682; $\alpha_D + 6° 43'$; E. V. 1,69 = 0,59 p. c. bornyl acetate; soluble in 7 vol. and more of 90 p. c. alcohol. Upon distillation (753 mm.) the following fractions were obtained: up to 160° 34 p. c., from 160 to 165° 36 p. c., from 165 to 170° 13 p. c., from 170 to 175° 3 p. c., from 175 to 190° 6 p. c., residue 8 p. c. The pure oil, when distilled in like manner, yields scarcely any fraction up to 160°.

59. Needle Oil of Pinus silvestris.

Origin. The needle oils of *Pinus silvestris,* L. (Ger. *Kiefer* or *Föhre*) differ in their properties according to their geographical source. Hence they will be discussed separately according to countries.

GERMAN "KIEFERNADELÖL." In an experimental way this oil has been distilled occasionally. Although it is but little inferior to other needle oils, particularly to *Latschenkieferöl,* it has not found application in perfumery and the soap industry. Hence its production is not a regular one. Occasionally it is obtained as a by-product in the production of the extract of the leaves of *Pinus silvestris.*

Fresh needles distilled by Schimmel & Co. in July yielded 0,55 p. c.[2]), those distilled in December 0,45 p. c. of oil[3]).

On another occasion the same firm distilled twigs collected in May and June, at which time the influence which the method of distillation exerted on the product was also ascertained. In one instance the dry material was distilled with steam, in another it was soaked. Of both distillations the fractions obtained du-

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[1]) Report of Schimmel & Co. Oct. **1905**, 59.

[2]) Report of Schimmel & Co. October **1896**, 62.

[3]) Bertram and Walbaum, Arch. der Pharm. **231** (1893), 300; M. Tröger and A. Beutin, *ibidem* **242** (1904), 521.

ring different time intervals were collected separately. These fractions as well as the bulked oils were examined and the bulked oils compared with oils obtained as a unit. The following table reveals the results obtained[1]).

	Oil %	d_{15°	α_D	n_{D20°	A.V.	E.V.	E. V. after acetyl.	Ester %	Total borneol %
1. Dry steam distillation.									
a) after 3 hrs. obtained	0,189	0,8721	+5° 36′	1,47568	1,8	6,3		2,2	
b) „ 4 addit. hrs. obt.	0,1	0,8797	+3° 45′	1,47917	2,8	2,3		0,8	
c) by cohobation obt. .	0,0075	0,8913	+1° 56′	1,48306	4,1	10,9		3,8	
d) a, b and c combined	0,2965	0,8755	+5°	1,47715	2,6	5,6	18,6	1,9	5,2
2. Water and steam distillation.									
I.									
a) after 3 hrs. obtained	0,173	0,8773	+5° 31′	1,47811	0,9	6,5		2,3	
b) „ 4 addit. hrs. obt.	0,152	0,8882	+5° 50′	1,48180	3,6	5,6		1,9	
c) a and b combined .	0,325	0,8824	+5° 41′	1,47996	2,4	6,0		2,1	
II.									
Total distillate after 7 hrs.		0,8822	+3° 10′	1,47899	2,8	9,3	26,0	3,3	7,3

Properties[2]). Pine needle oil has a specific gravity of 0,865 to 0,886 and an angle of rotation $\alpha_D + 5$ to $+ 10°$. Two Austrian oils have been found to be slightly lævogyrate (up to — 1° 55′). Upon fractional distillation 10 p. c. came over between 160 and 170°, and 46 p. c. between 170 and 185°. With 7 to 10 vol. of 90 p. c. alcohol the oil yields a clear solution. Ester content 1 to 3,5 p. c. (computed as bornyl acetate). Ester content after acetylation 15,1 p. c.[3]).

Composition. Like the needle oils already mentioned, German pine needle oil contains α-pinene, but unlike that of others it is dextrogyrate[2])[3]) (m. p. of nitrolbenzylamine 122 to 123°). It also contains *d*-sylvestrene. The dihydrochloride obtained at first melted below 50°, but after repeated crystallization attained the constant melting point of 72°. Hence the presence of dipentene

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[1]) Report of Schimmel & Co. April **1910**, 91.

[2]) Bertram and Walbaum, *loc. cit.* 300; Report of Schimmel & Co. October **1896**, 72.

[3]) M. Tröger and A. Beutin, Arch. der Pharm. **242** (1904), 521.

in the oil is also to be assumed, since the melting point of this compound has a decided depressing influence on that of sylvestrene dihydrochloride.

The saponification liquid of the oil contains acetic acid, which in the oil is combined with an alcohol not yet determined (presumably borneol or terpineol). In the highest fractions cadinene (m. p. of dihydrochloride 118°) has been found.

From the pine sprouts (male and female inflorescences) H. Hænsel[1]) distilled an oil of the following properties: d_{15° 0,8839; $\alpha_D - 22^\circ$; S. V. 19,5; S. V. after acetylation 58; boiling temperature 160 to 210°.

SWEDISH PINE NEEDLE OIL is distilled in the district Jönköping, Sweden, from pine needles by steam. It enters commerce as *Schwedisches Fichtennadelöl.* It is used for hygienic and medicinal purposes: for inhalations with diseases of the lungs, as ingredient for medicinal baths and for inhalations in sick rooms.

Properties. In its general properties and composition, Swedish pine needle oil agrees with the German oil. Sp. gr. 0,872; optical rotation $+10^\circ 40'$; upon fractionation it yields 44 p. c. between 160 and 170°, and 40 p. c. between 170 and 185°. It contains *d*-α-pinene (m. p. of nitrolbenzylamine 122 to 123°), *d*-sylvestrene (m. p. of dihydrochloride, 72°) and small amounts of an ester (3,5 p. c. computed as bornyl acetate), the nature of which has not yet been determined, but which, to judge from the odor, appears to be bornyl acetate[2]).

ENGLISH PINE NEEDLE OIL differs from the German and Swedish oils by its lævorotation.

Umney[3]) has distilled the needles of the Scotch fir (*Pinus silvestris,* L.) at different seasons. In June he obtained 0,5 p. c., in December 0,133 p. c. of volatile oil, the sp. gr. of which varied between 0,885 and 0,889, and the angle of rotation between $\alpha_D - 7,75$ and -19°. The ester content, computed as bornyl acetate, varied between 2,9 and 3,5 p. c. The fractional distillation of the two oils gave the following results:

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[1]) Apotheker Ztg. **20** (1905), 396.

[2]) Bertram and Walbaum, Arch. der Pharm. **231** (1893), 299.

[3]) Pharmaceutical Journ. **55** (1895), 161, 542.

	Oil distilled in June	 in December
from 157 to 167°	8 %	13 %
„ 167 „ 177°	27 %	24 %
„ 177 „ 187°	20 %	9 %
„ 187 „ 197°	3 %	6 %
„ 197 „ 240°	7 %	7 %
„ 240 „ 252°	6 %	4 %
Residue	29 %	37 %

Composition. The lowest fraction deviated the ray of polarized light 13° to the left (100 mm. tube) and possessed all of the properties of *l*-α-pinene. Fraction 171 to 175° was slightly dextrogyrate (+ 0,75°), behaved like dipentene[1]), and gave the sylvestrene reaction with glacial acetic acid and sulphuric acid.

Hence it may be assumed that, with the exception of the opposite rotation, English pine needle oil agrees in composition with the German and Swedish oils.

60. Siberian Fir Needle Oil.

Origin and Production. This oil is distilled in north eastern Russia from the needles and young twigs of *Abies sibirica,* Ledeb. *(Abies Pichta,* [Fisch.] Forb.; Ger. *sibirische Edeltanne).* The principal center of production is in the government Wjatka, whereas Siberia, on account of the high transportation charges, supplies but small amounts. The distillation is conducted during summer and fall. The amount produced is considerable and exceeds by far the total of all other fir needle oils.

Strictly speaking the designation Siberian fir needle oil is incorrect since the Siberian fir, *Picea obovata,* Ledeb. does not yield this oil. Hence this is one of the numerous instances in which the commercial designation of a coniferous oil is a contradiction to its botanical source.

Properties. d_{15° 0,905 to 0,925; α_D —37 to —43°; n_{D20° 1,470 to 1,472; ester content (bornyl acetate) 29 to 40 p. c.; A. V. up to 2,5; soluble in 10 to 14 vol. of 80 p. c. alcohol, mostly with slight turbidity, and in 0,5 to 1 vol. of 90 p. c. alcohol; in rare instances the solution is opalescent.

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[1]) Apparently derivatives of this hydrocarbon have not been prepared. Neither did Umney succeed in preparing sylvestrene dihydrochloride.

Composition. In the lowest fraction boiling below 145° a hydrocarbon C_9H_{14} (3 to 4 p. c.) is contained which O. Aschan[1]) recognized as santene. It possessed the following constants: b. p. 140°; d_{15° 0,8698; $n_{D19,2^\circ}$ 1,46960; optically inactive. The nitrosochloride melted at 109 to 111°, the nitrosite at 124 to 125°.

Like most of the coniferous needle oils, Siberian fir needle oil contains pinene, *viz.* *l*-α-pinene[2]) (m. p. of nitrolbenzylamine 122 to 123°) as well as β-pinene[3]).

It also contains about 10 p. c. of *l*-camphene which can be obtained in solid form by fractionation. As to its melting point, the opinion of the several observers vary. P. Golubew, who first isolated camphene from this oil, observed the melting point at 30°)[4]), later at 40 to 41°[5]) and at 50°[6]). J. Schindelmeiser[7]) observed it at 40°, and O. Wallach[8]) at 39° for the purified hydrocarbon. As a result of a detailed study, he arrived at the conclusion that the artificial and natural camphene represent two physically isomeric modifications.

The presence of α-phellandrene (m. p. of nitrite 106 to 107°) and of dipentene (m. p. of dibromhydrate 64°, of dichlorhydrate 49°; tetrabromide) was demonstrated by Schindelmeiser[9]). Both terpenes constitute together about 5,4 p. c. of the oil.

About 30 to 40 p. c. of the oil consists of *l*-bornylacetate[10]). In addition there is present the acetic acid ester of another terpene alcohol, probably of terpineol[2]).

From the highest boiling fraction O. Wallach and E. Grosse[11]) isolated a sesquiterpene, the trichlorhydrate of which melted at 79 to 80°. It is identical with bisabolene. (See vol. I, p. 328).

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[1]) Berl. Berichte **40** (1907), 4918.

[2]) Report of Schimmel & Co., October **1896**, 72.

[3]) E. Gildemeister and H. Köhler, *Wallach-Festschrift,* Göttingen 1909, p. 418.

[4]) Journ. russ. phys. chem. Ges. **20** (1888), 477; Chem. Zentralbl. **1903**, I. 835.

[5]) Chem. Zentralbl. **1905**, I. 95.

[6]) *Ibidem* **1910**, I. 30. Comp. also Chem. Ztg. **32** (1908), 922.

[7]) Chem. Zentralbl. **1903**, I. 835.

[8]) Nachr. K. Ges. Wiss. Göttingen 1907, Session of July 20.

[9]) Apotheker Ztg. **19** (1904), 815. — Chem. Ztg. **31** (1907), 759.

[10]) Hirschsohn, Pharm. Ztschr. f. Russland **30** (1892), 593; Chem. Zentralbl. **1892**, II. 793.

[11]) Liebig's Annalen **368** (1909), 19.

61. Aleppo Pine Needle Oil.

Upon distillation of the fresh shoots of the Aleppo pine (*Pinus halepensis,* Mill., *Pinus maritima,* Mill.) collected in southern France, E. Belloni[1]) obtained 0,681 p. c., and upon distillation of the dried shoots 0,517 p. c. of a light greenish oil with an aromatic taste and characteristic pine needle odor. It possessed the following constants:

A. Oil from fresh shoots: d_{15° 0,8810; α_D —23° 46′; $[\alpha]_{D15^\circ}$ —26,518°; A. V. 0; E. V. 7,9 = 2,77 p. c. ester (computed as $C_{10}H_{17}O \cdot CO \cdot CH_3$); combined alcohol 2,13 p. c.

B. Oil from dried shoots: d_{15° 0,8963; α_D — 20° 15′; $[\alpha]_{D15^\circ}$ — 22,355°; A. V. 5,43; E. V. 8,27 = 2,92 p. c. ester (computed as $C_{10}H_{17}O \cdot CO \cdot CH_3$); free alcohol 11,9 p. c.; combined alcohol 2,28 p. c.; total alcohol 14,18 p. c.

The oils are insoluble in 80 p. c. alcohol, soluble in 10 vols. of 90 p. c. alcohol. They are miscible with alcohol of 95 p. c. strength and stronger.

Upon fractionation from a Ladenburg flask the oils yielded the following results: Oil A: between 155 and 170° 58 p. c. (α_D — 27° 50′), between 170 and 190° 20 p. c. (α_D — 31° 40′), residue 20 p. c. Oil B: between 155 and 170° 42 p. c. (α_D — 26° 42′), between 170 and 190° 20 p. c. (α_D — 29° 34′), residue 37 p. c.

The oil contains no aldehydes. The free acid found in the oil distilled from the dry shoots consisted principally of caprylic acid (about 1,396 p. c.). The esters are principally those of the lower fatty acids, presumably acetic acid, propionic acid, caprylic acid and lauric acid. The bulk of the oil consists of *l*-α-pinene with the following properties: b. p. 155 to 157°; d_{15° 0,8618; $[\alpha]_{D15^\circ}$ — 29° 30′ (m. p. of nitrosochloride 103°, of nitrolpiperide 118°). Phellandrene and sylvestrene could not be identified in fraction 170 to 190° but limonene or dipentene probably is present. Of the alcoholic components Belloni[2]) identified *l*-borneol, m. p. 205°, by means of the phthalic acid anhydride method.

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[1]) *Sull' essenza di gemme di Pinus maritima,* Mill. Milano 1905. Annuario della Soc. chim. di Milano **11** (1905), fascic. 6; Chem. Zentralbl. **1906**, I. 360.

[2]) Boll. Chim. Farm. **45** (1906), 185; Chem. Zentralbl. **1906**, I. 1552.

In the Algerian needle oil of the Aleppo pine E. Grimal[1]) demonstrated the presence of phenyl ethyl alcohol, which previously had been observed only in the oils of neroli and rose. He saponified fraction 120 to 135° (10 mm.), shook out the saponified liquid with ether and fractionated the ethereal residue. Fraction 95 to 98° (8 mm.) was treated with phthalic acid anhydride and the resulting ester was saponified. A very aromatic liquid resulted which distilled between 218 and 220° under ordinary pressure and was characterized by the following constants: $d_{15°}$ 1,0187; $\alpha_D \pm 0°$; $n_{D18°}$ 1,52673. The alcohol was further characterized by elementary analysis, by its behavior during oxidation, and by its phenylurethane.

62. Needle Oil from Swiss Stone Pine.

Upon distillation with steam of the needles (without branches) of the Siberian cedar *(Pinus Cembra,* L., Ger. *Arve, Zirbelkiefer)* F. Flawitzky[2]) obtained 0,88 p. c. of volatile oil. It deviated polarized light to the right, $\alpha_D + 29{,}1°$ and consisted principally of *d*-α-pinene (m. p. of chlorhydrate 125°). Fraction 156° had the high specific angle of rotation $[\alpha]_D + 45{,}04°$.

63. Cone Oil from Abies Reginæ Amaliæ.

The cones of *Abies Reginæ Amaliæ,* Heldr. (*Abies cephalonica,* Lk.) growing in the forests of Arcadia contain so much volatile oil that it exudes upon the application of pressure. Upon distillation of the crushed fruit more that 16 p. c. of volatile oil have been obtained[3]).

Properties and Composition. The specific gravity of the oil is 0,868; its angle of rotation —5°. It begins to boil at 156°, the boiling temperature remains constant for some time at 170° and rises finally up to 192°.

As shown upon elementary analysis, the oil consists mostly of terpenes $C_{10}H_{16}$.

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[1]) Compt. rend. **144** (1907), 434.

[2]) Journ. f. prakt. Chem. II. **45** (1892), 115.

[3]) Buchner and Thiel, Journ. f. prakt. Chem. **92** (1864), 109.

64. Needle Oil from Pinus Laricio.

Two oils, reported to have been distilled from *Pinus Laricio,* Poir. (Ger. *Schwarzkiefer*), that had been sent to the firm of Schimmel & Co.[1]) possessed the following properties: —

a) d_{15° 0,8646; $\alpha_D + 8^\circ 17'$; E.V. 2,9 = 1,0 p.c. bornyl acetate; soluble in 8 to 9 vols. or more of 90 p.c. alcohol.

b) d_{15° 0,8701; $\alpha_D + 3^\circ 29'$; E.V. 9,8 = 3,4 p.c. bornyl acetate; soluble in 8 vols. of 90 p.c. alcohol.

Both oils were colorless and possessed a pleasant balsamic odor.

65. Hemlock Needle Oil.

True hemlock oil is the distillate from the young twigs of *Abies canadensis,* Michx. *(Tsuga canadensis,* Carr.; Ger. *Spruce-, Hemlock-,* or *Schierlings-tanne)* which is widely distributed over the American continent from Canada to Alabama and westward to the Pacific. With the hemlock there are frequently distilled the twigs of either the white spruce *Picea alba,* Lk. or the black spruce *Picea nigra,* Lk., or both. These two species with the hemlock constitute large forests, hence the twigs of all three species are, no doubt, frequently mixed, though but accidentally. Because of assumed identity the oils of the three species enter commerce under the common names of hemlock oil or spruce oil. Inasmuch as these oils agree largely, not only qualitatively but quantitatively, their common use may be of no disadvantage.

Properties and Composition. Hemlock oil is colorless, of pleasant balsamic odor; specific gravity 0,907 to 0,913[2]); $\alpha_D - 20^\circ 54'$[3]) to $- 23^\circ 55'$[4]). Fractional distillation yielded 11 p.c. between 150 and 170°, and 37 p.c. between 170 and 185°. Above this temperature decomposition set in with the liberation of acetic acid.

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[1]) Report of Schimmel & Co. April **1906**, 57.

[2]) Hanson and Babcock [Journ. Americ. chem. Soc. **28** (1906), 1198] observed d_{15° 0,9238 to 0,9273 for oils distilled from the needles and branches.

[3]) Bertram and Walbaum, Arch. der Pharm. **231** (1893), 294.

[4]) Power, Descriptive catalogue of essential oils. New York 1894, p. 58.

Hemlock oil contains *l*-α-pinene (m. p. of nitrolbenzylamine, 122 to 123°), 36 p.c. *l*-bornyl acetate and sesquiterpenes not yet identified.

C. G. Hunkel[1]) examined an oil that was distilled from fresh twigs of *Abies canadensis,* Michx. collected by himself in September. The oil had a sp. gr. of 0,9288 at 20°; $[\alpha]_{D20^\circ} - 18{,}399^\circ$; *l*-bornyl acetate content 51,5 to 52 p.c. *l*-α-Pinene was identified by means of its nitrolbenzylamine base (m. p. 122°).

66. Needle Oil from Black Spruce.

The oil of the black spruce, *Picea nigra,* Lk., already referred to in connection with the previous oil, is almost identical with hemlock oil. Sp. gr. 0,9228 at 20°; $\alpha_{D20^\circ} - 36{,}367^\circ$. Upon fractionation it distilled between 160 and 230°, the principal fraction passing over between 212 to 230°. It contains 48,85 p.c. bornyl acetate[2]).

67. Balsam Fir Needle Oil.

The fresh twigs and young cones of the Canada balsam fir, *Abies balsamea,* Mill. (Balm of Gilead fir) yield upon distillation with steam an oil closely resembling the two previous ones.

Properties and Composition. d_{20° 0,8881; $\alpha_{D20^\circ} - 28{,}91^\circ$. Upon fractional distillation 1,5 p.c. passed over up to 160°, 47,7 p.c. between 160 and 170°, 29,2 p.c. between 170 and 185°, 16,2 p.c. between 185 and 210°, residue 5,4 p.c.

The oil contains 17,6 p.c. bornyl acetate. The lævogyrate fraction 160 to 165° yielded a nitrosochloride (m. p. 101°). Although the amount was too small to prepare other derivatives, it may be assumed that the oil contains *l*-α-pinene[3]).

68. White Pine Needle Oil.

From the leaves of the white pine, *Pinus Strobus,* L. (Ger. *Weymouthkiefer*) collected during January in Wisconsin,

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[1]) Pharm. Review **14** (1896), 35.

[2]) Kremers, Pharm. Rundsch. **13** (1895), 135.

[3]) Hunkel, Americ. Journ. Pharm. **67** (1895), 9.

E. Kremers[1]) obtained 0,09 p.c. of volatile oil that boiled between 155 and 285°. In the first fraction, 155 to 170°, constituting 30 p.c. of the oil, α-pinene was contained (m. p. of nitrosochloride 105 to 106°).

Later J. Tröger and A. Beutin[2]) examined an oil distilled from spring shoots collected in Blankenburg in the Hartz mountains. It possessed the following properties: d_{15° 0,9012; optical rotation in a 200 mm. tube — 39,7°; n_{D20° 1,48274; ester content 8,6 p.c. (computed as $C_{10}H_{17}O \cdot COCH_3$); ester content after acetylation 15,25 p.c. corresponding to 5,2 p.c. of free alcohol in the original oil. Of 30 g. of oil 19 g. distilled over below 70° under 24 mm. pressure and boiled between 154 and 170° under atmospheric pressure. No terpenes in addition to *l*-α-pinene (m. p. of nitrolbenzylamine 122°) were identified. The fraction above 70° had an ester content of 23,5 p.c. In the acetylated oil the ester content had risen to 57,6 p.c. Attempts to isolate the alcohol gave negative results.

69. Douglas Fir Needle Oil.

The Douglas fir or red fir is one of the most common and most valuable trees of North America and constitutes a principal factor in the extensive coniferous forests of the Northwest of the United States. It is known by the following synonyms: *Pseudotsuga mucronata,* Sudworth, *P. Douglasii,* Carr., *P. Douglasii taxifolia,* Carr., *P. Douglasii denudata,* Carr., *P. Lindleyana,* Carr., *P. taxifolia,* Britton, *P. Douglasii* var. *glauca,* Mayr, *P. taxifolia* var. *elongata,* Lemmon, *Pinus taxifolia,* Lambert, *P. Douglasii,* D. Don, *P. canadensis,* B. Hooker, *P. Douglasii* var. *taxifolia,* Antoine, *P. Douglasii* var. *brevibracteata,* Antoine, *Abies taxifolia,* Poir., *A. mucronata,* Raf., *A. mucronata* var. *palustris,* Raf., *A. Douglasii,* Lindl., *A. Douglasii,* var. *taxifolia,* Loudon, *Picea Douglasii,* Lk., *Picea Douglasii,* Bertrand, *Tsuga Douglasii,* Carr., *T. Douglasii fastigeata,* Carr., *T. Lindleyana,* Rœzl.

From the fresh needles and twigs of small trees and underbrush, I. W. Brandel and M. Sweet[3]) obtained 0,8 to 1 p.c. of a

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[1]) Pharm. Review **17** (1899), 507.

[2]) Arch. der Pharm. **242** (1904), 528.

[3]) Pharm. Review **26** (1908), 326.

greenish-yellow oil. It had a limonene-like odor, d_{23° 0,8680; α_D — 62,5°; A. V. 0; S. V. 86,6, corresponding to 30,3 p. c. of bornyl acetate; S. V. after acetylation 92,1 (27,18 p. c. of borneol). Fractionation showed that the oil consisted principally of terpenes. The lower fractions though they possessed a pinene-like odor, yielded no nitrosochloride. Fraction 175 to 176° had the odor of limonene, but a tetrabromide could not be obtained, presumably because of the small amount. The fractions boiling between 161 and 169° constituted the bulk of the oil and contained camphene, m. p. 47°. The residue (b. p. above 190°), after saponification, boiled principally between 180 and 205°. The borneol present was oxidized to camphor (m. p. 171°; m. p. of oxime 113°).

70. Needle Oil from Pinus ponderosa.

On the Pacific coast the oil from the needles of the Oregon yellow pine, *Pinus ponderosa* is distilled as a by-product in the manufacture of so-called forest wool which is used in mattresses[1]. The yield amounts to 0,5 p. c. The properties of the oil are not recorded.

71. Several of the less common American Needle Oils.

The oils from the needles, cones and twigs of several American conifers, which however cannot be identified satisfactorily because the botanical author's names are not recorded, have been distilled by R. E. Hanson and E. N. Babcock[2].

Picea Mariana[3], or black spruce, yielded 0,57 p. c. of needle oil: d_{19° 0,9274.

Picea canadensis[4], or cat spruce, yielded 0,103 p. c. of needle oil: d_{15° 0,9216; 25,7 p. c. ester computed as bornyl acetate. From the odor of the oil the presence of limonene or dipentene may be inferred. The cones yielded 0,25 p. c. of a yellow oil that also had a limonene-like odor: d_{15° 0,899 (some time after the distillation).

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[1] Scientific American **84** (1901), 344; Pharm. Review **25** (1907), 364.

[2] Journ. Americ. chem. Soc. **28** (1906), 1198.

[3] *Picea Mariana*, Prel. = *Picea nigra*, Lk.

[4] *Picea canadensis*, Lk. = *Tsuga canadensis*, Carr.

Picea rubens[1]) or red spruce yielded 0,204 p. c. of needle oil: d_{16° 0,9539; 66,2 p. c. of bornyl acetate: 7,76 p. c. of free borneol. The cones yielded 0,38 p. c. of oil with a turpentine-like odor: d_{15° 0,860.

Pinus rigida (Mill.?) or pitch pine. 12 ko. of leaves and twigs yielded but 0,2 cc. of a yellowish, exceedingly pungent oil, insufficient for investigation.

Pinus resinosa (Sol.?), red pine or Norway pine. The yield was but 0,001 p. c. and the amount insufficient for a chemical investigation. The oil had a brownish-red color, its odor was pungent and unpleasant.

For an account of the larch needle oil investigated by the same chemists, see p. 134.

From the needles and twigs of several Colorado conifers J. Swenholt[2]) obtained the following oils by distillation with steam under pressure.

The oil of *Picea Engelmanni,* or Engelmann spruce, had a distinct odor of camphor. Its constants were: d 0,8950; $\alpha_D + 3^\circ 51'$ ($1^\circ 55' 38''$ in a 5 cm. tube); S. V. 24,15, corresponding to 8,5 p. c. of bornylacetate.

The oil of the lodge pole pine, *Pinus Murrayana,* had a pleasant odor that did not remind of turpentine oil. S. V. 51,87, corresponding to 18 p. c. of bornyl acetate.

The oil of *Pinus edulis* likewise had a pleasant odor that did not remind of turpentine. Constants: d 0,8653, $\alpha_D - 7^\circ 13'$ ($-3^\circ 36' 58''$ in a 5 cm. tube); S. V. 17,55, corresponding to 6 p. c. of bornyl acetate.

The aqueous distillate obtained upon cohobation presumably contains formic acid.

Oil of *Pinus flexilis:* d 0,8670; $\alpha_D + 8^\circ 1'$ ($+ 4^\circ 0' 28''$ in a 5 cm. tube); S. V. 43,14 corresponding to 15 p. c. bornyl acetate.

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[1]) *Picea rubens,* Sarg. = *P. rubra,* Lk.

[2]) Midland Drugg. and Pharm. Review **43** (1909), 611.

72. Oil of Pinus excelsa.

An "Oil of pine cone" sent to Schimmel & Co.[1]) from India, where it had been distilled from the cones of the Indian blue pine, *Pinus excelsa,* Wall., was of a pale yellow color and had the following constants: d_{15° 0,8757; $\alpha_D - 32^\circ 45'$; n_{D20° 1,47352; A. V. 0,5; E. V. 5,6, corresponding to 2,0 p. c. of bornyl acetate; soluble in 5 vol. and more of 90 p. c. alcohol.

73. Larch Needle Oil.

The needles of the European larch, *Larix decidua,* Mill. (*Larix europæa,* DC.) yield upon distillation but 0,22 p. c. of an oil, sp. gr. 0,878; $\alpha_D + 0^\circ 22'$[2]). It is soluble in 5 and more parts of 90 p. c. alcohol; S. V. 23,3; S. V. after acetylation 46.

Upon fractionation 30 p. c. distilled over between 160 and 165° ($\alpha_D + 4^\circ 15'$), 24 p. c. between 165 and 170°, 16 p. c. between 170 and 180°, 8 p. c. between 180 and 190°, 4 p. c. between 190 and 200°, 9 p. c. between 200 and 230°, residue 9 p. c.

The oil of the American larch, *Larix pendula,* Salisb. (*Larix americana,* Michx.) has been distilled by R. E. Hanson and E. N. Babcock[3]). The yield of oil from needles and twigs was 0,149 p. c.; d_{15° 0,8816; ester content 15,1 p. c. (computed as bornyl acetate). Fractional distillation yielded the following results: 20 p. c. distilled over between 155 and 170°, 38,4 p. c. between 170 and 180°, 11,2 p. c. between 180 and 190°, 9,2 p. c. between 190 and 200°, 14,8 p. c. between 200 and 240°, residue 6,4 p. c.

After repeated fractionation a fraction 155 to 162° was isolated that contained α-pinene (nitrosochloride, m. p. 108°). The investigators concluded that the oil contains about 15,1 p. c. of esters and that the remainder consists largely of pinene.

74. Lebanon Cedar Oil[4]).

Genuine cedar wood from *Cedrus Libani,* Barr. (*Pinus Cedrus,* L., *Abies Cedrus,* Poir., *Larix Cedrus,* Mill.) yields upon

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[1]) Report of Schimmel & Co. April 1911, 124.

[2]) *Ibidem* October 1897, 66.

[3]) Journ. Americ. chem. Soc. 28 (1906), 1198.

[4]) As revealed by a subsequent microscopic investigation, the oil described on p. 279 of the former edition of this work as Lebanon cedar oil, was distilled from a species of juniper.

distillation[1]) about 3,5 p. c. of a lemon-yellow oil that possesses an agreeable balsamic odor, reminding at the same time of methyl heptenone and thujone. It revealed the following constants: d_{15° 0,940 to 0,947; $\alpha_D + 68$ to 86°; n_{D20° 1,5125 to 1,5134; A. V. 0,5 to 1,5; E. V. 2 to 3,0; E. V. after acetylation 19,8; soluble in 5 to 6 vol. of 95 p. c. alcohol. It boils mainly between 270 and 290°. Distilled under 54 mm. pressure from an ordinary fractionating flask, the following amounts passed over: 30 p. c. between 270 and 275°, 40 p. c. between 275 and 280°, 14 p. c. between 280 and 285°, 6 p. c. between 285 and 290°, residue 10 p. c.

75. Atlas Cedar Oil.

Origin and Production. In Algeria the Atlas cedar oil is distilled from the wood of *Cedrus atlantica,* Manetti[2]), which is closely related to the Lebanon cedar. The yield varies between 3 and 5 p. c. The oil, which the manufacturer labels *"Libanol-Boisse"* is used as a medicament in bronchitis, tuberculosis, blennorrhœa, also for skin diseases.

Properties[3]. It is a somewhat viscid, light brownish, balsamic liquid: d_{15° 0,950 to 0,968; $\alpha_D + 46$ to $+ 62$°; n_{D20° 1,512 to 1,517; A. V. to 2,0; E. V. 3 to 11; E. V. after acetylation 30 to 46, corresponding to 12 to 19 p. c. of $C_{15}H_{26}O$[4]); soluble in 1 to 10 vol. of 90 p. c. alcohol. The solubility increases with the sesquiterpene alcohol content.

Composition. According to E. Grimal[5]) 80 p. c. of the oil distilled over between 270 and 295°. Small amounts of acetone were found in the lowest fraction. In fraction 180 to 215° about 5 p. c. of a ketone $C_9H_{14}O$ were found. It yielded a semicarbazone melting at 159 to 160° and a liquid oxime, which upon bromination yielded a dibromide melting at 132 to 133°.

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[1]) Report of Schimmel & Co. October **1909**, 132.

[2]) Dr. Trabut, *Sur l'huile de Cèdre de l'Atlas.* Bull. Sciences pharmacol. **1900**, 262; Report of Schimmel & Co. April **1901**, 58; April **1902**, 12; October **1902**, 25.

[3]) Observations made in the Laboratory of Schimmel & Co.

[4]) Comp. also Chemist and Druggist **61** (1902), 236.

[5]) Compt. rend. **135** (1902), 582 and 1057.

As the principal constituent of the higher fractions *d*-cadinene with the following properties was identified; b. p. 273 to 275°; d 0,9224; $[\alpha]_{D20^\circ} + 48^\circ 7'$; n_{D20° 1,5107. The chlorhydrate melted at 117 to 118°; $[\alpha]_{D20^\circ} + 25^\circ 40'$. The cadinene regenerated from the chlorhydrate with sodium acetate in glacial acetic acid solution revealed the following constants: b. p. 274 to 275°; d 0,9212; $[\alpha]_{D20^\circ} + 47^\circ 55'$; n_{D20° 1,5094. The bromhydrate melted at 124 to 125°.

76. Sequoia Oil.

Upon distillation of the needles of *Sequoia gigantea,* Torr. (*Wellingtonia gigantea,* Lindl.), the giant of California, obtained from a tree cultivated in Zürich, G. Lunge and Th. Steinkauler¹) obtained a volatile oil which congealed in part at ordinary temperature and which consisted principally of a hydrocarbon $C_{10}H_{16}$ boiling at 155°. The sp. gr. of the hydrocarbon was 0,8522; $[\alpha]_j + 23{,}8^\circ$. When hydrogen chloride was passed into the hydrocarbon, a white chlorhydrate (presumably pinene chlorhydrate) consisting of white needles resulted.

Fraction 227 to 230° had a sp. gr. of 1,045, an angle of rotation of + 6° and its odor reminded of that of peppermint oil. The results of the elementary analysis corresponded with the formula $C_{10}H_{20}O_3$. Between 280 and 290° a small amount of heavy yellow oil passed over that had an empyreumatic-aromatic odor.

Furthermore, the oil contains a hydrocarbon, named sequojene, that boils between 290 and 300° (uncorr.), is odorless, crystallizes in small laminæ and melts at 105°. Its composition is probably expressed by the formula $C_{13}H_{10}$, an isomer of fluorene.

77. Oil of Athrotaxis selaginoides.

Athrotaxis selaginoides, Don.²) occurs in Tasmania where it is known as King William pine. The leaves distilled in June yielded an oil characterized by the following properties: $d\frac{16^\circ}{15^\circ}$ 0,8765;

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¹) Berl. Berichte **13** (1880), 1656; **14** (1881), 2202.

²) Baker and Smith, A research on the pines of Australia, Sydney 1910, p. 303.

$\alpha_D + 74{,}8°$; $n_{D16°}$ 1,4905; E.V. 8,6 = 3 p.c. of ester $C_{10}H_{17}OCOCH_3$. The oil was difficultly soluble in ordinary alcohol, but soluble in all proportions in absolute alcohol. It consisted almost entirely of *d*-limonene ($[\alpha]_D + 112{,}2°$, m. p. of tetrabromide 104°). Traces of pinene, possibly also of cadinene, were likewise present, also a phenol, possibly carvacrol.

78. Oil of Cryptomeria japonica.

Origin. The wood of the Japanese cedar, *Cryptomeria japonica,* Don. (*Cupressus japonica,* L.) owes its pleasant odor to a volatile oil which can be obtained, with a yield of 1,5 p. c.[2]), upon distillation with steam.

Properties. Yellow oil; d 0,9453; $[\alpha]_D - 23° 1'$; A. V. 0; E. V. 3,88[1]).

Composition. According to C. Kimoto[2]), the oil contains a substance $C_{30}H_{48}O$(?), called sugiol, which boils at 264° and has a specific gravity of 0,935. K. Keimatsu[3]) found a dextrogyrate sesquiterpene, cryptene, closely related to cadinene, which adds two molecules of hydrohalogen and contains two ethylene linkages. The oil also contains a polyatomic phenol that yields a dibromide $C_{11}H_{14}Br_2O_3$.

An oil examined by H. Kimura[4]) boiled principally between 150 and 160° (17 mm.). It contained cadinene (m. p. of hydrochloride 117 to 118°), also another sesquiterpene, named suginene, which yielded nothing but liquid addition products with hydrogen chloride. Regenerated from the hydrochloride, suginene revealed the following constants: d 0,918; $[\alpha]_D - 10° 34'$. In addition the oil contains a sesquiterpene alcohol which, regenerated from its potassium compound, possesses the following properties: b. p. 162 to 163° (10 mm.); d 0,964; $[\alpha]_D - 37° 5'$.

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[1]) Kimura, Journ. of the pharm. Soc. of Japan **1905**, 189; Berichte d. deutsch. pharm. Ges. **19** (1909), 372.

[2]) Bull. Coll. Agric. (Tokio) **4** (1902), 403; Chem. Ztg. Rep. **26** (1902), 175.

[3]) Journ. of the Pharm. Soc. of Japan **1905**, 189; Report of Schimmel & Co. April **1906**, 23.

[4]) Kimura, Journ. of the pharm. Soc. of Japan **1905**, 189; Berichte d. deutsch. pharm. Ges. **19** (1909), 372.

It was named cryptomeriol by Kimura. When purified through its xanthogen derivative, it is changed to the isomeric alcohol, the *iso*cryptomeriol which melts between 135 and 136°. The oil is reported to consist of about 40 p. c. of alcohol and 60 p. c. of sesquiterpenes. Older oils are said to contain more alcohols than fresh oils.

79. Oil of Taxodium mexicanum.

The Mexican swamp cypress (*Taxodium mexicanum,* Carr.; *T. Montezumæ,* Decne.; *T. mucronatum,* Ten.) known as *Sabino* in Mexico occurs at altitudes of from 1600 to 2300 m. It is not widely distributed, but where it occurs constitutes large forests[1]). An oil sent to Germany by the Instituto Médico Nacional of Mexico, has been examined by Schimmel & Co.[2]). The distillate, which presumably had been obtained from the leaves, was light yellow in color, and resembles turpentine oil as to odor, to which it possibly is also closely related as to composition. d_{15° 0,8685; $\alpha_D - 10^\circ 20'$; n_{D20° 1,46931; A. V. 0,5; E. V. 5,7; soluble in 5,4 vols. and more of 90 p. c. alcohol.

80. Oil of Taxodium distichum.

Oil from the wood. From the sawdust of the southern cypress, *Taxodium distichum,* Rich. growing in the swamps of Virginia, A. F. Odell[3]) obtained with 95 p. c. alcohol an extract which, upon distillation under diminished pressure (35 mm.) yielded a fraction boiling between 180 and 190° and another between 217 to 222°. From the first fraction a substance with the following properties was isolated: b. p. 182 to 185° (35 mm.); $d\frac{20^\circ}{4^\circ}$ 0,9469; α_D dextrogyrate; n_{D20° 1,5040. As to elementary composition, it corresponded with the formula $C_{12}H_{20}O$. The molecular refraction (found 56,29, computed 53,16) indicated the

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[1]) The *Cypresse des Montezuma,* which occurs in the cemetery of Santa Maria del Tule near Oaxaca. It has a height of 40 m. and the circumference of its trunk is said to measure 30 m. De Candolle estimated the age of this tree at 6000 years, von Humboldt at 4000 years.

[2]) Report of Schimmel & Co. April **1909**, 98.

[3]) Journ. Americ. chem. Soc. **33** (1911), 755.

presence of two double bonds the presence of which was verified by the addition of four atoms of bromine. This new substance, named cypral by the author, is regarded as an aliphatic aldehyde, since it yields the characteristic reactions with silver nitrate and fuchsin sulphurous acid.

The higher boiling portions of the alcoholic extract contained a hitherto unknown sesquiterpene which Odell named cypressene, and which was characterized by the following constants: b. p. 218 to 220° (35 mm.), 295 to 300° (778 mm.); $d_{4°}^{18°}$ 0,9647; $[\alpha]_{D20°} + 6,53°$; $n_{D22°}$ 1,5240. The molecular refraction was found to be 64,66, indicating one double bond (computed 62,55). In accordance therewith the sesquiterpene added 2 atoms of bromine. With moderately concentrated nitric acid cypressene yielded a yellow, amorphous oxidation product, with concentrated sulphuric acid a decidedly red color.

OIL FROM THE CONES. The same investigator[1]) has likewise prepared and examined the oil from the cones. Cones distilled in September yielded one percent. of a greenish-yellow oil that had the odor of pinene. Cones collected later in the year yielded 1,5 to 2 p. c. of oil that was darker in color and more decidedly lemon-like as to odor. d 0,86 and 0,850; $\alpha_D + 18,0$ and $+ 35,5°$; alcohol content 2,5 p. c. The oil contained about 85 p. c. of *d*-α-pinene (b. p. 156 to 157°; $d_{4°}^{18°}$ 0,8616; $[\alpha]_D + 30,8°$; $n_{D20°}$ 1,4655; m. p. of nitrosochloride 103°), and 5 p. c. of *d*-limonene (m. p. 175 to 180°; $d_{4°}^{18°}$ 0,9567; $[\alpha]_{D20°} + 98,3°$; $n_{D20°}$ 1,4748; m. p. of tetrabromide 104°, of nitrosochloride 105°), also 2 p. c. of a fraction which probably contained a pseudoterpene alcohol as indicated by the flocculent precipitate produced upon the addition of Beckmann's reagent. In addition the distillate contained 3 p. c. of carvone ($d_{4°}^{18°}$ 0,960; $n_{D20°}$ 1,500; m. p. of semicarbazone 162 to 163°), also 3 p. c. of a dextrogyrate, tricyclic sesquiterpene probably identical with the cypressene of the wood oil, which had the following properties: $d_{4°}^{18°}$ 0,9335; $n_{D20°}$ 1,5039.

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[1]) Journ. Americ. chem. Soc. 34 (1912), 824.

81. Oil of Actinostrobus pyramidalis.

The leaves of *Actinostrobus pyramidalis,* Miq. (*Callitris actinostrobus,* F. v. M.)[1]), which occurs in isolated localities in western Australia, when distilled in July yielded 0,256 p.c. of volatile oil possessing the following properties: d_{15° 0,8726; $\alpha_D + 40{,}9^\circ$; n_{D19° 1,4736; S. V. 21,6 = 7,6 p. c. of ester $C_{10}H_{17}OCOCH_3$; S. V. cold 19,81 = 6,93 p. c. of ester $C_{10}H_{17}OCOCH_3$; soluble in 4 vols. of 90 p. c. alcohol.

Upon fractionation the oil was shown to be a terpene oil that consisted almost entirely of *d*-α-pinene which was characterized in the usual manner. Limonene seemed to be almost entirely absent. The oil also contains geranyl acetate, the geraniol being identified by its oxidation to citral.

82. Sandarac Resin Oil.

Origin and Production. Upon steam distillation of African sandarac from *Callitris quadrivalvis,* Vent. (*Thuja articulata,* Desf.) 0,26[2]) to 1 p. c.[3]) of volatile oil are obtained. Th. A. Henry[4]) obtained the oil by dissolving the resin in alcohol, making the solution slightly alkaline with potassa, distilling off the alcohol and shaking out the residual potassium salts with ether.

Properties. A golden yellow liquid; d_{15° 0,8781; $\alpha_{D20^\circ} + 67^\circ 60'$.

Composition[4]). Fraction 152 to 159° contains *d*-α-pinene (m. p. of nitrosochloride 103°, of nitrolpiperidine 118°). Fraction 270 to 280° contains a hydrocarbon which presumably belongs to the diterpenes (d_{15° 0,9386; $\alpha_D + 51^\circ 42'$; n_D 1,5215).

83. Sandarac Wood Oil.

Upon distillation of the sawdust from the wood of *Callitris quadrivalvis,* E. Grimal[5]) obtained 2 p.c. of a reddish-brown volatile

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[1]) Baker and Smith, A research on the pines of Australia. Sydney 1910, p. 291.

[2]) H. Hænsel, Pharm. Ztg. **48** (1903), 574.

[3]) Tschirch and Balzer, Arch. der Pharm. **234** (1896), 311.

[4]) Journ. chem. Soc. **79** (1901), 1149.

[5]) Compt. rend. **139** (1904), 927.

oil with a phenol-like odor. It is soluble in all proportions in 80 p. c. alcohol, deviates (in alcoholic solution) to the left, and has a sp. gr. of 0,991 at 15°. When distilled it boils between 230 and 306° leaving a resinous residue. It contains about 5 p. c. of phenols, which consist of carvacrol (m. p. of phenylurethane 141°) and hydrothymoquinone (oxidation to thymoquinone). In that portion of the oil which did not react with alkali the presence of thymoquinone (m. p. of *iso*nitrosothymol 161°, of mononitrothymol 137°) was demonstrated.

Australian Callitris Oils.

Many of the Australian species of *Callitris* yield economic woods which are very resistant toward termites, the so-called white ants. This property is very likely due to a content of a phenol, still unidentified, which R. T. Baker and H. G. Smith[1]) have named callitrol (see also p. 143).

Some of the species also secrete a resin similar in its properties to African sandarac (from *Callitris quadrivalvis*). In as much as no rational method of production has been worked out, the collection of the resin does not pay at present prices.

In the discussion of the individual oils, the specis of *Callitris* are grouped in such a manner that the botanical characteristics coincide with the occurrence of *d*-limonene, *l*-limonene and pinene.

84. Oil of Callitris robusta.

The leaves of *Callitris robusta,* R. Br.[2]) (*C. Preissii,* Miq.; *C. Suissii,* Preiss; *Frenela robusta,* A. Cunn.), which occurs in Western Australia, when distilled in July yielded 0,261 p.c. of oil that possessed the following properties: $d_{15°}$ 0,8825; $\alpha_D + 10,3°$; $n_{D19°}$ 1,4752; S. V. 49,59 = 17,35 p. c. of ester $C_{10}H_{17}OCOCH_3$; soluble in 10 vol. of 80 p. c. alcohol. Upon careful fractionation the investigators isolated much *d*-α-pinene, also *d*-bornyl acetate

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[1]) A research on the pines of Australia, Sydney 1910, p. 60.

[2]) Baker and Smith, *loc. cit.* p. 89.

and geranyl acetate. Presumably the oil contains small amounts of limonene and dipentene, likewise a sesquiterpene.

The fruits yielded 0,363 p. c. of an oil which possessed the following properties: $d_{15^\circ}^{16^\circ}$ 0,877; $\alpha_D - 17,9^\circ$; n_{D18° 1,4774; S.V. 16,8 = 5,88 p. c. of ester $C_{10}H_{17}OCOCH_3$.

85. Oil of Callitris verrucosa.

Callitris verrucosa, R. Br.[1] (*Frenela verrucosa,* A. Cunn.), known as cypress or turpentine pine, occurs principally in New South Wales, but is also found in the interior of Australia and in West Australia.

The oil from the leaves (distilled in September with a yield of 0,331 p. c., in December with a yield of 0,266 p. c.) possessed the following constants: d_{23° 0,8591 and 0,8596; $\alpha_D + 44,2^\circ$ and 47,5°; n_{D19° 1,4809 and n_{D20° 1,4809; S. V. 8,93 and 10,87; E. V. after acetylation 21,27; insoluble in 10 vols. of 90 p.c. alcohol.

After careful fractionation the following constituents were found: *d*-α-pinene (m. p. of nitrolbenzylamine 122 to 123°), *d*- and *l*-limonene and dipentene. The limonene and dipentene tetrabromides were obtained from fraction 170 to 180° (d_{23° 0,8624; $\alpha_D + 51,7^\circ$). In addition the oil contains small amounts of geranyl and bornyl acetates, also traces of free borneol, likewise the same sesquiterpene which was found in the oil of *Callitris robusta.*

The oil from the fruits, distilled in December with a yield of 0,44 p. c., had the following properties: d_{22° 0,8608; $\alpha_D + 0,3^\circ$; n_{D19° 1,4738; S. V. 5,1 = 1,78 p. c. ester $C_{10}H_{17}OCOCH_3$.

According to Th. A. Henry[2] the volatile oil of Australian sandarac resin from *Callitris verrucosa* contains *d*-α-pinene.

86. Oil of Callitris propinqua.

Callitris propinqua, R. Br.[3] (*Frenela Moorei,* Parlat.), known as cypress pine, occurs in New South Wales, South Australia and in the Kangaroo islands.

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[1] Baker and Smith, *loc. cit.* p. 101.

[2] Journ. chem. Soc. 79 (1901), 1161, 1163.

[3] Baker and Smith, *loc. cit.* p. 112.

The leaf oil, distilled in May with a yield of 0,41 p. c., had the following properties: $d_{15^\circ}^{19^\circ}$ 0,8662; $\alpha_D + 32,4^\circ$; n_{D19° 1,4752; S. V. hot 34,88; S. V. cold 25,27; with 10 vols. of 90 p. c. alcohol no clear solution resulted.

The constituents of this oil are almost identical with those of the oil of *Callitris glauca.*

An oil distilled from the twigs with fruits (yield 0,326 p. c. in March) showed: $d_{15^\circ}^{20^\circ}$ 0,8709; $\alpha_D + 20,5^\circ$; n_{D19° 1,4749; S.V. 32,24.

87. Oil of Callitris glauca.

Callitris glauca, R. Br.[1]) (*C. Preissii,* Miq.; *C. Huegelii,* ined.; *Frenela crassivalvis,* Miq.; *F. canescens,* Parlat.; *F. Gulielmi,* Parlat.) is known as white, cypress or Murray river pine. It grows over the entire Australian continent, but always at some distance from the coast.

Distilled with water vapor, the wood yields 0,82 p.c. of a volatile oil which in the crude state constitutes a semisolid mass. When pressed through cloth, the larger portion of the solids remains as a cake. The liquid portion has d_{16° 0,9854; is soluble in an equal volume of 70 p. c. alcohol, but the solution becomes turbid upon the addition of more than 3 vol.; with 80 p.c. alcohol a clear solution results at first, but this solution also becomes turbid upon the addition of more solvent. Repeated careful fractionation resulted in the separation of a fraction between 250 and 252° (d_{15° 0,9266; n_{D15° 1,4926; insoluble in 90 p. c. alcohol), which appears to consist chiefly of sesquiterpenes. In addition, the oil contains free acids, esters, also a phenol callitrol, characterized by color reactions. Thus, if sulphuric acid be added to a glacial acetic acid solution, a red color results. The composition of callitrol has not yet been ascertained. The solid constituent, referred to above, crystallizes from alcohol in hexagonal prisms, melts at 91°, and, as was revealed by elementary analysis, consists of guaiol, $C_{15}H_{26}O$; $[\alpha] - 29^\circ$ (in 5 p.c. alcoholic solution).

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[1]) Baker and Smith, *loc. cit.* p. 63 and 118. Comp. also Roy. Soc. New South Wales, Abstract of Proceedings, August 1908, 3; Journ. Soc. chem. Industry **27** (1908), 1039.

The leaf oil, which agrees with the better pine needle oils as to odor and taste, was distilled in December with a yield of 0,532 p.c. and in March with a yield of 0,635 p.c. It had the following constants: $d_{16°}$ 0,8813; $\alpha_D + 27{,}9°$; $n_{D16°}$ 1,4771; ester content (hot) 13,82 p.c., (cold) 6,26 p.c., computed as $C_{10}H_{17}OCOCH_3$. The freshly distilled oil is soluble in 10 vols. of 90 p.c. alcohol, the old oil frequently no longer soluble in 10 vols. In the several fractions the presence of the following substances was demonstrated: *d*-α-pinene (m. p. of nitrosopinene 132°), *d*-limonene (m. p. of tetrabromide 116°)[1], dipentene, *d*-bornylacetate, free *d*-borneol; in the saponification liquid acetic acid and probably butyric acid.

88. Oil of Callitris arenosa.

Callitris arenosa, A. Cunn.[2] (*Frenela robusta,* A. Cunn. var. *microcarpa,* Benth.; *F. Moorei,* Parlat.; *F. arenosa,* A. Cunn.; *F. microcarpa,* A. Cunn.; *F. columellaris,* F. v. M.) occurs in isolated spots in New South Wales, also in Queensland. Like many other species of *Callitris,* it is known as cypress pine.

The oil from the leaves, obtained with a yield of from 0,249 p.c. (in January) to 0,402 p.c. (in September), had the following constants $d_{23°}$ 0,8491; $\alpha_D + 35{,}8°$; $n_{D23°}$ 1,4760; and $d_{26°}$ 0,8452; $\alpha_D + 18{,}9°$; $n_{D26°}$ 1,4764. It is colored a light lemon yellow and does not dissolve in 10 vols. of 90 p.c. alcohol. Upon fractionation it was shown to consist of about 85 p.c. *d*- and *l*-limonene and dipentene. After fractional crystallization of the tetrabromide, its melting point was 115 to 116° and 121 to 122°. In late summer the oil contains more *l*-limonene than in winter, an observation that has also been made in connection with other species of *Callitris.* In addition the oil appears to contain small amounts of bornyl and geranyl acetate.

89. Oil of Callitris intratropica.

The occurrence of *Callitris intratropica,* Benth. et Hook.[1] (*Frenela intratropica,* F. v. Muell.; *F. robusta,* A. Cunn. var.

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[1] In this oil, as in several others, the investigators infer the presence of dipentene from the high melting point of the limonene tetrabromide.

[2] Baker and Smith, *loc. cit.* p. 157.

microcarpa, Benth.) appears to be restricted to Northern Australia and to its Northwest coast. Like the previous species, it also is known as cypress pine.

The oil from the leaves was distilled with a yield of 0,11 p.c. (in November); d_{22° 0,8481 to 0,8570; $\alpha_D - 21{,}6^\circ$; n_{D18° 1,4768; ester content 3,81 to 4,75 (computed as $C_{10}H_{17}OCOCH_3$); insoluble in 10 vols. of 90 p.c. alcohol. In the carefully fractionated oil, the presence of the following substances was ascertained: α-pinene, *l*-limonene, dipentene, borneol and geraniol, the two alcohols probably as acetate. The bulk of the oil consists of terpenes.

The oil from the wood contains callitrol and guaiol. The wood is so rich in guaiol that crystals of it frequently appear when the surface is cut.

90. Oil of Callitris gracilis.

Callitris gracilis, R. T. Baker[2]), known as cypress or mountain pine, occurs only in the vicinity of Rylstone, New South Wales.

Upon distillation, the leaves yielded 0,723 p.c. of volatile oil with the following properties: $d\frac{20^\circ}{15^\circ}$ 0,8683; $\alpha_D + 8{,}7^\circ$; n_{D20° 1,4752; ester content 12,1 p.c. computed as $C_{10}H_{17}OCOCH_3$; soluble in 10 vols. of 90 p.c. alcohol. After repeated fractionation the following constituents were identified: *d*-α-pinene (m. p. of nitrosochloride 107 to 108°, of nitrosopinene 131 to 132°), *l*-limonene, *d*-bornyl acetate and very probably α-terpineol (identified by means of dipentene dihydriodide, m. p. 78°, when shaken with hydriodic acid), apparently present as butyrate. In the saponification liquid acetic and butyric acids were found. In addition the oil probably contains geraniol and a phenol related to callitrol.

91. Oil of Callitris calcarata.

Callitris calcarata, R. Br.[3]) (*C. sphæroidalis,* Slotsky; *C. fruticosa,* A. Br.; *Frenela calcarata,* A. Cunn.; *F. Endlicheri,*

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[1]) Baker and Smith, *loc. cit.* p. 172.

[2]) *Ibidem, loc. cit.* p. 181.

[3]) *Ibidem, loc. cit.* p. 192.

Parlat.; *F. fruticosa,* Endl.; *F. pyramidalis,* A. Cunn.; *F. ericoides,* Hort.; *F. australis,* Endl.; *Cupressus australis,* Persoon; *Juniperus ericoides,* Noisette) is widely distributed in the Southern states of Australia and known as black, red, or mountain pine.

The oil from the leaves (yield 0,162 p.c. in April, 0,168 p.c. in March) had the following properties; d_{17° 0,8863[1]) to 0,8949; α_D — 4,5 to + 11,7°; n_{D19° 1,4747 to 1,4760; ester content (hot) 38,6 to 46,58 p.c., (cold) 27,08 to 39,4 p.c., computed as $C_{10}H_{17}OCOCH_3$. It was soluble in an equal vol. of 80 p.c. alcohol, but the solution became turbid upon the addition of more solvent. In the carefully fractionated oil geranylacetate and *d*-bornyl acetate were found as the principal constituents. In the saponification liquid acetic acid and possibly butyric acid were present. The geraniol was identified by its oxidation to citral (naphthocinchoninic acid). In addition, the oil contains *d*-α-pinene, dipentene, *d*- and *l*-limonene. This species likewise contains more *l*-limonene in late summer than in winter.

The oil from the branches and fruits (yield 0,164 p.c. in December) had the following properties: $d_{15^\circ}^{23^\circ}$ 0,8803; α_D — 4,5°; n_{D19° 1,4752; S. V. 110,38 = 38,6 p. c. ester computed as $C_{10}H_{17}OCOCH_3$. In the several fractions the following substances were found: *d*-borneol (as acetate?), geraniol, resp. geranylacetate, *l*-limonene, dipentene (m. p. of tetrabromide 118°), and acetic acid in the saponification liquid.

The oil from the fruits was distilled in December with a yield of 0,229 p.c. It is practically identical with the oil from the leaves. $d_{15^\circ}^{23^\circ}$ 0,8797; α_D + 2,15°; n_{D23° 1,4744; S. V. (hot) 95,35 = 33,37 p.c. of ester computed as $C_{10}H_{17}OCOCH_3$ (cold 31,18 p.c.). The geraniol was identified by its oxidation to citral.

92. Oil of Callitris rhomboidea.

Callitris rhomboidea, R. Br.[2]) (*C. (?) cupressiformis,* Vent.; *C. arenosa,* Sweet; *Frenela rhomboidea,* Endl.; *F. Ventenatii,* Mirb.; *F. arenosa,* A. Cunn.; *F. triquetra,* Spach; *F. attenuata,* A. Cunn.; *Cupressus australis,* Desf.; *Thuja australis,* Poir.;

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[1]) Computed for 17°.

[2]) Baker and Smith, *loc. cit.* p. 220.

T. articulata, Tenore) is also known as cypress pine and occurs in certain localities of Queensland and New South Wales.

The yield of oil from the leaves distilled in January amounted to 0,0335 p.c.: $d_{15^\circ}^{22^\circ}$ 0,8826; $\alpha_D - 19{,}2^\circ$; n_{D25° 1,4747; ester content (hot) 30,43 p.c., (cold) 29,78 p.c., computed as $C_{10}H_{17}OCOCH_3$; soluble in 7 vol. of 80 p.c. alcohol. Of borneol the oil contains but traces. The ester consisted almost exclusively of geranyl acetate. Probably α-pinene, *l*-limonene and dipentene are present.

93. Oil of Callitris Tasmanica.

Callitris Tasmanica, Baker et Smith[1]) (*Frenela rhomboidea,* R. Br. var. *Tasmanica,* Benth.) occurs in Tasmania, also locally in Victoria and New South Wales. In Tasmania it is known as Oyster Bay pine.

The oil from the leaves distilled in March with a yield of 0,14 p.c. and in June with a yield of 0,208 p.c., had the following properties: d_{15° 0,8976 and d_{22° 0,9036; $\alpha_D + 1{,}0^\circ$ and $-5{,}8^\circ$; n_{D25° 1,4738 and n_{D15° 1,4739; ester content (hot) 59,95 and 62,75 p.c., (cold) 59,91 and 62,2 p.c., computed as $C_{10}H_{17}OCOCH_3$: insoluble in 10 vol. of 70 p.c. alcohol, soluble in 1 vol. and more of 80 p.c. alcohol. The oil consists to the extent of 70 p.c. of geranylacetate and free geraniol. Upon fractionation the presence of the following constituents was ascertained: *d*-α-pinene, probably mixed with *l*-α-pinene, ($d_{15^\circ}^{23^\circ}$ 0,857; $\alpha_D + 9{,}9^\circ$; n_{D24° 1,4706; m. p. of nitrosochloride 107 to 108°, of benzylamine base 122 to 123°), *l*-limonene, dipentene (m. p. of tetrabromide 118°). In the saponification liquid acetic acid only was found. In addition the oil contained a small amount of phenol which probably is identical with that found in the oil of *Callitris gracilis.*

94. Oil of Callitris Drummondii.

Callitris Drummondii, Benth. et Hook. fil.[2]), (*Frenela Drummondii,* Parlat.) grows in West Australia. Like *C. arenosa, C. glauca, C. intratropica* and *C. gracilis* it is known as cypress pine.

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[1]) Baker and Smith, *loc. cit.* p. 233.

[2]) *Ibidem, loc. cit.* p. 253.

The leaf oil, distilled in June (yield 0,547 p. c.), revealed the following properties: d_{17° 0,8591; $\alpha_D + 42,2^\circ$; n_{D19° 1,4739; 1,85 p. c. ester $C_{10}H_{17}OCOCH_3$. In the several fractions the presence of the following substances was ascertained: *d*-*α*-pinene (m. p. of nitrosochloride 108°; of nitrosopinene 132°), *d*-limonene and dipentene, also borneol and geraniol as ester, presumably as acetate. The oil contained more than 90 p. c. pinene.

The oil from the fruits is almost identical with that from the leaves: d_{15° 0,8663; $\alpha_D + 45,1^\circ$; n_{D19° 1,4798; ester content 2,4 p. c., computed as $C_{10}H_{17}OCOCH_3$.

95. Oil of Callitris Muelleri.

Callitris Muelleri, Benth. et Hook. fil.[1]), (*Frenela fruticosa,* A. Cunn.; *F. Muelleri,* Parlat.) is known as Illawarra pine and occurs in isolated localities of New South Wales.

The oil from the leaves was distilled in September with a yield of 0,103 p. c.; d_{24° 0,8582; $\alpha_D - 4,7^\circ$; n_{D20° 1,4749; ester content 2,76 p. c., computed as $C_{10}H_{17}OCOCH_3$. The oil which consisted almost exclusively of terpenes and which resembles turpentine oil as to odor, was insoluble in 10 vols. of 90 p. c. alcohol. The following constituents were identified: *d*- and *l*-*α*-pinene, also *d*- and *l*-limonene.

The fruits contain no volatile oil.

96. Oil of Callitris oblonga.

The occurrence of *Callitris oblonga,* Rich.[2]) (*C. Gunnii,* Hook.; *Frenela australis,* R. Br.; *F. Gunnii,* Endl.; *F. variabilis,* Carr.; *F. macrostachya,* Gord.) is restricted to Tasmania where it is known as native cypress.

Distilled in June, the leaves yielded 0,054 p. c. of volatile oil of the following properties: d_{16° 0,8735; $\alpha_D + 38,1^\circ$; n_{D16° 1,4783; ester content (hot) 6,05 p. c., (cold) 5,6 p. c., computed as $C_{10}H_{17}OCOCH_3$. The oil, which is insoluble in 10 vols. of 90 p. c.

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[1]) Baker and Smith, *loc. cit.* p. 262.

[2]) *Ibidem, loc. cit.* p. 271.

alcohol, yielded upon fractionation mostly *d*-α-pinene (b. p. 155 to 156° and characterized by the nitrosochloride) and very likely contained limonene, probably also a sesquiterpene or a similar compound.

97. Oil of Callitris Macleayana.

In New South Wales, *Callitris Macleayana,* F. v. M.[1]) (*C. Parlatorei,* F. v. M.; *Frenela Macleayana,* Parlat.; *Octoclinis Macleayana,* F. v. M.; *Leichhardtia Macleayana,* Shep.) is known as stringy bark or Port Macquarie pine.

The leaf oil distilled in October (yield 0,172 p. c.) had the following properties: $d_{15^\circ}^{20^\circ}$ 0,8484; $\alpha_D + 42{,}5^\circ$; n_{D20° 1,4791; ester content (hot) 3,5 p. c., (cold) 3,2 p. c., computed as $C_{10}H_{17}OCOCH_3$; insoluble in 10 vols. of 90 p. c. alcohol. After careful fractionation, the following constituents were identified; *d*-α-pinene (m. p. of nitrosochloride 107 to 108°), *d*-limonene (m. p. of tetrabromide 117 to 118°), dipentene (?), also a hydrocarbon the odor and properties of which suggest *d*-menthene (b. p. 162 to 165°; d_{22° 0,837; $\alpha_D + 58{,}7^\circ$; n_{D22° 1,4703). In addition the oil appears to contain cadinene (d_{22° 0,9203; n_{D22° 1,5052) for it gave the color reaction with chloroform and sulphuric acid; a dichlorhydrate, however, was not obtained.

The wood yielded 0,558 p. c. of oil. It consists of a semisolid reddish liquid, the crystalline constituent of which is guaiol.

98. Thuja oil.

Oleum Thujæ. — Thujaöl. — Essence de Thuya.

Origin and Production. Thuja oil is obtained by distillation of the leaves and twigs of the *arbor vitæ* or *Thuja occidentalis,* L., known in North America as white cedar or swamp cedar. According to E. Jahns[2]), the yield varies, according to the season, between 0,4 and 0,65 p. c. It is greatest in spring (March) and diminishes greatly in summer (June). The small amount of oil that is demanded for the market is principally distilled in North America where, according to Ayer[3]), the leaves and branches

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[1]) Baker and Smith, *loc. cit.* p. 278.

[2]) Arch. der Pharm. 221 (1883), 749, footnote.

[3]) Oil, Paint and Drug Reporter June, 1906, 17.

yield up to 1 p. c. of oil. The oil is distilled primarily in the Northern and Eastern districts of Vermont. Those trees which are exposed to sunlight on all sides are the best. The distillation equipment is frequently very primitive. Care should be taken to pack the still properly so that no free spaces are afforded the steam during distillation. The yield also increases with the steam pressure. At times the oil is water-white, sometimes, when the trees have stood in the shade, it is dark in color. Cold weather does not, however, lower the yield of oil from the leaves, but that from the wood.

Although it is very different in its properties, the oil of *Thuja occidentalis* is frequently confounded with that of *Juniperus virginiana,* L.

Properties. Thuja oil is colorless or yellow to greenish-yellow in color, limpid, and possesses a strong characteristic, camphor-like odor reminding of male fern, and has a bitter taste. d_{15° 0,915 to 0,935; α_D — 5 to — 14°; A. V. 0,6; E. V. 20,6; E. V. after acetylation 41,1 (one single observation). It forms a clear solution with 3 to 4 parts of 70 p. c. alcohol. It boils between 160 and 250°, the bulk of the oil distilling between 180 and 205°. The first fraction contains acetic acid¹) with little formic acid.

Composition. Thuja oil was first examined in 1843 by Schweizer²), however, without any definite results. More successful was Jahns³) who succeeded in isolating three constituents by fractional distillation. He obtained a dextrogyrate terpene fraction which boiled between 156 and 161°, a dextrogyrate fraction which boiled between 195 and 197°, and a lævogyrate fraction which boiled between 197 and 199°. The latter fractions contained oxygen and corresponded to the formula $C_{10}H_{16}O$. Inasmuch as they appeared to be optically isomeric, they were designated *l*- and *d*-thujol.

The later investigations by Wallach⁴) definitely cleared up the situation. The identity of the terpene of fraction 160° with *d*-*α*-pinene (nitrosochloride) was established. The fraction up to

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¹) Jahns, *loc. cit.*

²) Journ. f. prakt. Chem. **30** (1843), 376. — Liebig's Annalen **52** (1844), 398.

³) *Loc. cit.*

⁴) Liebig's Annalen **272** (1892), 99.

190° contains a substance that is acted upon by potassium hydroxide with the formation of potassium acetate. Presumably it is an acetic ester. Fraction 190 to 200° contains two chemically distinct ketones of the formula $C_{10}H_{16}O$, *viz.* *l*-fenchone and *d*-thujone.

From the fraction distilling about 220°, Wallach[1]) obtained an inactive oxime that melted at 93 to 94° and which proved to be a derivative of carvotanacetone[2]). Inasmuch as Semmler[3]) had shown that thujone, when heated to higher temperatures, is converted into carvotanacetone, it is probable that carvotanacetone is not present as such in the oil but results from the thujone upon fractional distillation.

While preparing the semicarbazone of *l*-fenchone from thuja oil, Wallach[4]) later found that this fenchone, which had been treated with nitric acid for the purpose of removing thujone, contained *l*-camphor. This discovery led to a renewal of the investigation of thuja oil which revealed that it does not contain camphor but *l*-borneol or its ester. When the oil was treated in the conventional manner for the isolation of fenchone, the borneol was oxidized to *l*-camphor.

99. Thuja Root Oil.

The oil from the root of *Thuja orientalis,* L. is dark brown in color and possesses an odor reminding of thymoquinone. Sp. gr. 0,979. Yield 2,75 p. c.[5]).

100. Oil of Thuja plicata.

Origin. The American *arbor vitæ* or Washington cedar is known botanically by a number of synonyms: *Thuja plicata,* Lamb. non Don, *Th. gigantea,* Nutt., *Th. Menziesii,* Dougl., *Th. Douglasii,* Nutt. and *Th. Lobii* hort. or more correctly *Th. Lobbi* hort., after Lobb, who in 1853 introduced the tree into Europe from western America.

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[1]) Liebig's Annalen **275** (1893), 182.

[2]) Wallach, Liebig's Annalen **279** (1894), 384.

[3]) Berl. Berichte **27** (1894), 895.

[4]) Liebig's Annalen **353** (1907), 213.

[5]) Report of Schimmel & Co. April **1892**, 57.

OIL FROM THE LEAVES AND TWIGS.

Properties and Composition. From the air dried leaves of the Pacific *arbor vitæ,* also known as red cedar or canoe cedar along the Pacific coast of North America, W. C. Blasdale[1]) obtained 2,8 p. c. of a volatile oil of terpene-like odor and the following constants: $d_{15°}$ 0,8997; $\alpha_D + 1° 45'$; n_D 1,4575; b. p. 150 to 225°. Besides thujone, which was isolated from fraction 198 to 200° ($d_{15°}$ 0,9142; $\alpha_D - 0° 52'$; n_D 1,4532) and characterised in the usual manner, no other constituents of the oil could be identified.

According to J. C. Frye, the material distilled by I. W. Brandel and A. H. Dewey[2]) was obtained from *Thuja plicata = Th. gigantea = Th. Menziesii.* Upon distillation with water vapor the leaves and twigs yielded 0,8 to 1,4 p. c. of a light yellow oil, with a slightly pungent camphor-like odor. $d_{25°}$ 0,9305; $\alpha_{D25°} - 6,9°$; A. V. 0,518; S. V. 5,7; E. V. after acetylation 6,2; soluble in all proportions in 70 p. c. alcohol. More than 75 p. c. of the oil distilled between 190 and 203°. It is remarkable that each and every fraction of the oil, which was lævogyrate originally, after fractionation was dextrogyrate. Terpenes were present to the extent of about 3 p. c. Of these α-pinene was identified by its nitrosochloride melting at 103°. The presence of cymene was not definitely established since fraction 175 to 180° upon oxidation yielded only a small amount of an acid melting at 121°. Thujone was found principally in fraction 200 to 203°. It was characterized by its tribromide and by the boiling point of the ketone (203°) regenerated from the acid sulphite addition product. After the thujone had been removed, the presence of fenchone in the principal fraction, mainly 190 to 197,5°, was established by its oxime melting at 164°. The residue remaining above 220° revealed a high saponification value and doubtless contained borneol ester since, upon oxidation with nitric acid, camphor was obtained. After reduction with sodium and alcohol, the oil yielded upon acetylation an ester value of 96,83 p. c. corresponding to about 28,5 p. c. of alcohols.

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[1]) Journ. Americ. chem. Soc. **29** (1907), 539.

[2]) Pharm. Review **26** (1908), 248.

The leaves distilled by Schimmel & Co.[1]) were sent by Prof. Heckel of Marseilles and labled *Thuja Lobii*.

About 1,32 p. c. of an oil of a light yellow color and a strong thujone odor were obtained. Like the oil discribed by Blasdale, it was dextrogyrate: d_{15° 0,9056; $\alpha_D + 5^\circ 4'$; n_{D20° 1,45721; A. V. 0,8; E. V. 16,9; soluble in 70 p. c. alcohol (about 1 : 8) but always with opalescence; with 1,2 vol. and more of 80 p. c. alcohol it, however, forms a clear solution. The thujone, isolated by means of the semicarbazone, revealed itself as *l*-α-thujone. After twofold recrystallization from alcohol, the semicarbazone melted at 185 to 186°. The optical rotation of the thujone regenerated therefrom with phthalic acid anhydride amounted to $\alpha_D - 5^\circ 12'$.

Finally, R. E. Rose and C. Livingston[2]) have distilled an oil from the leaves and twigs with a yield of 1 p. c. which possessed the following properties: d_{20° 0,913; $[\alpha]_{D20^\circ} - 4,77^\circ$; n_{D20° 1,4552; A. V. 0,518; E. V. 2,28; E. V. after acetylation 8,8. It was soluble in 70 p. c. alcohol in all proportions. 85 p. c. of the oil boiled between 100 and 110° (40 mm.) and consisted of α-thujone (m. p. of the tribromide 121 to 122°; of the semicarbazone 186 to 188°). In addition the oil contained 3 to 5 p. c. of *d*-α-pinene, which was identified by means of its physical constants and its nitrosochloride. These investigators also found 1 to 3 p. c. of *d*-tanacetyl alcohol which was characterized by its physical constants: b. p. 210 to 220°; d_{25° 0,9266; $[\alpha]_{D25^\circ} + 29,8^\circ$; n_{D25° 1,46207. It appears to exist in the oil as acetate. Fenchone was not found.

OIL FROM THE WOOD.

Upon distillation of the shavings of the wood with water vapor and shaking out of the aqueous distillate with ether, Blasdale[3]) obtained white crystals which melted at 80°, which had the characteristic pungent odor of the wood, and which possibly have the formula $C_{10}H_{12}O_2$.

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[1]) Report of Schimmel & Co. April 1909, 89.

[2]) Journ. Americ. chem. Soc. 34 (1912), 201.

[3]) *Loc. cit.*

101. Oil of Cypress.

Oleum Cupressi. — Cypressenöl. — Essence de Cyprès.

Origin and Production. Cypress oil is distilled from the leaves and young twigs of *Cupressus sempervirens,* L., (*C. fastigiata,* DC.). According to the season, the freshness of the material and the method of distillation, the yield varies from 0,2 to 1,2 p. c.

Properties. Cypress oil is a yellowish liquid with a pleasant odor of cypress, which, after evaporation leaves a distinct ambra-like odor reminding of labdanum. The physical constants of the oils distilled in Germany differ materially from those obtained in southern France, the German oils being denser than the French oils. This variation may be due partly to the difference in the freshness of material, but appears to be traceable principally to the difference in the method of distillation.

German distillates revealed the following constants: d_{15° 0,88 to 0,90; $\alpha_D + 4$ to $+ 18^\circ$; n_{D20° 1,474 to 1,480; A. V. 1,5 to 3,0; E. V. 13 to 22; E. V. after acetylation 36 to 51; soluble in 2 to 7 vol. and more of 90 p. c. alcohol, occasionally with slight turbidity.

In connection with French oils the following were observed: d_{15° 0,868 to 0,884; $\alpha_D + 12$ to $+ 31^\circ$; n_{D20° about 1,471 to 1,476; A. V. up to 2; E. V. 3 to 14; E. V. after acetylation 9 to 32; soluble in from 4 to 7 vol. of 90 p. c. alcohol, occasionally with slight turbidity.

An Algerian oil had the following properties: d_{15° 0,8764; $\alpha_D + 22^\circ 18'$. It did not yield a clear solution with 10 vol. of 90 p. c. alcohol.

Composition. As the result of a detailed investigation in the laboratory of Schimmel & Co.[1] a considerable number of constituents have been isolated.

The oil that was subjected to examination had the following properties: d_{15° 0,8922; $\alpha_D + 16^\circ 5'$; n_{D20° 1,7416; S. V. 25,3; E. V. after acetylation 50,5. These values correspond to an ester

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[1] Report of Schimmel & Co. April 1904, 36; October 1904, 22; April 1910, 46.

content of 8,8 p. c. computed as $C_{10}H_{17}OCOCH_3$ and of 14,4 p. c. of alcohols computed in $C_{10}H_{17}OH$. The oil did not yield a clear solution with 14 parts of 80 p. c. alcohol.

Furfurol. When distilled in a vacuum (10 mm.), the first drops came over at 44°. With a solution of aniline hydrochloride in aniline they afforded the purple color reaction characteristic of furfurol.

d-α-Pinene. This terpene, the presence of which had previously been established[1], was again identified in fractions possessing all of the properties of pinene ($d_{15°}$ 0,8587; $\alpha_D + 28° 4'$). (M. p. of nitrosochloride 102 to 103°; of benzylamine derivative 122 to 123°).

d-Camphene. In all of the fractions between 160 and 170°, which constituted the bulk of the oil, this terpene was identified by means of the *iso*borneol reaction. Hence camphene is one of the principal constituents. The crude *iso*borneol isolated from the *iso*bornyl actetate upon saponification, had a strong mouldy odor which was probably due to a small admixture of *iso*fenchyl alcohol which, however, could not be isolated as such. Hence it is not improbable that fenchene also is contained in the oil since — analogous to camphene — it yields *iso*fenchyl alcohol when treated with the mixture of glacial acetic acid and sulphuric acid. The *iso*borneol, after repeated purification from petroleum ether and sublimation, melted at 206 to 207°.

Reactions for limonene, dipentene and phellandrene performed on fractions between 170 and 180° gave negative results.

d-*Sylvestrene.* M. p. of the dihydrochloride 72°. The bromide, recrystallized from acetic ester, was obtained in flat, colorless prisms that melted at 134 to 135°.

Cymene is present in small amounts only. It was identified in fraction 174 to 180°. Oxidation with 5 p. c. permanganate solution yielded p-hydroxy *iso*propyl benzoic acid melting at 155 to 156°. When boiled with concentrated hydrochloric acid, it was changed to propenyl benzoic acid melting at 160 to 161°.

Ketone. Fraction 80 to 90° (3 to 4 mm.) contains a ketone not further characterized that has a peculiar odor reminding of

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[1] Report of Schimmel & Co., October 1894, 64.

menthone as well as of thujone. M. P. of the semicarbazone 177 to 178°.

Sabinol (?). Fraction 70 to 74° (3 to 4 mm.), which boiled between 208 and 212° under ordinary pressure, had the properties of sabinol: d_{15° 0,9433; $\alpha_D + 14° 8'$. Upon oxidation there resulted a mixture of acids, part of which melted between 130 and 140° and part of which did not melt at 250°. α-Tanacetogen dicarboxylic acid, the oxidation product of sabinol, melts at 140°.

Alcohol. From fraction 90 to 95° (4 mm.) a few drops of an alcohol with a rose-like odor were obtained, when this was treated in benzene solution with phthalic acid anhydride at waterbath temperature. Its phenylurethane melted at 142 to 144°[1]).

Esters of Terpineol. Fractions above 95° (3 to 4 mm.) were rather rich in esters. The S. V. of an oil which after repeated fractionation boiled between 96 and 98° (4 mm.) was 191,0 corresponding to an ester content of 66,85 p. c. computed as $C_{10}H_{17}OCOCH_3$. Saponification with alcoholic potassa yielded *d*-α-terpineol, m. p. 35° (d_{15° 0,938; $\alpha_{D22^\circ} + 36° 32'$; m. p. of the phenylurethane 112°). The acids found in the several ester fractions were acetic acid, valeric acid, and an acid which boiled between 210 and 260° and crystallized in long silky needles that melted at 129°.

Free terpineol was not found in cypress oil.

Sesquiterpenes. In addition to appreciable amounts of cypress camphor, which can be removed by freezing and by washing out with dilute alcohol, the high boiling portions contain *l*-cadinene. It was identified by its dihydrochloride that melted at 117 to 118°[2]).

Cedrol. The cypress camphor already referred to is found in the fractions above 135° (5 mm.). After recrystallization for 5 to 6 times from dilute alcohol and two subsequent purifications from petroleum ether it is obtained free from odor. It crystallizes in the rhombic system (0,98844 : 1 : 0,71772; well-defined cleavage in the direction of {001}, less so in the direction of {110})[3]);

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[1]) Report of Schimmel & Co., oct. **1904**, 22.

[2]) *Ibidem*, October **1904**, 22.

[3]) C. Blaß, Chem. Zentralbl. **1910**, II. 872.

m. p. 86 to 87°; b. p. 290 to 292°. Its composition is that of a sesquiterpene alcohol (elementary analysis, molecular weight determination according to E. Beckmann). As the result of a false determination of its optical rotation, cypress camphor was at first regarded as the inactive modification of cedar camphor or cedrol. Later[1]) it was shown that cypress camphor is dextrogyrate ($[\alpha]_D + 10° 5'$ in 10 p. c. chloroform solution) and that when treated with dehydrating agents it yields a lævogyrate sesquiterpene ($\alpha_D - 85° 57'$), hence in no way differs from cedrol (Vol. I, p. 401) but is identical with it.

As distillation residue a tough, brown substance is obtained that has an odor reminding of labdanum and ambra.

Upon cohobation of the aqueous distillate of cypress oil a readily volatile, yellow distillate is obtained. In it the presence of methyl alcohol (acid oxalic acid ester), diacetyl (monophenylhydrazone) and furfurol (phenylhydrazone; m. p. of semicarbazone 197°) were established[2]).

Medicinal Uses. In the Childrens Hospital, Leipzig, O. Soltmann[3]) has made extensive investigations of the use of cypress oil as a remedy against whooping cough. The remedy is applied by sprinkling an alcoholic solution of the oil (1 : 4) over the bedding, pillow and night gowns of the children four times daily.

102. Oil of Cypress Fruits.

An oil distilled in southern France from the fruits of *Cupressus sempervirens*, L. had the following properties: $d_{15°}$ 0,8686; $\alpha_D + 30° 48'$; A. V. 0; E. V. 6,74; E. V. after saponification 11,78; soluble in 6 vols. and more of 90 p. c. alcohol[4]).

Upon distillation of the cones deprived of their seeds, Roure-Bertrand Fils[5]) obtained 0,415 p. c. of a light amber colored oil

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[1]) Report of Schimmel & Co., April **1910**, 46.

[2]) *Ibidem*, April **1903**, 29.

[3]) *Keuchhusten und Cypressenöl.* Therapie der Gegenwart, March 1904. — Comp. also H. Winterseel, *Das Cypressenöl. Inaug. Dissert. d. med. Fakultät.* Bonn, 1908.

[4]) Report of Schimmel & Co. April **1905**, 26.

[5]) Report of Roure-Bertrand Fils April **1912**, 26.

of the following properties: $d_{15°}$ 0,8734; $\alpha_D + 29° 52'$; A. V. 1,0; S. V. 9,8; E. V. after acetylation 21,0; soluble in 4 vols. and more of 90 p. c. alcohol.

The seeds contain no volatile oil.

103. Oil of Cupressus Lambertiana.

The leaves of *Cupressus Lambertiana,* Carr. (*C. macrocarpa,* Hartw.), a tree often met with in the gardens of the Riviera, yield upon distillation about 0,1 p.c. of oil; $d_{15°}$ 0,8656; $\alpha_D + 31° 53'$; A. V. 1,5; E. V. 13,9; E. V. after acetylation 50,82; forms a turbid solution with 9 to 10 vol. of 80 p. c. alcohol, a clear solution with 0,5 vol. and more of 90 p.c. alcohol. The greenish-yellow oil has a balm-like odor, due probably to the presence of citronellal. When shaken with acid sodium sulphite solution, the presence of aldehyde-like constituents could be demonstrated, but their amount was too small for identification. The non-aldehydic constituents have a peppermint like odor and may contain cymene[1]).

104. Oil of Cupressus lusitanica.

Cupressus lusitanica, Mill. (*C. glauca,* Lamk.; *C. pendula,* l'Hérit.; *C. Uhdeana,* Gord.; *C. sinensis,* Hort.) is cultivated in the gardens of Portugal, Spain and Italy. It is reported to have been brought to France in 1683. From 400 kg. of twigs Roure-Bertrand Fils[2]) obtained 1 kg. (0,25 p.c.) of oil possessing the following properties: $d_{15°}$ 0,8723; $\alpha_D + 9° 10'$; A. V. 1,05; S. V. 9,8; S. V. after acetylation 26,6; soluble in 3 vol. and more of 90 p.c. alcohol.

105. Hinoki Oil.

The white wood of the hinoki tree, *Chamæcyparis obtusa,* Endl. (*Retinospora obtusa,* Sieb. et Zucc.) is cultivated in Japan and is used in the construction of Shintô temples and in the manufacture of lacquered wares[3]). The oil distilled from the

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[1]) Report of Schimmel & Co. April 1905, 83.

[2]) Report of Roure-Bertrand Fils April 1912, 8, 25.

[3]) Rein, *Japan.* Leipzig 1896. Vol. 2, p. 277.

leaves resembles those from savin and thuja as to odor. Its low boiling temperature is remarkable. About one half of the oil distils over between 110 and 160°, the remainder between 160 and 210°[1]).

106. Oil of Chamæcyparis Lawsoniana.

The oil from *Chamæcyparis Lawsoniana,* Parl. (*Cupressus Lawsoniana,* A. Murr.) which is frequently cultivated in the gardens of Germany, has been distilled by Schimmel & Co.[2]). The material for distillation was obtained from Holstein and yielded about 1 p. c. of a lemon-yellow oil, the odor of which reminded of savin and cypress. Its other properties were: d_{15° 0,9308; $\alpha_D + 23° 48'$; n_{D20° 1,48844; A. V. 3,7; E. V. 61,6; E. V. after acetylation 78,8; soluble in one-half its volume of 90 p. c. alcohol; with 1 to 3 vol. it produces temporary turbidity. With bisulphite solution small amounts of an aldehyde were removed which, to judge by its odor, may be lauric aldehyde.

107. Juniper Oil.

Oleum Juniperi. — Wacholderbeeröl. — Essence de Genièvre.

Origin and Production. *Juniperus communis,* L., the common juniper, is distributed throughout Europe. It occurs more abundantly in the northern portions where it prefers heaths and pine forests. It also occurs in the mountains of central and southern Germany, in the Alps, the Apennines and Pyrenees to an altitude of 1500 m. and more. It also occurs more abundantly in Hungary, between the Danube and the Theiss, more particularly in the Waag valley, the Little Carpathians, the Tatra mountains, the "Forest" Carpathians, also in the East Carpathians (Siebenbürgen) and in Bosnia. The so-called juniper berries are the berry-like cones which are collected in the second year when they are ripe.

The distillation of juniper oil is conducted hand in hand with the production of juniper extract. After the crushed berries have been distilled with steam, the residue in the still is extracted

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[1]) Report of Schimmel & Co. April 1889, 44.

[2]) *Ibidem,* October 1910, 144.

with hot water. The aqueous extract is evaporated in vacuum to extract consistence and enters the trade as *Succus*[1]) or *Roob Juniperi,* Ger. *Wacholderbeersaft.* The yield of both oil and extract varies considerably in different years, as does the composition of the extract. In some years it is so rich in sugar that it congeals to a solid mass.

The average yield of oil is 1 to 1,5 p. c. for the Italian berries, 2 p. c. for the French and Bosnian, 1 to 1,2 p. c. for the Bavarian, and 0,8 p. c. to 1 p. c. for the Hungarian berries. The oil content of the berries from East Prussia, Poland, Thuringia and Franconia is less, *viz.* 0,6 to 0,9 p. c. A distillation of Swedish berries yielded only 0,5 p. c. of oil, Russian berries even less.

Juniper oil in not inconsiderable quantities enters the market from Trencsin. This Hungarian oil, as experience has shown, is of inferior quality and not normal. It is obtained as a by-product in the distillation of gin (Borowiczka). The annual production of juniper oil in Hungary is estimated at 30,000 kg. by A. Ströcker[2]), an estimate that appears decidedly too high.

The oil of juniper berries is used principally in the production of gin *(Wacholderbranntwein, Steinhäger, genièvre)* and liquors, but is also used to a limited extent in medicine, more particularly in veterinary practice.

Properties. Oil of juniper berries is limpid and either colorless or slightly greenish in color. Old oil is viscid, reacts acid and has a more or less rancid odor. The fresh oil has a peculiar odor reminding of turpentine and a balsamic, burning, somewhat bitter taste. According to its origin and method of production, the oil reveals considerable variation as to its physical properties. The specific gravity lies between 0,865 and 0,882 and for normal oil varies mostly between 0,867 and 0,875[3]). As a rule the oil is lævogyrate (up to —11°) rarely, inactive and occasionally

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[1]) The extract thus obtained does not correspond to the *Succus Juniperi* of the German Pharmacopœia. The method of preparation of the official extract is such that at least a small amount of oil remains in the extract.

[2]) Pharm. Post 38 (1905), 236.

[3]) Umney and Bennett record 0,870 to 0,900 as the specific gravity of the English oil. Chemist and Druggist 71 (1907), 171.

dextrogyrate[1]), $n_{D20°}$ 1,479 to 1,484; A. V. up to 3,0; E. V. 2 to 8; E. V. after acetylation 18 to 23. In alcohol, more particularly in in dilute alcohol, oil of juniper berries is but sparingly soluble. To dissolve 1 part of oil, 5 to 10 parts of 90 p. c. alcohol are required. With some oils, however, a clear solution cannot be effected with 90 p. c. alcohol. Freshly distilled oils yield, as a rule, a clear solution, older ones do not.

The Hungarian oil referred to has a specific gravity of 0,860 to 0,880; an optical rotation of up to — 18° 45′[2]). As to solubility it is like the German.

So-called extra strong oil of juniper berries, which is obtained either by fractional distillation or by shaking out with alcohol of varying strength, loses its original greater solubility within a short time.

Composition. Fraction 156 to 159° of juniper oil contains α-pinene[3]) (m. p. of nitrosochloride 109 to 110°, of nitrolbenzylamine 123 to 124°)[4]), but no β-pinene[5]). In fraction 161° ($d_{15°}$ 0,8697; $\alpha_D + 2° 32'$) the presence of camphene[6]) was ascertained. The *iso*borneol obtained by hydration according to Bertram and Walbaum, although recrystallized repeatedly from petroleum ether, melted at 205 to 206°; $[\alpha]_D - 6° 28'$ in a 17,8 p. c. alcoholic solution. A more careful investigation revealed the

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[1]) Two oils from Russia deviated + 7° 17′ and + 7° 50′; an oil distilled from needles and berries, likewise Russian, deviated + 8° 46′ (Report of Schimmel & Co., April **1907**, 60). The conclusion may be drawn that the first two oils were also partly distillates from needles and that presumably dextrogyration is always attributable to leaf oil. At least the Russian source of the berries does not appear to be the cause of the dextrorotation, for a distillate from Russian berries (yield 0,48 p. c.) had the following properties: $d_{15°}$ 0,8818; $\alpha_D - 0° 32'$; $n_{D20°}$ 1,48112; A. V. 1,8; E. V. 5,6; soluble in 6 vols. of 90 p. c. alcohol, the solution being slightly turbid.

[2]) In connection with individual oils an even higher angle of rotation, up to — 21° 20′, has been observed. According to the statement of the purveyor, these oils had been distilled from Bosnian berries. The subsequent distillation of berries from Bosnia yielded a slightly lævogyrate oil ($\alpha_D - 0° 35'$). Hence the suspicion that the oils in question had been adulterated was not removed.

[3]) Wallach, Liebig's Annalen **227** (1885), 288.

[4]) Report of Schimmel & Co. October **1910**, 72.

[5]) Comp. H. Hænsel, Chem. Zentralbl. **1908**, II. 1437.

[6]) Report of Schimmel & Co. October **1910**, 72.

fact that the product was a mixture of borneol and *iso*borneol. The amount of *iso*borneol was ascertained by converting it into the methyl ether and determining the methyl value. The amount of borneol was ascertained by Tschugaeff's nitric acid test[1]); also by means of Bertram and Walbaum's methyl ether reaction as modified by A. Hesse[2]).

Another examination, likewise conducted in the laboratory of Schimmel & Co.[3]) revealed that a large portion of the oxygenated constituents consists of terpinenol. In order to secure the oxygenated constituents, the oil was repeatedly shaken with 70 p. c. alcohol. From the alcoholic solution the solvent was removed by distillation. Thus an oil was obtained which possessed a pleasant juniper-like odor and the following constants: d_{15° 0,9300; $\alpha_D - 3^\circ 44'$; E. V. 21,8; E. V. after acetylation 136 corresponding to 41,65 p. c. alcohol $C_{10}H_{17}OH$. Diluted with xylene, the alcohol content was found to be 56,2 p.c. $C_{10}H_{17}OH$. When fractionated under 8 mm. pressure, 70 p.c. came over between 86 and 110°, and 30 p. c. between 110 and 155°. Repeated fractionation of the principal fraction resulted in the separation of a portion that consisted essentially of terpinenol-4 and possessed the following properties: b. p. 93 to 95° (8 mm.); 215 to 220° (750 mm.); d_{15° 0,9400; $\alpha_D + 13^\circ 6'$. When oxidized with dilute permanganate solution while keeping the reaction mixture cool, 1,2,4-trihydroxy terpane, m. p. 114 to 116°, resulted, a glycerol which Wallach[4]) had obtained from terpinenol-4. This glycerol was further identified by its conversion into carvenone (m. p. of semicarbazone 202°. Comp. vol. I, p. 383).

In addition to terpinenol, but in much smaller amount, oil of juniper berries contains another alcohol with the following properties: b.p. 105 to 110° (8 mm.); 218 to 226° (ordinary pressure); d_{15° 0,9476; $\alpha_D - 4^\circ 30'$; n_{D22° 1,48248. It combines readily with phthalic acid anhydride[5]) and was separated from fraction 95

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[1]) Chem. Ztg. **26** (1902), 1224.

[2]) Berl. Berichte **39** (1906), 1141.

[3]) Report of Schimmel & Co. October **1909**, 71.

[4]) Liebig's Annalen **362** (1908), 278.

[5]) As has been pointed out by H. Hænsel the higher boiling fractions contain traces of a primary alcohol $C_{10}H_{18}O$ that can be removed with phthalic acid anhydride (Chem. Zentralbl. **1908**, II. 1437).

to 130° in the form of the acid phthalic ester. Its odor reminds of geraniol and borneol and it is probable that the substance is not a definite chemical compound but a mixture of several alcohols. Finally the oil contains a small amount of a substance of a particularly characteristic odor which is met with in fraction 72 to 88° (8 mm.).

Cadinene[1]) is a constituent the presence of which in this oil has been known for some time. It is found in fraction 260 to 275° (m. p. of dihydrochloride 118°).

In the tailings of a juniper berry oil that had stood in a cool place for a long period, a separation was observed. After repeated crystallizations from alcohol, fine needle-shaped crystals melting at 165 to 166° were obtained[2]). Similar crystal formations have been observed repeatedly and have been described in the older literature[3]) as juniper camphor, juniper stearoptene and juniper berry hydrate[4]).

108. Oil of Juniper Leaves.

The twigs of *Juniperus communis,* L. deprived of their berries were distilled by R. E. Hanson and E. N. Babcock[5]) in May. They obtained 0,15 to 0,18 p. c. of a light yellow oil ($d_{20°}$ 0,8531), which had a characteristic odor of juniper.

109. Oil of Juniper Wood.

The so-called oil of juniper wood is now a days used only in veterinary practice and as an external remedy in domestic medication. It is mostly a turpentine oil that has been distilled over juniper wood or twigs, some times it is a juniper berry oil diluted with turpentine oil. Hence the properties of commercial "juniper wood oil" vary with these practices.

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[1]) Bericht von Schimmel & Co. April 1890, 43.

[2]) *Ibidem*, October 1895, 46.

[3]) Of the earlier investigations of juniper oil the following should here be mentioned: Blanchet, Liebig's Annalen 7 (1833), 167; Dumas, Liebig's Annalen 15 (1835), 159; Soubeiran and Capitaine, Liebig's Annalen 34 (1840), 324.

[4]) Blanchet, *loc. cit.;* the crystalline deposit observed by Zaubzer [Repert. f. d. Pharm. 22 (1825), 415] differed according to Buchner (*ibidem* 425) from turpentine camphor or terpin hydrate.

[5]) Journ. Americ. chem. Soc. 28 (1906), 1201.

A sample of juniper wood oil that was marked genuine had the same properties as juniper berry oil: d_{15° 0,8692; $\alpha_D - 21^\circ 2'$; n_{D20° 1,47111; A. V. 0,9; E. V. 6,7; soluble in 7 vols. and more of 90 p. c. alcohol with slight turbidity.

110. Juniper Oil from Juniperus Oxycedrus.

OIL FROM THE FRUITS. The reddish-brown fruits of *Juniperus Oxycedrus,* L., which grows along the Mediterranean, yield 1,3[1]) to 1,5 p. c.[2]) of an oil that has a turpentine-like and but faintly juniper-like odor. Specific gravity 0,851[1]) to 0,854[2]); $\alpha_D - 4^\circ 40'$[2]) to $-8^\circ 30'$[1]). It does not form a clear solution with 95 p. c. alcohol.

OIL FROM THE TWIGS. A Spanish oil distilled from the tips of the branches had an odor resembling the better pine needle oils[3]).

111. Cedar Oil from Hayti.

A cedar wood received by Schimmel & Co.[4]) from Hayti yielded 4,33 p. c. of a lemon-yellow oil with an odor that resembled that of the ordinary cedar oil from *Juniperus virginiana,* L. Nothing definite could be ascertained as to the botanical origin of the wood, but a microscopical examination revealed it as coniferous. The oil obtained differed, however, from the ordinary cedarwood oil by its higher specific gravity (d_{15° 0,9612), its lower optical rotation ($\alpha_D - 14^\circ 58'$), and its larger alcohol content (E. V. after acetylation 64,0). The A. V. was 2,7, E. V. 5,0. The oil was not completely soluble in 10 vols. of 90 p.c. alcohol but soluble in every proportion in 95 p. c. alcohol.

112. Oil of Red Cedar Wood.

Oleum Ligni Cedri. — Cedernholzöl. — Essence de Bois de Cèdre.

Origin and Production. The red or Virginia cedar, *Juniperus virginiana,* L. is a shrub or tree that attains a height of 15 m. It is distributed throughout the United States of North America. For a long time its wood has been used in the manufacture of

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[1]) Hænsel, Apotheker Ztg. **13** (1898), 510.

[2]) Observations made in the works of Schimmel & Co.

[3]) Bericht von Schimmel & Co. October **1889**, 54.

[4]) Report of Schimmel & Co. April **1906**, 17.

cigar boxes, lead pencils and minor wooden ornaments. The forests of Georgia and Florida, which formerly supplied most of the wood, are almost exhausted. At present Tennessee is the principal center of production and Nashville the principal market for cedar wood. Here also the saw dust and other waste, also the knots, which are said to be particularly rich in oil, are distilled.

The oil which is collected in the drying kilns as a by-product is of inferior quality. These kilns are so arranged that the escaping vapors can be condensed. The higher boiling constituents remain in the wood and only the lower boiling constituents are thus obtained. As a result, the oil is limpid and its odor less delicate and permanent than the normal. Hence it cannot be used in perfumery.

In Germany the waste of the lead pencil factories is used for distillation, a yield of from 2,5 to 4,5 p.c. being obtained. The exhausted chips are used in factories in which skins are prepared for the fur trade.

Properties. Cedarwood oil is wellnigh colorless, somewhat viscid and occasionally studded with crystals of cedar camphor. It has a mild, peculiar but persistent odor. Inhalation of the vapors imparts a violet odor to the urine. d_{15° 0,943 to 0,961; α_D — 25 to — 42°; n_{D20° about 1,504; A. V. up to about 1; E. V. up to 6,5; E. V. after acetylation 26 to 42. In alcohol the oil is soluble with relative difficulty, for 1 vol. of oil required 10 to 20 vols. of 90 p.c. and up to 6 vols. of 95 p.c. alcohol.

American oils, presumably from the drying kilns of lead pencil manufacturers (see above), had the following properties; d_{15° 0,940 to 0,944; α_D — 40 to — 46° 22′; S. V. 2 to 4; E. V. after acetylation 14 to 18; soluble in 5 to 6 vol. of 95 p.c. alcohol.

Composition. The most interesting constituent of the oil, *viz.* cedrol (see vol. I, p. 401) or cedar camphor was first examined by Walter¹) who converted it into cedrene by dehydration with phosphoric acid anhydride. The formula $C_{16}H_{28}O$ suggested by him was declared improbable by Gerhardt²) who suggested $C_{15}H_{26}O$.

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¹) Liebig's Annalen **39** (1841), 247.

²) Gerhardt, *Lehrbuch der organischen Chemie.* Vol. IV, p. 378.

Chapman and Burgess[1]) studied the liquid portions of the oil. By means of fractional distillation they separated cedrene (b. p. 261 to 262°; d 0,9359; $\alpha_D - 60°$) and compared it with the hydrocarbon of fraction 301 to 306° of sandalwood oil. According to Chapoteaut[2]) the hydrocarbons were supposed to be identical. Chapman and Burgess, however, arrived at the conclusion that both hydrocarbons were very similar but not identical.

Rousset[3]) examined cedarwood oil with the following results: Cedrene, obtained by fractionation — hence natural cedrene — is a sesquiterpene $C_{15}H_{24}$ (comp. vol. I, p. 340). Under 10 mm. pressure it boils at 131 to 132°; $[\alpha]_D - 47° 54'$. Upon oxidation of cedrene with chromic acid in acetic acid solution a liquid ketone resulted, to which Rousset assigned the formula $C_{15}H_{24}O$ and which he named cedrone. Reduction converted it into an alcohol $C_{15}H_{26}O$, *iso*cedrol. Isomeric with this is the cedar camphor or cedrol (m. p. 84°). If cedrol be heated in a sealed tube with acetic acid anhydride, only a part thereof is converted into the ester, the other part is dehydrated to the sesquiterpene. If cedrol be treated with benzoyl chloride no ester whatever results but only the hydrocarbon $C_{15}H_{24}$. Since cedrol yields neither a ketone nor aldehyde upon oxidation it must be regarded as a tertiary alcohol.

Cedrol is not always contained in cedarwood oil. For years it was sought for in vain in the laboratory of Schimmel & Co. Apparently it is formed when the sawdust or shavings are exposed to the (moist?) atmosphere for a prolonged period.

More recent investigations by F. W. Semmler, together with his students A. Hoffmann[4]), F. Risse[5]), K. E. Spornitz[6]) and E. W. Mayer[7]) yielded results that differ somewhat from the above.

The natural cedrene was studied first. The results of these investigations are already recorded in vol. I, pp. 340 and 341. The following supplementary statements should be recorded.

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[1]) Proceed. chem. Soc. No. 168 (1896), 140.

[2]) Bull. Soc. chim. II. **37** (1882), 303; Chem. Zentralbl. **1882**, 396.

[3]) *Ibidem* III. **17** (1897), 485.

[4]) Berl. Berichte **40** (1907), 3521.

[5]) *Ibidem* **45** (1912), 355.

[6]) *Ibidem* 1553.

[7]) *Ibidem* 786.

When natural cedrene (b.p. 123 to 124° under 12 mm.) was oxidized with ozone, there resulted as indifferent products a ketone (not determined whether $C_{14}H_{24}O$ or $C_{14}H_{22}O$) and a keto-aldehyde $C_{15}H_{24}O_2$. Of acid oxidation products an acid $C_{15}H_{24}O_3$, cedrene keto-acid was isolated, the methyl ester of which possessed the following constants: b. p. 165 to 170° (10 mm.); d_{20° 1,0509; α_{D20° — 32° 24′; n_D 1,4882. When oxidized with nitric acid of 27 p.c. strength, this cedrene keto-acid yielded an acid $C_{14}H_{22}O_4$ (m.p. 182,5°), the cedrene dicarboxylic acid, the dimethyl ester of which revealed the following constants: b. p. 179 to 183° (13 mm.); d_{20° 1,0778; α_D — 31° 36′; n_D 1,48084.

That the cedrene keto-acid $C_{15}H_{24}O_3$ is a methyl keto-acid which is closely related to the dicarboxylic acid $C_{14}H_{22}O_4$, was demonstrated by the oxidation of the former to the latter by means of alkaline bromine solution.

The question as to the identity of natural and artificial cedrene already alluded to has been solved by the study of their oxidation products by Semmler.

The artificial cedrene was obtained by heating cedrol (m.p. 79 to 80°) with an equal volume of 100 p.c. formic acid for ¹/₄ hour[1]). It boiled at 112 to 113° (7 mm.): α_D — 85°. Upon oxidation with ozone, in glacial acetic acid solution, this hydrocarbon yielded the cedrene keto-acid which was characterized by its methyl ester (b. p. 166 to 168° under 11 mm.; d_{19° 1,0501; α_D — 35°; n_D 1,48482).

The cedrene dicarboxylic acid obtained from the artificial cedrene was also identical with the cedrene dicarboxylic acid from natural cedrene. The two products when triturated together revealed no lowering of the melting point.

These experiments demonstrate that the strongly optically active artificial cedrene is contained in the natural cedrene. Inasmuch as the natural product has a higher boiling point, it presumably contains other isomeric sesquiterpenes, probably some semicyclic cedrene.

Semmler[2]) likewise succeeded in isolating from cedar wood oil another oxygenated constituent which he named cedrenol.

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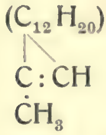
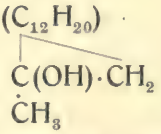
[1]) Berl. Berichte 45 (1912), 1554.

[2]) *Ibidem* 786.

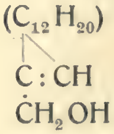
This is a primary sesquiterpene alcohol. It occurs in fraction 152 to 170° (7 mm.) ($\alpha_{D20^\circ} + 17,5^\circ$) of the oil, from which it can be isolated with phthalic acid anhydride in benzene solution. The alcohol, purified through the acetate, has the following properties: b. p. 166 to 169° (9,5 mm.); d_{20° 1,0083; $\alpha_{D20^\circ} \pm 0^\circ$; n_{D20° 1,5212. The acetate is a colorless liquid, b. p. 165 to 169° (9,5 mm.); d_{20° 1,0168; $\alpha_D - 2^\circ$; n_{D20° 1,5021. Cedrenyl chloride boils between 150 and 165° (10 mm.); d_{20° 1,001. Heated with sodium and alcohol, the chloride yields a hydroxyethyl ether and a hydrocarbon which was found to be identical with cedrene, as was shown by its oxydation products cedrene keto-acid and cedrene dicarboxylic acid. Cedrenol is related to cedrene as the two primary alcohols of the santalol series to the santalenes, sesquiterpenes $C_{15}H_{24}$; and as myrtenol and gingergrass alcohol are related to pinene and limonene. Presumably the primary alcohol group CH_2OH of the cedrenol molecule occupies the same position held by the CH_3 group in both cedrene and cedrol. Their relationship is readily expressed by the following formulas:



Cedrene, $C_{15}H_{24}$



Cedrol, $C_{15}H_{26}O$



Cedrenol, $C_{15}H_{24}O$.

In addition to cedrenol, Semmler and Mayer[1]) have shown the presence of a saturated alcohol in cedarwood oil, *viz.* pseudocedrol. This alcohol is contained in fraction 145 to 155° (10 mm.) from which the cedrenol has been removed by means of phthalic acid anhydride. It boils between 147 and 152° (9 mm.), constitutes a very viscid oil of the composition $C_{15}H_{26}O$, and is characterized by the following constants: d_{20° 0,9964; $\alpha_{D20^\circ} + 21,5^\circ$; n_{D20° 1,5131. It is tertiary in character, for when heated with zinc dust in a sealed tube to 225 to 235°, oxygen was abstracted with the formation of the corresponding saturated hydrocarbon, dihydrocedrene. Moreover, it contained 50 p. c. of cedrene as impurity. In order to purify the dihydrocedrene, ozone was

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[1]) Berl. Berichte **45** (1912), 1384.

passed into the chloroform solution of the hydrocarbon mixture until added bromine was no longer decolorized. Dihydrocedrene boils between 109 and 112° (10 mm.) d_{20° 0,907; $\alpha_D + 37^\circ$; n_D 1,4882. It differs in its physical properties from the dihydrocedrene which had been obtained by the reduction of cedrene with platinum and hydrogen and which revealed the following constants: b. p. 122 to 123° (10 mm.); d_{20° 0,9204; $\alpha_{D20^\circ} + 2^\circ$; n_{D20° 1,4929. When acted upon by formic acid, pseudocedrol yields cedrene which was characterized by its keto acid and its dicarboxylic acid.

Cedrol and pseudocedrol are chemically identical and physically isomeric.

Tests and Detection. Adulterations of cedarwood oil have thus far not been observed. Frequently, however, this cheap oil is used for the adulteration of other oils, to which purpose it is admirably suited because of its faint odor. Its presence is recognized by its high specific gravity, its high boiling point, its strong lævorotation and by its relatively difficult solubility in alcohol. Adulteration with cedarwood oil may be chemically established by oxidation of the cedrene to cedrene keto-acid and cedrene dicarboxylic acid. The suitable fraction (b. p. about 123 to 124° under 12 mm. pressure or 263 to 264° under ordinary pressure) of the oil to be examined is oxidized with potassium permanganate or ozone to cedrene keto-acid $C_{15}H_{24}O_3$ (See also vol. 1, p. 340). This is further oxidized by means of alkaline bromine solution or nitric acid to cedrene dicarboxylic acid, m. p. 182,5°[1]).

113. Cedar Leaf Oil.

Oleum Foliorum Cedri. — Cedernblätteröl. — Essence des Feuilles de Cèdre.

Origin. According to observations made in the laboratory of Fritzsche Bros.[2]), the cedar leaf oil of the American market is never what it ought to be, *viz.* the oil from the leaves of *Juniperus virginiana,* L. This is partly due to the fact that in North America the term cedar is applied to two distinct trees, *viz.* to

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[1]) Semmler and Risse, Berl. Berichte 45 (1912), 355.

[2]) Report of Schimmel & Co. April 1898, 14.

Juniperus virginiana and to *Thuja occidentalis.* It is true that these two species are differentiated as "red" and "white" cedar. The distillers of the oil, however, pay no attention to this distinction and use the leaves of both species, frequently even with the leaves of other conifers. Hence the cedar oil of commerce reveals appreciable differences in its properties.

Genuine cedar leaf oil is but rarely distilled. In one instance the yield amounted to 0,2 p. c.[1]).

Properties. d_{15° 0,887[2]) to 0,900[2]); $\alpha_D + 59° 25'$; S. V. 10,9; E. V. after acetylation 39,1. It was not soluble in 10 vols. of 80 p. c. alcohol. The odor was pleasant, somewhat sweetish. When fractionated, the bulk distilled below 180°.

The specific gravities of a number of commercial oils varied between 0,863 and 0,920; the angle of rotation between $-3° 40'$ and $-24° 10'$. Some of these oils were soluble in 4 or 5 vols. of 70 p. c. alcohol, others not. All of these commercial oils had a more or less thuja-like odor.

Composition[3]). The lowest fractions appear to contain α-pinene (nitrosochloride). One fraction (b. p. 173 to 176°; $\alpha_D + 89°$) consisted almost entirely of pure *d*-limonene (m. p. of tetrabromide 104 to 105°). The higher boiling fractions contained borneol (m. p. 103 to 104°), partly free, partly as ester (valeric acid?). The highest fractions contained cadinene (hydrochloride).

114. Oil of Juniperus chinensis.

According to the investigations of H. Kondo[4]) the oil of *Juniperus chinensis* resembles chemically that of *Juniperus virginiana.* Both the cedrol and the cedrene isolated from the oil were chemically identical with the corresponding compounds isolated from *J. virginiana.* In their physical properties, however, they revealed considerable deviations.

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[1]) Distilled in the factory of Fritzsche Bros. in Garfield, N. J. Comp. also Report of Schimmel & Co. April 1894, 56.

[2]) Hanson and Babcock, Journ. Americ. chem. Soc. 28 (1906), 1201.

[3]) Report of Schimmel & Co. April 1898, 14.

[4]) Journ. of the pharm. Soc. of Japan 1907, 236; Report of Schimmel & Co. October 1907, 57.

115. East African Cedarwood Oil.

Juniperus procera, Hochst. is a tree that is found in the mountains of Abyssinia and Usambara also on the Kilimandjaro and Kenia. It grows at an altitude of 1500 to 3000 m. and in Usambara constitutes extended forests. Anatomically, the wood reveals great resemblance to that of *Juniperus virginiana.*

From the sawdust of the wood, which is used in the manufacture of lead pencils, Schimmel & Co.[1] obtained 3,2 p.c. of a dark yellowish-brown oil with an odor reminding very much of vetiver, and which possessed the following constants: d_{15° 0,9876; n_{D20° 1,50893; A. V. 14,9; E. V. 8,4; E. V. after acetylation 70. Inasmuch as the oil was too dark, the optical rotation was determined for a solution of equal volumes of alcohol and oil. For a 20 mm. tube it was found to be $-3^\circ 43'$, which corresponds to $-37^\circ 10'$ for the original oil in a 100 mm. tube. The oil was soluble in 1,6 vols. and more of 80 p.c. alcohol and in ½ vols. and more of 90 p.c. alcohol.

From the comminuted small boards 3,24 p.c. of oil were obtained which at ordinary temperature consisted of a semi-solid mass permeated with crystals. The oil from which the crystals had been removed had the following properties: d_{15° 1,0289; n_{D20° 1,51011; A. V. 27,06; E. V. 7,93; E. V. after acetylation 89,6. In this case also it was impossible to determine the optical rotation of the original oil. Diluted with an equal volume of alcohol, it showed $-3^\circ 15'$ in a 20 mm. tube ($= -32^\circ 30'$ for the original oil in a 100 mm. tube). It is soluble in 2 vol. and more of 80 p.c. alcohol and in ½ vol. of 90 p.c. alcohol. The crystals consisted of cedar camphor. Recrystallized from alcohol, they melted at 86 to 87°; $[\alpha]_D + 10,12^\circ$ (2,5517 g. solution dissolved in 25 cc. of chloroform). The phenyl urethane melted at 106,5°.

116. Oil of Savin.

Oleum Sabinæ. — Sadebaumöl. — Essence de Sabine.

Origin. The savin, *Juniperus Sabina,* L. is a tree-like shrub[2] that grows wild in the mountains of Central and Southern Europe and that is occasionally cultivated.

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[1] Report of Schimmel & Co. October 1911, 105.

[2] P. Guigues, *Une forêt de sabines dans les Hautes-Alpes.* Bull. Sciences pharmacol. 9 (1902), 33.

Production. The oil is obtained by the steam distillation of the leaves and ends of twigs, the *Summitates Sabinæ.* The yield varies, according to the time of collection and the freshness of the material, between 3 and 5 p.c.[1]). The leaves used for distillation are obtained primarily from the Tirol. In Southern France also oil of savin is distilled, but there the leaves and branches of related species *(J. phœnicea* and *J. thurifera* var. *gallica)* are mostly used[2]). Hence the constants of the French oils are different. In consequence it was formerly supposed that they represented true oil of savin adulterated with oil of turpentine.

Properties. Oil of savin is a colorless or yellowish liquid of a disagreeable narcotic odor and a bitter, pungent, camphor-like taste. d_{15° 0,907 to 0,930; $\alpha_D + 38$ to $+ 62^\circ$[3]); n_{D20° 1,473 to 1,479; A. V. up to 3; E. V. 107 to 138; E. V. after acetylation 127 to 154. It is soluble in $^1/_2$ and more parts of 90 p.c. alcohol. Of 80 p.c. alcohol 5 to 15 vol. are required, but the solution thus obtained is not always perfectly clear. Upon repeated fractionation, 25 to 30 p.c. are obtained below 175°[4]).

Composition. Concerning the hydrocarbons of the lower fractions there has been much ambiguity for a long time. The results of an investigation published by Dumas[5]) in 1835 indicated the presence of pinene or camphene. Dumas had isolated a fraction 155 to 161° that had the composition $C_{10}H_{16}$. Upon the oxidation of the terpene that boiled at about 161°, Grünling[6]) obtained terephthalic and terebic acids which indicated pinene. Fromm[7]) then obtained about 25 p.c. of a terpene fraction below

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[1]) With regard to the abnormally low yields from fresh and dry twigs see E. F. Ziegelmann, Pharm. Review **23** (1905), 22.

[2]) E. Perrot and Mongin, *A propos de la Sabine et des espèces botaniques de Juniperus fournissant la drogue commerciale.* Bull. Sciences pharmacol. **9** (1902), 38. The authors demonstrate that the French drug is a mixture of the twigs of *Juniperus Sabina, J. phœnicea* and *J. thurifera* var. *gallica,* of which *J. phœnicea* constitutes the bulk. Similar conditions prevail in the distillation of French savin.

[3]) In connection with an English oil Umney and Bennett observed $\alpha_D + 68^\circ$.

[4]) Berl. Berichte **33** (1900), 1192 and 1463.

[5]) Liebig's Annalen **15** (1835), 159.

[6]) *Beiträge zur Kenntnis der Terpene.* Inaug. Diss., Straßburg 1879, p. 27. — See also Levy, Berl. Berichte **18** (1885), 3206.

[7]) Berl. Berichte **33** (1900), 1192.

165°, but he did not succeed in identifying pinene or any other known terpene. Inasmuch as it is important to know in the testing for adulterations whether the oil contains pinene or not, Schimmel & Co.[1]) refractionated the portion that distilled below 160°. From 25 kg. of oil they thus obtained but 13 g. of a hydrocarbon with the boiling point of pinene. However, a part of this consisted of sabinene. Neither did it give the reactions characteristic for pinene. Thus it was shown that savin oil contains at most traces of pinene and that the investigations by Dumas and Grünling were conducted either upon an oil adulterated with pinene or upon an oil that had been obtained from other species of *Juniperus* (see above). The proof of the presence of very small amounts of α-pinene was accomplished by J. W. Agnew and R. B. Croad[2]) who obtained upon the oxidation of fraction 160° with mercuric acetate a mixture of pinol hydrate (m. p. 131°, of dibromide 131 to 132°; m. p. of pinol dibromide 94°) and 8-hydroxycarvotanacetone (m. p. of semicarbazone 175°)[3]).

In 1900 Semmler[4]) discovered in savin oil a new terpene, sabinene $C_{10}H_{16}$, which boils between 162 and 165°. (See vol. 1, p. 300), and which he oxidized to sabinene glycol (m. p. 54°) and to sabinic acid (m. p. 57°). Whereas until recently only *d*-sabinene had been found in savin oil (comp. vol. 1, p. 300), Agnew and Croad found *l*-sabinene. In fraction 170 to 180° Schimmel & Co.[5]) proved the presence of α-terpinene (m. p. of nitrosite 156°).

The principal constituent is an alcohol $C_{10}H_{16}O$ which was first isolated by E. Fromm[6]) and named sabinol by him. It is contained in the oil partly free, partly as ester, the acetate (silver salt[7])) predominating. According to Fromm[8]) the higher boiling acids are a mixture of a liquid, dibasic acid which boils at 255° and which probably has the composition $C_{20}H_{36}O_5$, and a solid acid $C_{14}H_{16}O_8$ which boils at about 260° and melts at 181°.

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[1]) Report of Schimmel & Co. April 1908, 97.

[2]) Analyst **37** (1912), 295.

[3]) Comp. Henderson and Agnew, Journ. chem. Soc. **95** (1908), 289, and Henderson and Eastburn, *ibidem* 1465.

[4]) Berl. Berichte **33** (1900), 1463.

[5]) Report of Schimmel & Co. April 1911, 106.

[6]) Berl. Berichte **31** (1898), 2025.

[7]) Report of Schimmel & Co. October 1895, 44.

[8]) Berl. Berichte **33** (1900), 1210.

Sabinol (see vol. I p. 390) has a specific gravity of 0,950 at 15° and boils between 210 and 213° (b. p. 77 to 78° under 3 mm.)[1]. When oxidized with permanganate, it yields α-tanacetogen dicarboxylic acid (m. p. 140°). Sabinol acetate is characterized by its very high optical rotation. A sabinol with $\alpha_D + 6°$ yielded an acetate (b. p. 81 to 82° under 3 mm.; $d_{15°}$ 0,972) of $\alpha_D + 79°$[1].

The fraction above 220° contained a substance that combined with bisulphite. It had an odor that reminded of cuminic aldehyde and boiled between 127 and 129° (20 mm). This substance ($d_{16°}$ 0,9163; $\alpha_D + 11° 40'$), about the composition of which nothing is known, yields a phenyl hydrazone that melts at 40 to 45° and an oxime that melts at 85°[2].

In fraction 220 to 237° Schimmel & Co.[3] found citronellol (m. p. of the silver salt of the acid phthalate 126 to 127°). In one of the tailings F. Elze[4] found geraniol (m. p. of diphenylurethane 82°) and dihydrocuminic alcohol (m. p. of naphthylurethane 146 to 147°).

In the highest fractions of savin oil Wallach[5] ascertained the presence of cadinene.

In the aqueous distillates resulting from cohobation, Schimmel & Co.[6] found methyl alcohol, furfurol and diacetyl. In the first fraction of the oil Elze[4] found traces of *n*-decyl aldehyde (m. p. of semicarbazone 102°; m. p. of *n*-caprinic acid 31°).

Test. The principal adulterant of savin oil is the oil of *Juniperus phœnicea*[7] (probably also that of *J. thurifera* var. *gallica*). As to its properties this oil is like a mixture of savin oil and French turpentine oil.

Like that of French turpentine oil, the presence of added oil of *J. phœnicea* may be recognized by lowering of the specific gravity, reduction or reversion of the angle of rotation to the left, lowering of the saponification value and diminution of the

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[1] Elze, Chem. Ztg. **34** (1910), 767.

[2] Report of Schimmel & Co. April **1900**, 43.

[3] *Ibidem* October **1907**, 80.

[4] Chem. Ztg. **34** (1910), 767.

[5] Liebig's Annalen **238** (1887), 82.

[6] Report of Schimmel & Co. October **1900**, 62 and April **1903**, 73.

[7] Umney and Bennett, Pharmaceutical Journ. **75** (1905), 827.

solubility in alcohol. In both cases the exact proof of their presence is supplied by the isolation and identification of pinene, since, as has already been pointed out, oil of savin contains but traces of this terpene.

117. Oil of the Leaves of Juniperus phœnicea.

Origin. It was first pointed out by J. C. Umney and C. T. Bennett¹) that the French savin oil of commerce is not a distillate from *Juniperus sabina,* but in the main is obtained from the tips of branches of *Juniperus phœnicea,* L. which is closely related to the savin. In southern France this shrub is popularly known as *sabine.* From twigs partly in flower and without berries, J. Rodié²) obtained 0,45 to 0,5 p. c. of oil.

Properties. As to odor, the oil resembles more closely juniper berry oil than savin oil. The following constants have been observed by Rodié as well as by Schimmel & Co.³): d_{15° 0,863 to 0,872; $\alpha_D + 2^\circ$ to $+ 7^\circ 20'$; E.V. 0 to 2,1; E.V. after acetylation 4,7 to 11; soluble in 5 to 6,5 vols. and more of 90 p.c. alcohol. The properties of the oil examined by Umney and Bennett⁴) varied somewhat, *viz.* d_{15° 0,892; $\alpha_D + 4^\circ 30'$; E. V. 26 (9 p. c. acetate); E. V. after acetylation 60 (17 p. c. alcohol $C_{10}H_{17}OH$). These figures would seem to indicate that some genuine savin was used in the distillation.

Composition. According to Rodié, 90 p. c. of the oil consists of terpenes of which α-pinene (m. p. of nitrosochloride 107°, of hydrochloride 125°) constitutes the bulk. In addition Rodié has shown the presence of very small amounts (about 0,1 p. c.) of *l*-camphene (m. p. of *iso*borneol 212°), and phellandrene (m. p. of nitrite 101°). Only 6,5 p. c. of the oil boiled above 180°. They constituted a brownish-red thick liquid of a peculiar odor reminding of juniper; d_{15° 0,946; $\alpha_D - 1^\circ 10'$; E.V. 18,2, corresponding to 6,37 p.c. ester $C_{10}H_{17}OCOCH_3$; E. V. after saponification 85,4 corresponding to 25,17 p. c. alcohol $C_{10}H_{17}OH$. Of this

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¹) Umney and Bennett, Pharmaceutical Journ. 75 (1905), 827.

²) Bull. Soc. chim. III. 35 (1906), 922.

³) Report of Schimmel & Co. April 1907, 95.

⁴) Pharmaceutical Journ. 75 (1905), 827.

5,03 p. c. are present as ester and 20,14 p. c. as such. With the aid of bisulphite solution Rodié[1]) isolated small amounts of an aldehyde which was not identified. This substance which constitutes about 0,0166 p. c. of the oil of *J. phœnicea* and which appears to be wanting in other species of juniper, is, judging by its odor, a new aldehyde. Its naphthocinchoninic acid decomposes without melting, at 275 to 276°. The oxime is liquid. In the saponification liquid Rodié established the presence of acetic acid. Of water-insoluble acids, the presence of caproic acid was established in fraction 190 to 210° (732 mm.).

118. Oil of the Berries of Juniperus phœnicea.

A lot of red juniper berries imported from Smyrna and presumably referable to *Juniperus phœnicea,* L. yielded upon distillation 1 p. c. of oil with a specific gravity of 0,859 and an optical rotation $\alpha_D - 4° 55'$ at 16°. In all of its properties the oil corresponded with those of the berries of *Juniperus communis,* L.[2]).

119. Oil of Juniperus thurifera.

On account of their similarity, *Juniperus thurifera* var. *gallica,* De Coincy, a shrub that is widely distributed in southern France, is readily confounded with *J. Sabina.* Hence, like *J. phœnicea,* it is probably used in the distillation of savin oil[3]).

The oil is almost unknown. A small sample obtained by Schimmel & Co. from Professor Dr. P. Guigues of Beyrout, had a pleasantly aromatic odor that reminded faintly of savin. $d_{15°}$ 0,9246; α_D between $+1$ and $+2°$.

120. Oil of Juniperus Species (Kaju garu).

From a *Kaju garu* [*Kajoe garoe*[4]) = scented wood] of Macassar, the botanical origin of which was unknown, Van Rom-

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[1]) Bull. Soc. chim. IV. **1** (1907), 493.

[2]) Report of Schimmel & Co. October 1895, 30.

[3]) Holmes, Pharmaceutical Journ. **75** (1905), 830. — P. Guigues, Bull. Sciences pharmacol. **9** (1902), 33. — Report of Schimmel & Co. October 1906, 70 and April 1907, 94.

[4]) *Kaju garu* is also the designation for the wood of *Gonystylus Miquelianus* or *Aquilaria Moskowskii.* According to de Clercq (*Nieuw plantkundig woor-*

burgh obtained by steam distillation an oil that was studded with crystals and which was examined by P. A. A. F. Eyken[1]. After isolation and purification, the crystals were identified as guaiol (m. p. 93°; analysis; $[\alpha]_D - 30°$; molecular refraction). A comparison with guaiol from guaiac wood oil confirmed the identity. In the liquid oil free acids, more particularly formic and acetic acids, were found. Eyken also himself distilled the oil from a wood which he regards as possibly derived from a species of juniper. The oil (yield 1,3 p. c.) soon solidified, but, contrary to the oil first examined, contained no fractions below the boiling point of guaiol. The fractions with a higher boiling point than guaiol also remained liquid and hence rendered its isolation more difficult. In spite of these differences, Eyken regards both oils as identical and attributes the variations to the fact that one oil had stood for several years whereas the other was a fresh distillate.

The same wood was later examined by W. G. Boorsma[2]. It revealed the structure of the wood common to the junipers, but its species could not be identified. The wood, deprived of its oil by steam distillation, yields upon extraction with ether 5 p. c. of an amorphous mass which burns with an aromatic odor.

Another aromatic wood is the *Kaju kasturi*[3], which is derived from a species of *Juniperus* or some other conifer. The heartwood is reddish to dark red, the sap wood white. Upon distillation the red wood yielded a light yellow oil with a guaiol-like odor. Inasmuch as Boorsma could not cause it to crystallize he regarded it as free from guaiol.

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denboek voor Nederlandsch Indië, Amsterdam 1909, p. 170) *Kajoe gaharoe* is the Malay name for *Aquilaria malaccensis*, Lam. (*Kajoe* = wood). The wood, with or without frankincense, is used as incense by the natives. For *Aquilaria malaccensis* many other designations are current which, however, apparently are also used for *Gonystylus Miquelianus*.

[1] Recueil trav. chim. des P.-B. **25** (1906), 40, 44; Chem. Zentralbl. **1906**, I. 841.

[2] Bulletin du Département de l'Agriculture aux Indes Néerlandaises (Pharmacologie III.) **1907**, No. 7, p. 37.

[3] According to Clercq (*loc. cit.* p. 344) *Kajoe kastoeri* is the Malay name for the wood of *Xanthophyllum adenopodum* Miq. *(Polygalaceæ)*.

Family: PANDANACEÆ.

121. Pandanus Oil.

In India, Arabia and Persia, the flowers of *Pandanus odoratissimus,* L. (Fam. *Pandanaceæ*) are highly esteemed because of their fragrance and supposed medicinal virtue[1]. An infusion of the bruised stems is applied by the Mohammedan physicians against a variety of diseases. The Hindoos regard the aqueous distillate of the flowers as a prophylactic against small-pox. If the aqueous distillate is to be used as perfume, the flowers — to which sandalwood has been added — are occasionally distilled with rose water. An aromatic infused oil is also prepared with the aid of sesamum oil.

According to Holmes[2] the volatile oil has a very pleasant, decidely honey-like oder. Nothing more is known about the properties of the oil.

Family: GRAMINEÆ.

Cymbopogon Oils (Andropogon Oils).

122. Palmarosa Oil.

Oleum Palmarosæ seu Geranii Indicum. — Oil of East Indian Geranium. — Essence de Géranium des Indes. — Palmarosaöl.

Origin. Palmarosa oil, also known as Indian grass oil, rusa oil, Indian or Turkish geranium oil[3], is distilled from the overground portions of the rusa or geranium grass designated as *Cymbopogon Martini,* Stapf[4]. The numerous synonyms of this herb are: *Cymbopogon Martinianus,* Schult., *Andropogon*

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[1] Dymock, Warden and Hooper, Pharmacographia indica. Part IV, p. 535.

[2] Pharmaceutical Journ. III. 10 (1880), 635.

[3] The erroneous designation "Turkish geranium oil", which has practically been abandoned, dates back to a time when the oil entered the European market via Constantinople. From Bombay it was transported by ships to the ports of the Red Sea and thence by overland routes through Arabia to Constantinople. After having been specially prepared it was here used on a large scale to adulterate rose oil. (See also p. 189).

[4] Kew Bull. 1906, 335.

Martini, Roxb., *A. pachnodes,* Trin., *A. Calamus aromaticus,* Royle, *A. nardoides, α,* Nees, *A. Schœnanthus,* Flück. et Hanb., non L., *A. Schœnanthus* var. *genuinus,* Hack., *A. Schœnanthus* var. *Martini,* Hook. f. The popular designation rusa, applied to this grass, is probably traceable to the reddish-brown color taken on by the panicles in fall.

Cymbopogon Martini occurs in two varieties which are known in India as *motia* and *sofia.* According to Stapf¹) they cannot be differentiated morphologically when dried specimens are compared. J. H. Burkill²), however, states that in the fields they can be distinguished by their different habits. The greatest difference between these two varieties becomes apparent in the composition of their volatile oils. The *motia* (= pearl, precious) yields the palmarosa oil, and the *sofia* (= mediocre) the gingergrass oil. Burkill regards this difference as sufficient justification to designate the two varieties as *Cymbopogon Martini* var. *motia,* and *C. M.* var. *sofia.*

With the exception of the deserts and steppes of the Punjab, the outer slopes of the West Ghat and apparently a large portion of North Karnatik, the rusagrass, according to Stapf, grows from the Rajmahal mountains (at the turn of the Ganges) up to the Afghanistan border and from the subtropical zone of the Himalaya to the twelth degree of latitude.

According to Forsyth, the grass begins to bud about the latter part of August and flowers to the end of October. The distillation must be conducted during this season, more particularly during the early flowering period, since the yield suffers an appreciable diminution later and its quality likewise depreciates.

So far as the conditions favorable to their vegatation are concerned, Burkill has found that the *motia* thrives best on dry ground, either at the foot of the hills or at moderate altitudes on the southern slopes but moderately covered with trees. The *sofia,* however, demands moisture and grows preferably where this is supplied by abundant dew and fog. It prefers higher altitudes up to the tops of the hills, but is also found on the

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¹) Report of Schimmel & Co., April 1907, 58.

²) J. H. Burkill, First notes on *Cymbopogon Martini,* Stapf. Journal of the Asiatic Society of Bengal, March 1909, Vol. V, No. 3 (N. S.); Report of Schimmel & Co., October 1909, 90.

lower slopes, however, not on those with southern exposure. Its favorite haunts are the teak forests (*Tectona grandis,* L. or East Indian oak), in which the rapid evaporation at night causes a decided reduction in the temperature of the atmosphere and hence abundant formation of dew. However, it should be stated that both *motia* and *sofia* may occur at any altitude, provided the other conditions are favorable.

So far as the regional distribution of the two grasses is concerned, Burkill ascertained that indeed *motia* and *sofia* occurred side by side at different altitudes near Asirgarh, Chandni and in the Melghat region. However, in Deogaon and Belkhera, to the west and northwest of Ellichpur, an important commercial center for palmarosa oil, also in Dhamangaon *motia* occurs almost exclusively. Further up in the mountains he found more *sofia.* Beyond the watershed in the Sipna valley as far as Tapti he found *sofia* exclusively.

The differences between *motia* and *sofia* vary with the region, according to the more favorable conditions found by the one or the other variety. Hence the statements made by collectors vary accordingly. Thus, on the one hand, in the vicinity of Asirgarh and Chandni *motia* is more erect and attains a height of from 6 to 8 feet, whereas *sofia* is but 3 to 4 ft. high and produces dense bushy ears. On the other hand, in the Melghat region, sofia is the higher plant. The width of the leaves and the intensity of the color increase with the height. As opposed to *motia,* the *sofia* is characterized by the large number of radical leaves. The *sofia* leaves also form a different angle with the sheath than do the *motia* leaves. Of further interest is Burkill's observation that in certain regions grasses occurred that were neither *motia* nor *sofia* but which he regarded as cross forms. Until the study being made of *C. Martini* has been completed, he regards it too early to make a final statement, since, no doubt, other varieties may be found.

Production[1]). Taking into consideration the wide distribution of this grass, the territory in which it is distilled for its oil is rather limited. In the Bombay presidency, palmarosa oil is

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[1]) Comp. David Hooper, Chemist and Druggist 70 (1907), 207 also G. Watt, The commercial products of India, London 1908, p. 452.

distilled principally in the Khandesh district, more particularly in the vicinities of Pimpalner, Akrani, Nandurbar, Shahada and Taloda. In Berar province, the oil is distilled in the districts of Nagpur, Jebalpur, Akola, Buldana, Ellichpur, Basim, Wunn and Amraoti. The city of Ellichpur is the principal market of this province. Oil distilleries are also found in Radschputana, *e. g.* in Ajmere; furthermore in the British Central Provinces: in the districts of Nimar, Hoshangabad, Betul, Mandla and Seoni. The Nimar district has always been an important center, the oil being designated Nimar oil.

For the past eighty years the oil has been distilled as it is to-day. Concerning the oil distilleries in the Amraoti district, J. H. Burkill¹) has issued an interesting report based on his own observations. The oil distilling industry about Ellichpur is worked in the following way. The forest lands where *Cymbopogon Martini* var. *motia* grows are leased out to men of substance-generally Mohammedans, who for the most part sub-lease them again piece-meal to men who go out to selected valleys in the Melghat with stills and engaging villagers send some out to cut the grass tops at so much per hundred bundles brought in, and with others set up open-air distilleries on the banks of the streams. There is built first a row of stone fire-places and the cauldrons are set up on them, generally 3 or 4 in a row. The cauldrons are sometimes of iron and sometimes of copper. If they are of copper they are generally somewhat smaller than those of iron and depressed globose; the iron cauldrons are cylindrical and rivetted; they are about $2^1/_2$ feet in diameter. The top of the iron cauldrons is slightly conical with a central lid. Out of the lid emerges the bamboo elbowed tube by which the distillate passes off.

The cauldron once set in place ready for the fire, is never moved.

The elbowed tube has a bamboo peg run through it at the angle and is wrapped from end to end in string. From the elbow the longer part is about six feet.

The receivers are generally long necked, more than a foot in diameter below, not so deep as broad (neck excluded). But

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¹) Report of Schimmel & Co., October 1909, 87.

sometimes they are without a neck, in which case a pad of cloth on the bamboo closes the mouth. They are generally made of copper. They are placed in the water quite up to the neck. A framework of wood lies in the stream which is generally dammed to deepen the water. Into the interspaces of this framework the receivers fit, being held in place by means of two sticks of wood which are tied on either side of the neck and are placed under the cross bars of the framework. Further, stones are heaped round each receiver to help to keep them under water.

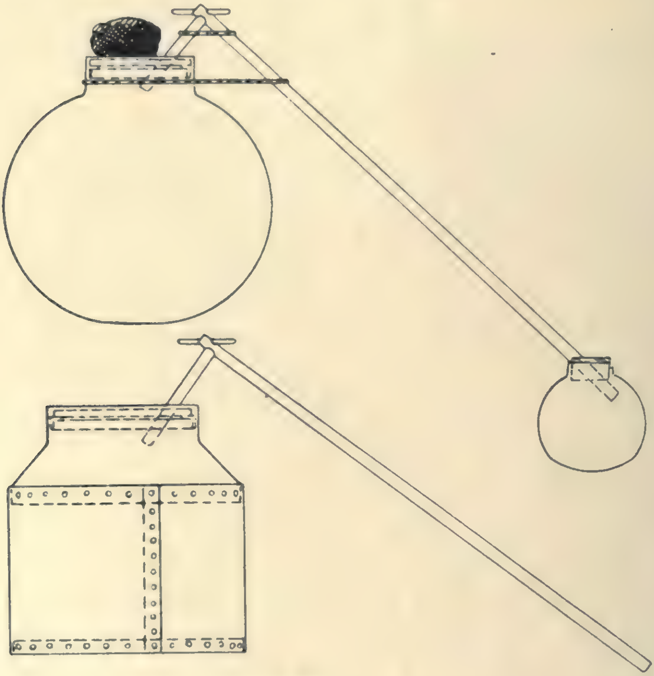

Fig. 19.

Copper (above) and iron (below) still for palmarosa oil.

The method of work is as follows. We will suppose that the cauldron has just been emptied of a charge and lies with the lid off and with the fire drawn from below it. A workman standing on the stone walls round the cauldron, with a rod measures the depth of the water in it. This water is brown and holds a considerable amount of tannin derived from previous charges of grass. Next he pours enough clean water into the cauldron to bring the depth up to about (for a large cauldron) 10—12 inches and next packs in the grass often trampling it down in order to get as much as possible in.

Fig. 20.

Distillation of palmarosa oil in the neighborhood of Ellichpur (Nearer India).

The stills are of different sizes. The larger one takes a charge of about 200 bundles of grass (each bundle containing about 300 stems) and the smaller takes about half the quantity. Next the lid is replaced and the joint luted up with a paste of flour of *udid (Phaseolus)* and a muddy bandage. The bamboo tube is inserted into the hole in the lid where it fits and is similarly luted in. Next, fire is put under the cauldron and boiling recommences.

The boiling lasts two or three hours; and according to the arrangements which the masters make with the men, five or six boilings are done in the twenty-four hours.

The bamboo passes into the receiver for a distance of about six inches. After a while the bubbling of the steam through the increasing distillate begins to give what the workmen describe as the sound "tit-tit". The sound deepens and when it becomes what they call "bul-bul" they know to stop the boiling. In doing this the fire is removed, cold water is thrown over the lid of the cauldron, the bamboo tube removed, the lid lifted, and the receiver taken out of the stream. The pressure of the steam in the cauldron is at the time not inconsiderable.

While some men with a hay-fork are removing the exhausted grass from the cauldron, the master takes with a spoon the oil from off the top of the water in the receiver and using a funnel of tin he separates it from any water which the spoon brings up with the oil.

In some stills lime juice is used now to help to clarify the oil.

Three large cauldrons give about a pint and a half of oil, which on standing deposits a sediment of a copper salt.

All the oil of each small distillery is mixed together and carried to the nearest trade centre — Ellichpur, for most of the stills examined.

Table salt to the extent of half a pound is thrown into each cauldron every few days.

Figures 21 and 22 illustrate the distilleries found in the Khandesh[1]) circuit to the west of Amraoti. It is customary to

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[1]) A description of the oil distillation in Khandesh can be found in the book Pharmacographia indica by Dymock, Warden and Hooper, part VI, p. 558; comp. Arch. der Pharm. **234** (1896), 321.

Fig. 21.

Fig. 22.

Palmarosa distillation in Khandesh (Nearer India).

build a roof over the stills. A large piece of wood is used as top or cover of the still. The method of procedure is the same as that described above. Whereas in Amraoti salt is frequently added to the still, this is done but rarely in Khandesh. In the latter place the period of each distillation is also extended. In Khandesh both palmarosa and gingergrass oils are distilled, the former in the lower regions, the latter on the Akrani plateau. At medium altitudes the available palmarosa grass is distilled first, then the gingergrass.

Properties. Palmarosa oil is colorless or light yellow, occasionally it is colored green by copper. It has a pleasant odor reminding of roses. Its sp. gr. is 0,887 to 0,90. Its optical properties vary, some oils being slightly dextrogyrate, others slightly lævogyrate, still others optically inactive. $\alpha_D + 6$ to $-3°$, mostly between $+1$ and $-2°$; $n_{D20°}$ 1,472 to 1,476; A. V. 0,5 to 3,0; E. V. 12 to 48; E. V. after acetylation 226 to 274 corresponding to 74,8 to 94,8 p.c. of total geraniol. In 1,5 to 3 and more parts of 70 p.c. alcohol it dissolves to form a clear solution; in very rare instances opalescence to turbidity has been observed. Oils with a higher geraniol content are soluble in from 3 to 4 vols. and more of 60 p.c. alcohol.

Examination. Palmarosa oil of commerce is frequently adulterated. As adulterants gurjun balsam oil, cedar oil, turpentine oil, petroleum (kerosene, paraffin oil) and cocoanut oil have been observed[1]). All of them betray their presence by the insolubility of the oil in 70 p.c. alcohol. Oils adulterated with cocoanut oil as a rule congeal when placed in a freezing mixture. Petroleum and turpentine oil reduce the specific gravity, whereas fatty oil raises it. In doubtful cases it is advisable to make an acetylation test. Oils with a lower geraniol content than 75 p.c. are to be rejected.

An adulteration with alcohol, together with another admixture (citronella oil fraction), has been observed by Schimmel & Co.[2]).

Composition. The older statements concerning the botanical source and the physical properties of palmarosa oil are so con-

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[1]) Schimmel's Bericht April 1888, 22; April 1889, 20; Report of Schimmel & Co. October 1890, 35.

[2]) Report of Schimmel & Co. April 1907, 56.

flicting that it seems doubtful whether the investigators really worked with palmarosa oil or not[1]).

The first investigation with unquestionable material was conducted by O. Jacobsen[2]). He demonstrated that the bulk of the oil consists of an alcohol $C_{10}H_{18}O$ which boils between 232 and 233° and which he designated geraniol. He also discovered the compound of geraniol with calcium chloride, which has become so important in the isolation of the pure alcohol, since it is readily decomposed into its components by water. Later Semmler[3]) verified the formula $C_{10}H_{18}O$ and recognized the aliphatic character of geraniol. Thus geraniol became the first representative of the aliphatic terpene alcohols, a new class of compounds that has acquired such importance in the study of the volatile oils.

The amount of geraniol in palmarosa oil varies between 75 and 95 p. c. Of this the greater part is free, and from 3 to 13 p. c. are ester. As determined by E. Gildemeister and K. Stephan[4]) by means of the silver salts, the acid components of these esters, acetic and *n*-capronic acids, occur in about equal parts.

Of terpenes palmarosa oil contains but very little, *viz.* about 1 p.c. of dipentene (m. p. of tetrabromide 125°, of nitrolbenzylamine 109 to 110°). Of methylheptenone (m. p. of semicarbazone 135°)[5]) traces are also present.

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[1]) J. Stenhouse (Liebig's Annalen **50** [1844], 157) reports on an investigation of an East Indian grass oil from *Andropogon Iwarancusa,* the odor of which reminded of rose oil, and the taste of which resembled lemon oil. Upon distillation it yielded a hydrocarbon $C_{10}H_{16}$ boiling at 170°. It may be assumed with a fair degree of certainty that this grass oil was not palmarosa oil but citronella oil from *Andropogon Nardus,* L., also known as *Andropogon Iwarancusa,* Roxb. Citronella oil contains a terpene boiling at 160° (camphene) whereas such low boiling constituents are wanting in palmarosa oil.

J. H. Gladstone (Journ. chem. Soc. **17** [1864], 1 ff.; Jahresb. f. Chemie **1863**, 548) describes an Indian geranium oil of the sp. gr. 0,943 at 21°, which he regarded as identical with the East Indian grass oil from *Andropogon Iwarancusa.* It does not become apparent from the statements of this author what oil he had in hand.

[2]) Liebig's Annalen **157** (1871), 232.

[3]) Berl. Berichte **23** (1890), 1098.

[4]) Arch. der Pharm. **234** (1896), 328.

[5]) Report of Schimmel & Co. April **1905**, 47.

In addition to geraniol, Flatau and Labbé[1]) claim to have found a second alcohol, *viz.* citronellol. As Schimmel & Co.[2]) have pointed out, this statement is incorrect as is likewise the statement by the same investigators[3]) that palmarosa oil contains a fatty acid $C_{14}H_{28}O_2$ of the m. p. 28°. According to the investigations of Schimmel & Co.[4]) pure palmarosa oil contains no such acid and the findings of the French chemists can be explained only by assuming that their oil was adulterated with cocoanut

Fig. 23.

Copper containers for palmarosa and gingergrass oils.

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[1]) Compt. rend. 126 (1898), 1725. — Bull. Soc. chim. III. 19 (1898), 633.

[2]) Report of Schimmel & Co. October 1898, 59.

[3]) Compt. rend. 126 (1898), 1726.

[4]) Report of Schimmel & Co. October 1898, 28.

oil or some other fatty oil. Hence the acid $C_{14}H_{28}O_2$ is not a constituent of palmarosa oil, but an adulterant.

According to Elze[1]), farnesol (comp. vol. I, p. 399) is contained in palmarosa oil.

Production and Commerce. The principal commercial and export center is Bombay. Most of the oil is shipped to Europe. Formerly the oil was shipped to the ports of the Red Sea, from there overland to Cairo and thence to Constantinople and the rest of Europe. On this account the oil was formerly designated "Turkish geranium oil" without, however, any justification. At present palmarosa oil is shipped from Bombay directly to Europe. In Bombay the oil is graded and filled into large tin-lined copper *ramières* or pots. Formerly these averaged from 100 to 200 lbs., now most of them have a net capacity of 250 lbs. These containers are protected by a net work of ropes (fig. 23) and are not crated. It is estimated that the export from Bombay averages 50,000 lbs. annually. Inasmuch, however, as the actual exports for the year 1902/3 amounted to 125,595 lbs., the above figure would seem to refer to the production of Bombay and the Central Provinces. The balance probably came from the southern provinces in which the production has increased materially in recent years.

The exports in volatile oil from Bombay (principally palmarosa oil with about one-fourth gingergrass oil) are given in the following table:

1896/97	8 199	gals. at a value of	149 553	rupees
1897/98	10 776	„ „ „ „ „	209 691	„
1898/99	16 000	„ „ „ „ „	404 140	„
1899/00	10 400	„ „ „ „ „	278 005	„
1900/01	12 834	„ „ „ „ „	341 670	„
1901/02	19 641	„ „ „ „ „	610 783	„
1902/03	18 872	„ „ „ „ „	523 630	„
1903/04	20 680	„ „ „ „ „	538 774	„
1904/05	18 742	„ „ „ „ „	465 209	„
1905/06	23 436	„ „ „ „ „	551 425	„

Formerly the principal import countries were England, Egypt and Turkey. Arranged according to the amount imported, they are at present Germany, France, England and the United States of America.

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[1] Chem. Ztg. **34** (1910), 857.

123. Gingergrass Oil.

Gingergrasöl. — Essence de Gingergrass.

Origin and Production. Only a comparatively short time ago[1]), gingergrass oil was regarded as a poorer quality of palmarosa oil, more particularly since it entered the market from Bombay and in the same kind of container. It was mostly adulterated with considerable amounts of turpentine or mineral oils, additions, the presence of which was readily recognized by its sparing solubility in alcohol, more particularly in diluted alcohol. Occasionally, however, a gingergrass oil was observed that formed a clear solution with 70 p. c. alcohol, but the odor of which was very different from that of palmarosa oil[2]). The examination of such an oil[3]) revealed a composition differing materially from that of palmarosa oil. Hence the assumption that gingergrass oil was but a poorer grade of palmarosa oil could no longer be maintained. J. H. Burkill then succeeded in clearing up the botanical source of gingergrass oil. He sent samples of oil distilled from *Cymbopogon Martini,* Stapf var. *motia* and *C. M.* var. *sofia* to Schimmel & Co., who identified the oil from *sofia* as gingergrass oil and that from *motia* as palmarosa oil[4]). Thus the fact was established that gingergrass oil is obtained from *Cymbopogon Martini,* Stapf var. *sofia.* (Comp. palmarosa oil, p. 179).

The distillation of gingergrass oil is like that of palmarosa oil. Under the former the distribution of the two grass varieties has been discussed in detail. The yield of an oil distilled in Java amounted to 0,1 p. c.[5]).

Properties. d_{15° 0,90 to 0,953; $\alpha_D + 54$[6]) to -30°; n_{D20° 1,478 to 1,493; A. V. up to 6,2; E. V. 8 to 29 (in one case 54,5)[7]); E. V. after acetylation 120 to 200. Soluble in 2 to 3 vols. of 70 p. c. alcohol. Additional alcohol mostly produces opalescence

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[1]) Gildemeister and Hoffmann, The volatile oils. Ist ed. p. 285.

[2]) E. Gildemeister and K. Stephan, Arch. der Pharm. **234** (1896), 326.

[3]) H. Walbaum and O. Hüthig, Journ. f. prakt. Chem. II. **71** (1905), 459.

[4]) Report of Schimmel & Co. April **1907**, 58.

[5]) Jaarb. dep. landb. in Ned.-Indië, Batavia **1910**, 49.

[6]) An oil distilled in Java had $\alpha_D + 46^\circ 5'$ (footnote 5).

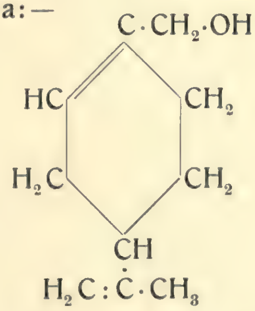
[7]) Report of Schimmel & Co. October **1912**, 67.

or even turbidity. Soluble in 0,5 to 1,5 vols. and more of 80 p. c. alcohol. In isolated instances opalescence is observable.

Composition. Our knowledge of the composition of this oil is based on an investigation by H. Walbaum and O. Hüthig in the laboratory of Schimmel & Co.1). Of terpenes the following are present: d-*α-phellandrene*2) (m. p. of nitrite 120°), *dipentene* (m. p. of tetrabromide 125°, of α-dipentene nitrolpiperidide 153°) and d-*limonene* (m. p. of α-limonene nitrolpiperidide 93°, of α-limonene nitrolbenzylamine 93°). Fraction 80 to 90° contains an *aldehyde* $C_{10}H_{16}O$, the odor of which reminds of heptaldehyde and citronellal, and the properties of which have been described on p. 432 of vol. I. The amount present is estimated at only 0,2 p.c. A slightly higher boiling fraction contains *i*-carvone which was identified by its semicarbazone, m. p. 153 to 154°.

As becomes apparent from the high acetylation values, the bulk of the oil consists of *alcoholic* substances. They are contained in fractions 85 to 95° (5 mm.) and consist of a mixture of *geraniol* (oxidation to citral; m. p. of diphenylurethane 82°) and a *dihydrocuminic alcohol* (for properties and derivatives see vol. I. p. 374) the odor of which reminds of both linalool and terpineol (m. p. of naphthylurethane3) 146 to 147°).

The constitution of the dihydrocuminic alcohol obtained from gingergrass oil, which, according to F.W. Semmler and B. Zaar4), is identical with the perilla alcohol from perilla aldehyde, is expressed by the following formula:—



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1) *Ibidem* April 1904, 55; October 1904, 44; April 1905, 41; (see also footnote 3 on the previous page).

2) Phellandrene had previously been found by Gildemeister and Stephan (footnote 2 on the previous page).

3) Report of Schimmel & Co. October 1906, 40.

4) Berl. Berichte 41 (1911), 460.

Adulterations. Gingergrass oil is so universally subject to adulteration that, at times, a pure oil cannot be had. Turpentine oil, mineral oil and gurjun balsam oil are the principal adulterants. All of these additions betray themselves by the lowering of the solubility, also by the change in density. Gurjun balsam oil[1]) also strongly influences the optical rotation.

Lemongrass Oils.

124. East Indian Lemongrass Oil.

Malabar, Travancore or Cochin Lemongrass Oil. — Oleum Andropogonis citrati. — Ostindisches Lemongrasöl. — Essence de Lemongrass. — Essence de Verveine des Indes.

Origin and Production. As to the botanical origin of the lemongrass oils of commerce there existed, for a long time, considerable uncertainty and ambiguity. The situation was finally cleared up by the investigations of O. Stapf[2]) referred to on p. 217. It has been known for some time that the oils distilled on the Malabar coast differed as to greater solubility in 70 p. c. alcohol and frequently also by their higher citral content from other oils, *e. g.* those produced in the West Indies, Brazil, Ceylon, Java and numerous other places. According to Stapf this is due to the fact that the two oils are derived from different species of *Cymbopogon.* Whereas the East Indian oil, the lemongrass oil of commerce, is obtained from *Cymbopogon flexuosus,* Stapf, the more difficultly soluble oil is derived from *C. citratus,* Stapf[3]).

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[1]) Report of Schimmel & Co. April 1908, 56.

[2]) Kew Bull. 1906, 297.

[3]) By means of experiments made by J. F. Jowitt in Bandarawela (Ceylon) with the cultivation of both lemongrass species, Stapf's assumption has been proven experimentally. The oils distilled from the cultivated grasses were examined in the Imperial Institute in London by S. S. Pickles (Circulars and Agricultural Journal of the Royal Botanic Gardens, Ceylon. Vol. V, N° 12, November 1910, 137. Comp. also Bull. Imp. Inst. 8 [1910], 144). The grasses themselves were once more carefully examined as to their botanical identity by Stapf himself. As to the solubility of the oils, it became apparent that the oil from *C. citratus* did not give a clear solution with even 10 vols. of 90 p. c. alcohol, whereas *C. flexuosus* yielded an oil that was soluble in 2,2 vols. and more of 70 p. c. alcohol.

Cymbopogon flexuosus, Stapf (*Andropogon flexuosus,* Nees et Steud.; *A. Nardus* var. *flexuosus,* Hack.) known as Malabar- or Cochin grass, occurs in the Tinnevelly district and in Travancore. Whereas formerly it occurred wild only, in recent years larger areas have been cultivated with this grass since the wild plant no longer sufficed to supply the demand for oil[1]. The distillation has also been extended northward so that at present considerable amounts of oil are also distilled in Malabar. Inasmuch as the grass[2] demands much moisture but does not flourish unless the soil is drained, it is cultivated principally on the foothills of the Ghats. The principal distillation areas are the *"Hinterland"* of Anjengo, the hilly shores of the Periyar river in Travancore, and the plantation districts Peermade in Travancore and Nellampatty in the state of Cochin. On the east side of the Ghats and in the Palmi mountains lemongrass oil is also distilled in isolated places. Because of high prices, the production of lemongrass oil had been greatly increased, later, because of price reduction due to overproduction, it was largely cut down. More particularly was this true of the distilleries on large plantations where the distillation was carried on with expensive equipments and labor. In some districts, *e. g.* in Wynaad, the low aldehyde content of the oil had a discouraging effect on the production. The native farmers, however, appear to work at a profit even at the low price of 2 d. per ounce.

The distillation of the oil begins shortly after the beginning of the rainy season, *i. e.* about the beginning of July, and continues, according to the course of the monsoon which follows the Southwest monsoon, up to and into January. Inasmuch as the Northeast monsoon is scant on the west coast and at times fails altogether, the distillation is discontinued in January on account of the drought. The dried grass is destroyed by fire since the ashes afford a good fertilizer. In the lower places, *i. e.* when artificial irrigation is possible, the lemongrass must give way to the cultivation of winter crops, principally rice.

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[1] Comp. also D. Hooper, Chemist and Druggist **70** (1907), 208.

[2] The description which follows has kindly been placed at the disposal of Schimmel & Co. by Mr. Werner Reinhart, of the firm of Volkart Brothers in Winterthur, who made a trip into the lemongrass oil districts. Report of Schimmel & Co. October **1910**, 77.

A distillery of the natives, such as is illustrated on this page, fig. 24, usually remains standing all year around. It is always covered by a straw roof resting on bamboo poles. A copper cylinder about 6 ft. in height and 3 ft. in diameter rests on a fire place built of stones and about 1 ft. high. It is not provided with a chimney, but the air has access through the openings between the loosely piled stones. At about one-half its height, the cylinder is provided with a lateral opening, that can be closed by a door through which the grass is introduced into the still and through which it is also removed. The top of the cylinder is closed by a removable helmet, which is connected by means of a copper tube with the serpentine condenser which rests in a wooden vat about 6 ft. high. By means of a wooden trough, water is conducted from a well to the condenser. As receiver a vessel is used that is constructed upon the principle

Fig. 24.

Distillation of lemongrass oil in the neighborhood of Alwaye (Travancore).

of the Florentine flask, with this difference, however, that it consists of a very wide open cylinder as shown in fig. 25.

In this manner a large surface is created on which the oil collects and can be skimmed off by means of a spoon. The aqueous distillate flows off through a lateral tube which is fastened to the lower end of the cylinder and passes upward at an acute angle. Contrary to the usual practice, this aromatic water is not used over again for the distillation of a new charge of grass, but is allowed to flow away.

For the distillation the freshly collected grass tops, tied in bundels, are transferred into the still both through the lateral opening and from above until it is about $^3/_4$ full. For such a charge 1000 bundels with a total weight of about 750 lbs. are required. Then the still is filled to about $^1/_4$ its height with water (about 40 gals.). After the lateral opening has been closed, the helmet placed in position and all cracks luted with cow's dung, fire is started beneath the still. The distillation of a charge lasts from 5 to 6 hrs. and yields 1 to $1\,^1/_2$ bottles of 22 oz. each of oil. The oil is allowed to remain in the bottles for some time in order that it may separate from any admixed water, also from deposits (copper salts), and is later transferred to tin-lined iron drums for shipment.

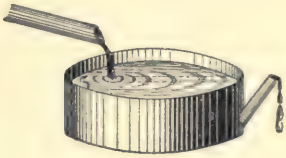

Fig. 25.

Attempts to cultivate lemongrass in other countries have mostly been carried on with *Cymbopogon citratus,* Stapf (See p. 202) which yields the inferior West Indian oil.

With the object in view of obtaining a lemongrass oil in every respect the equal of the Malabar oil, the botanical experiment stations in the Leeward Islands have, according to F. Watts and H. A. Tempany[1]), attempted the cultivation of the genuine Cochin grass of *Cymbopogon flexuosus.* The grass is said to flourish. However, four experimental distillations made with Cochin grass cultivated in Antigua and Montserrat yielded oils that did not possess the required citral content but 53, 63, 64

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[1]) West Indian Bulletin 9 (1908), 267; Report of Schimmel & Co. April 1909, 64.

and 68 p. c. respectively. Watts and Tempany attribute this to insufficient maturity of the grass since experiments with West Indian grass have shown that both yield of oil as well as citral content increase with maturity. 72,5 kg. of a three months old grass cultivated in Antigua yielded upon distillation 139 cc. of oil with a 58 p. c. citral content, whereas the like amount of grass one year old yielded 206 cc. oil with a 69 p. c. citral content. Additional experiments are going to be made to ascertain the conditions most favorable to the harvest of Cochin grass. From the experiments thus far made at the botanical experiment station it becomes apparent that 2 to 3 cuts can be made in a year and that each cut yields about 6000 to 8000 lbs. of grass per acre. The oil yield was determined at 0,2 to 0,26 p. c.

Similar experiments made in Barbados[1]) had yielded very favorable results. From a grass raised from Cochin seed, the local government laboratory distilled a readily soluble oil rich in citral.

Composition. Up to 1888 the chemical composition of lemongrass oil was quite unknown. At that time an aldehyde $C_{10}H_{16}O$ was discovered as its principal constituent in the laboratory of Schimmel & Co.[2]). Because of its decided lemon-like odor, the name citral was given to this substance (For properties see vol. I, p. 408). Three years later F. D. Dodge[3]) described the same aldehyde as citriodora aldehyde. He, however, did not work with the pure aldehyde since he describes it as a dextrogyrate substance boiling at 225°.

Inasmuch as Barbier and Bouveault[4]) obtained three distinct semicarbazones[5]) (m. p. 171°, 160° and 135°) by the action of semicarbazide on lemongrass oil, they arrived at the conclusion that the citral of lemongrass oil consists of three isomeric

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[1]) Report of Schimmel & Co. October 1908, 82.

[2]) Bericht von Schimmel & Co. October 1888, 17.

[3]) Americ. chem. Journ. 12 (1890), 553; Berl. Berichte 24 (1891), 90 Ref.; Chem. Zentralbl. 1891, I. 88.

[4]) Compt. rend. 121 (1895), 1159.

[5]) The formation of different semicarbazones from citral was first observed by Wallach. Berl. Berichte 28 (1895), 1957; comp. also Tiemann and Semmler, Berl. Berichte 28 (1895), 2133 and Tiemann, Berl. Berichte 31 (1898), 821.

aldehydes. Tiemann[1]), however, showed that the semicarbazone melting at 135° is a mixture of the other two, a fact later substantiated by Bouveault[2]). Hence the case is one not of isomeric aldehydes but of isomeric semicarbazones.

W. Stiehl[3]) also assumed the existence of three isomeric aldehydes $C_{10}H_{16}O$ in lemongrass oil, *viz.,* citral (geranial), citriodora aldehyde and allolemonal. According to Schimmel & Co.[4]) this citriodora aldehyde corresponds, as to its method of preparation, to the citral of commerce. Inasmuch as this, as was shown by Semmler[5]), is identical with the geranial from geraniol, the citral and citriodora aldehyde of Stiehl are identical. In addition Dœbner[6]) found that the allolemonal of Stiehl consists of about equal parts of citral and non-aldehyde substances.

From the investigations of Tiemann[7]) it becomes apparent that the bulk of the aldehyde of lemongrass oil is citral. He, however, had to modify his original view of the unity of citral and assumed the presence of two stereoisomeric citrals, a and b (vol. I, pp. 408 and 413), which are readily changed one into the other.

In addition to citral, lemongrass oil possibly contains traces of citronellal[8]). Furthermore, Schimmel & Co.[9]) have demonstrated the presence of traces of an isomeric aldehyde $C_{10}H_{16}O$ (b. p. 68° under 6 mm.; d_{15° 0,9081; $\alpha_D + 0^\circ 50'$; n_{D20° 1,45641), the semicarbazone of which melts at 188 to 189°. Upon oxidation with moist silver oxide an acid $C_{10}H_{16}O_2$ (b. p. 130° under 9 mm.) was obtained. Still another aldehyde constituent of lemongrass oil, of which likewise mere traces are present, is the *n*-decylic aldehyde (m. p. of semicarbazone 102°) which upon oxidation yields *n*-caprinic acid[10]).

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[1]) Berl. Berichte **32** (1899), 115. — Chem. Ztg. **22** (1898), 1086.

[2]) Bull. Soc. chim. III. **21** (1899), 419.

[3]) Journ. f. prakt. Chem. II. **58** (1898), 51; **59** (1899), 497.

[4]) Report of Schimmel & Co. October **1898**, 58.

[5]) Berl. Berichte **24** (1891), 203. — Comp. also *ibidem* **31** (1898), 3001.

[6]) *Ibidem* **31** (1898), 3195.

[7]) *Ibidem* **31** (1898), 3278, 3297, 3324; **32** (1899), 107, 115; **33** (1900), 877.

[8]) Dœbner, Berl. Berichte **31** (1898), 1891.

[9]) Report of Schimmel & Co. October **1905**, 45.

[10]) *Ibidem* 43.

In the first fractions of lemongrass oil, Barbier and Bouveault[1]) found a methylheptenone which, according to their opinion, differed from the substance obtained by Wallach[2]) from cineolic acid. However, as demonstrated by Schimmel & Co.[3]), the methylheptenone isolated from lemongrass oil is identical with the ketone of Wallach and that described by Tiemann and Semmler[4]).

Geraniol[4]), the alcohol corresponding to citral, is contained in the highest fractions of the oil, partly free, partly as ester. It was isolated by means of its calcium chloride compound (m. p. of diphenylurethane 82°).

The presence of linalool[5]) in fraction 198 to 200° may be regarded as probable.

Barbier and Bouveault observed the presence of a terpene (b. p. 175°; $\alpha_D - 5°48'$) in some oils but not in others. It formed a liquid bromide from which small amounts of a solid substance, m. p. 85°, separated. Presumably it got into lemongrass oil by adulteration.

According to Stiehl[6]), lemongrass oil contains dipentene and possibly also limonene.

Properties. As its name indicates, lemongrass oil has an intensive lemon-like odor and taste. It is a reddish-yellow to reddish-brown, mobile liquid; sp. gr. 0,899 to 0,905, exceptionally a density of 0,895 and up to 0,910 has been observed in otherwise good oils; $\alpha_D + 1°25'$ to $-5°$; $n_{D20°}$ 1,483 to 1,488; soluble in 1,5 to 3 vols. of 70 p. c. alcohol, in isolated cases slight opalescence or turbidity was observable resulting from the separation of paraffin.

Characteristic of the quality of an oil is its citral content, its principal constituent. This is determined either according to the bisulphite method (vol. I, p. 582) or according to the sulphite method (vol. I, p. 584). According to the first method, other

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[1]) Compt. rend. 118 (1894), 983.

[2]) Liebig's Annalen 258 (1890), 319 ff.

[3]) Report of Schimmel & Co. October 1894, 33. Comp. also Tiemann & Semmler, Berl. Berichte 28 (1895), 2126, footnote.

[4]) Berl. Berichte 26 (1893), 2721.

[5]) Report of Schimmel & Co. October 1894, 33; April 1899, 65.

[6]) *Loc. cit.*

aldehydes and a part of the methylheptenone are determined with the citral. Consequently higher results are obtained by this method than by the sulphite method.

The aldehyde content of a normal oil varies between 70 and 85 p. c. when determined according to the bisulphite method and between 65 and 80 p. c. when assayed according to the sulphite method. Hence, in recording assays, or when purchasing according to guaranteed aldehyde content, the method of assay should always be mentioned. If the same oil is assayed according to both methods, the bisulphite method gives results that are higher by 2 to 5,5 p. c.[1]. Upon prolonged storage the citral content is reduced[2].

Adulterations. Although adulteration of lemongrass oil is not very common, unwarranted additions have been observed occasionally. Petroleum and cocoanut oil are recognized by the incomplete solubility of the oil. Upon distillation of the oil with steam, the latter remains in the flask and can readily be recognized as such[3]. More difficult is the detection of citronella oil which Parry[4] as well as Schimmel & Co.[5] have found. The oils adulterated with citronella oil had a remarkably low citral content and after the citral had been removed the odor of citronella oil was distinctly perceptible.

Easier was the detection of an adulteration with acetone observed by Parry[6]. The oil in question attracted attention because of its low specific gravity, but had an apparent citral content of 76 p. c. The acetone was separated by fractional distillation. In as much as it combines with bisulphite, it apparently increased the citral content.

Production and Commerce. The principal seat of production lies in Southern India, more particularly in the province Travancore, south of Cochin, with Trivandrum as principal collecting center. The principal port of export, however, is Cochin.

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[1] Report of Schimmel & Co. October 1908, 82.

[2] *Ibidem* October 1909, 75.

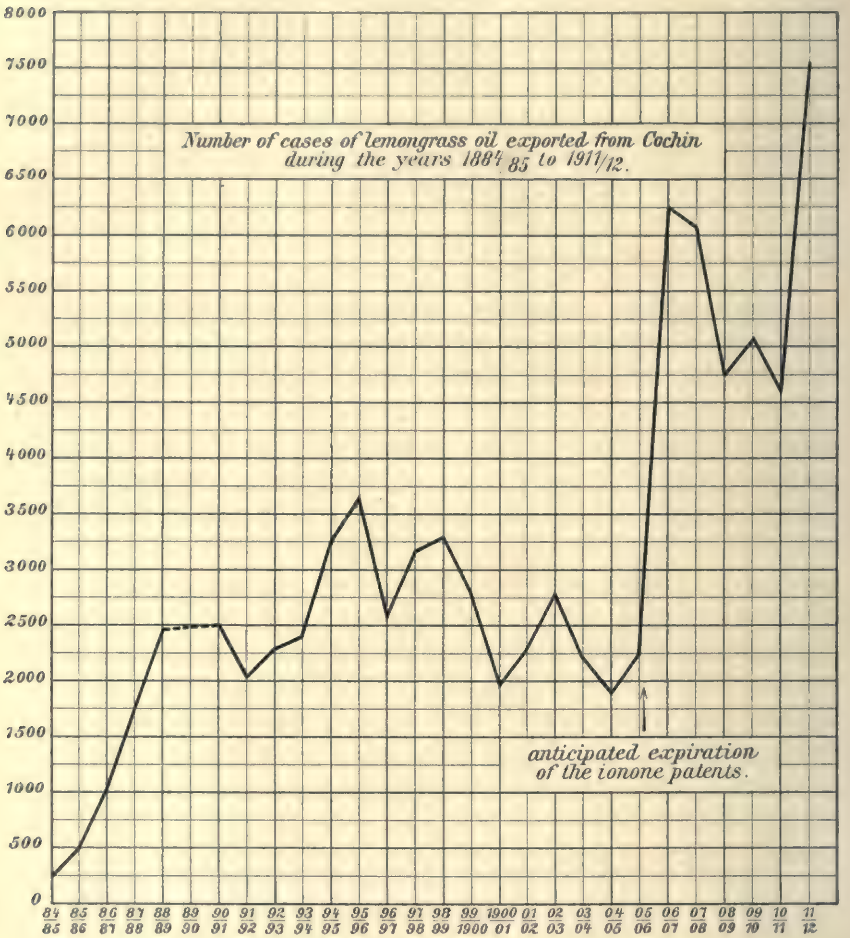
[3] *Ibidem* October 1905, 45.

[4] Chemist and Druggist 66 (1905), 140.

[5] Report of Schimmel & Co., April 1907, 68.

[6] Chemist and Druggist 62 (1903), 768.

Calicut and Quilon also export lemongrass oil[7]. The accompanying curve illustrates the exports, with the exception of 1889/90, from the beginning to the present time.


Number of cases of lemongrass oil exported from Cochin during the years 1884/85 to 1911/12.

anticipated expiration of the ionone patents.

Whereas in 1884 the exports amounted to but 228 cases of 12 bottles of 22 oz. each (7½ kg. in all), they rose materially in recent years as shown by the following table. The sudden rise in 1906 would seem to be associated with the prospective

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[7] Watt, The commercial products of India. London 1908. p. 458. — Hooper, Chemist and Druggist **70** (1907), 208.

termination of the ionone patents in Germany. The exports in cases to the several ports are recorded in the following table:

Year	Total	London	Liverpool	Havre	Marseilles	Bremen	Hamburg	New-York	Antwerp	Asiat. ports[1]
1899/00	2792	—	—	—	—	—	—	—	—	—
1900/01	1933	—	—	—	—	—	—	—	—	—
1901/02	2322	—	—	—	—	—	—	—	—	—
1902/03	2806	—	—	—	—	—	—	—	—	—
1903/04	2220	—	—	—	—	—	—	—	—	—
1904/05	1882	246	—	76	375	—	252	115	21	797
1905/06	2269	190	—	100	200	—	—	331	—	1230
1906/07	6240	609	—	1268	1734	—	1923	351	130	225
1907/08	6081	1650	540	904	1876	199	561	301	50	—
1908/09	4755	663	860	213	1638	—	215	1166	—	—
1909/10	5089	846	100	794	1791	101	1148	309	—	—
1910/11	4622	676	—	1158	1538	250	765	235	—	—
1911/12	7563	681	—	1343	3491	183	893	972	—	—

In Ceylon also some lemongrass oil is distilled, but only in isolated places and in small amount only. Statistics are not available.

In the Straits Settlements the distillation of lemongrass oil is still conducted on a small scale only. In 1903 it amounted to not more than 200 gals. (abt. 900 l.[2]).

125. West Indian Lemongrass Oil.

Origin. The designation "West Indian lemongrass oil" was adopted at a time when its botanical origin was unknown in order to distinguish it from the regular lemongrass oil of commerce. Repeatedly oils from the West Indies were offered for sale which deviated from the East Indian oil by their lesser solubility in alcohol, particularly in dilute alcohol. It was only later that O. Stapf[3] ascertained that the two oils were obtained from different plants and that the plant from which the West Indian oil is obtained is more widely distributed if anything in the East Indies than the plant from which the commercial oil is

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[1] Bombay and other ports, presumably for further shipment to Europe.

[2] Bull. Imp. Inst. 3 (1903), 13.

[3] Kew Bull. 1906, 297.

obtained. Hence, strictly interpreted, the designation West Indian oil is not justified. However, inasmuch as the name has established itself fairly well, it may be allowed to remain.

The plant from which the oil here to be discussed is obtained is *Cymbopogon citratus,* Stapf (*Andropogon citratus,* D. C.; *A. Schœnanthus,* L.; *A. citriodorum,* Desf.; *A. Roxburghii,* Nees; *A. ceriferus,* Hack.; *A. Nardus* var. *ceriferus,* Hack.; *Schœnanthum amboinicum,* Rumph.), lemongrass, Malay *„Sereh betoel"*. Contrary to Malabargrass *C. citratus,* according to Stapf, is found cultivated only[1]). It is found in most tropical countries, more particularly in Ceylon and the Straits Settlements, also in Nether-Burma and Canton, in Java, in Tonquin, Africa, Mexico, Brazil, the West Indies, French Guiana, in Mauritius, Madagascar, Guinea &c. On the largest scale the grass is cultivated in the Malay peninsula, more particularly about Singapore. It is used here not only for the production of oil, but for culinary purposes as well.

This grass seldom reaches the flowering stage, hence has been observed little or not at all by botanical collectors. This explains why it has been but insufficiently characterized in spite of its wide distribution.

Lemongrass oils which, judging from their behavior[2]), were derived from *Cymbopogon citratus,* have been examined frequently. They were obtained from the following countries and islands: S. Thomé[3]), Brazil[4]), the West Indies[5]), Mexico[6]), Kamerun[7]), Java[8]), Amani[9]), Ceylon[10])[11]), Cochinchina[12]), the

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[1]) According to Tschirch, *Handbuch der Pharmakognosie,* vol. II, p. 819 the grass occurs in the wild state in Java, according to Bacon, likewise in the Philippines (see p. 205).

[2]) Compare footnote 2 on p. 192.

[3]) Berichte d. deutsch. pharm. Ges. 7 (1897), 501; 8 (1898), 23.

[4]) Report of Schimmel & Co. April **1896**, 63.

[5]) *Ibidem* April **1902**, 48; Oct. **1902**, 50; April **1903**, 49.

[6]) *Ibidem* Oct. **1903**, 49.

[7]) Berichte d. deutsch. pharm. Ges. **13** (1903), 86; Report of Schimmel & Co. Oct. **1903**, 46; Oct. **1904**, 55.

[8]) Report of Schimmel & Co., Oct. **1904**, 56. — Journ. d'Agriculture tropicale 5 (1905), 42; Report of Schimmel & Co. Oct. **1905**, 46.

[9]) Report of Schimmel & Co. April **1905**, 84.

[10]) Chemist and Druggist **68** (1906), 355; Report of Schimmel & Co. April **1906**, 43; April **1911**, 78.

[11]) Bull. Imp. Inst. **9** (1911), 339; Report of Schimmel & Co. April **1912**, 79.

[12]) Report of Schimmel & Co. Oct. **1906**, 89.

Seychelles[1]) New Guinea[2]), Uganda[3])[5]), the Philippines[4]), Bengal[5]), also the Congo Free State, West Africa, Tongkin and Bermuda[6]).

Concerning the cultivation of the so-called West Indian lemongrass, a number of reports have been made which are herewith abstracted.

In Porto Allegre[7]), Brazil, an oil has been distilled from cultivated grass. In rainy years four cuts could be harvested, in dry years not more than three. The yield from fresh grass varied according to the season, from 0,24 to 0,4 p. c.

Some years ago, the *Times of Malaya*[8]) recommended the cultivation of lemongrass in place of citronella grass, since the former affords a larger crop. A sandy clay is best adapted to the cultivation of lemongrass but it also flourishes on well drained pure sandy soil. It prefers a certain amount of moisture, but cannot endure standing water. Hence, in order to expect a good harvest, rain and sunshine must prevail in the right proportion. The harvest may begin in the third year, moreover during the cool season, when two cuts can be made. The cutting should be followed immediately by distillation which is carried on in copper stills according to the common primitive method. Under normal conditions an annual output of 8000 oz. per acre may be expected.

Wright and Bamber[9]) report on the experiences in lemongrass cultivation gathered at the experimental stations in Ceylon. Whereas the cultivation of *Andropogon citratus,* DC. was formerly restricted to the southern part of the island, lemongrass is now successfully cultivated in Peradeniya at an altitude of 1600 ft. with an annual rainfall of 82 in. and a mean temperature

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[1]) Bull. Imp. Inst. **6** (1908), 108; Report of Schimmel & Co. Oct. **1908**, 82.

[2]) Berichte d. deutsch. pharm. Ges. **19** (1909), 25; Report of Schimmel & Co. April **1909**, 77; April **1910**, 68.

[3]) Report of Schimmel & Co. April **1909**, 65.

[4]) Philippine Journ. of Sc. **4** (1909), A, 111; Report of Schimmel & Co. Oct. **1909**, 76.

[5]) *Ibidem* Oct. **1909**, 75; Oct. **1910**, 77.

[6]) Bull. Imp. Inst. **9** (1911), 339; Report of Schimmel & Co. April **1912**, 89.

[7]) Report of Schimmel & Co. April **1896**, 63.

[8]) Kew Bull. **1906**, 364; Report of Schimmel & Co. April **1907**, 69.

[9]) Bull. Imp. Inst. **5** (1907), 300; Report of Schimmel & Co. April **1908**, 67.

of 75,5° F. for the year. The soil is a clay, poor in organic material and nitrogen. It contains an abundance of magnesia and potash, but no lime and little phosphoric acid.

The cultivation is very simple. Tufts of grass are divided into plants suitable for transplanting and planted in holes 2 to 3 feet apart. The grass grows rapidly and can be cut 5 to 9 months after planting. Thereafter it can be cut three times each year. Inasmuch as lemongrass greatly exhausts the soil, the stumps must be transplanted every three years. 10,000 lbs. of lemongrass contain about 65 lbs. potash, 12 lbs. nitrogen, 12 lbs. lime and 9 lbs. phosphoric acid. The distilled grass is used as fuel and the ashes as fertilizer. Ordinarily the grass is distilled in the fresh condition. The distillation lasts from 4 to 5 hrs. 496 lbs. of fresh lemongrass yield 1 lb. of crude oil (0,2 p. c.). The annual yield per acre amounts to about 20 lbs. of crude oil.

In order to ascertain the oil content in the several stages of development and thus to learn the most favorable time for harvest and distillation, A.W. K. de Jong¹) has made a series of investigations with *Andropogon citratus.* According to these the leaves are richest in oil. Moreover the leaf last formed contains relatively the most oil, and the oil content diminishes with the increasing age of the leaf. However, the citral content of the oil increases slightly with the age of the leaf, averaging 77 to 79 p. c. in the youngest and going as high as 83 p. c. in the oldest. The sheaths likewise contain oil, but much less than the leaves. The roots of *Andropogon citratus* also contain volatile oil. While the fibrous roots are devoid of oil, it is found in the thick tubers, of which the younger ones contain more (abt. 0,5 p. c.) than the older ones (abt. 0,35 p. c.). Hence De Jong recommends that the roots be distilled with the grass. (Concerning the properties of this root oil see p. 207). It is said not to be advisable to postpone the distillation after the formation of the 4th or 5th leaf.

In Java, according to P. Serre²), lemongrass oil is distilled principally in Tjitjoeroek, Kediri and Tjiaoei, the yield amounting to about 0,33 p. c.

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¹) Teysmannia 1907, No. 8; Report of Schimmel & Co. October 1908, 81.

²) Journ. d'Agriculture tropicale 5 (1905), 42; Report of Schimmel & Co. October 1905, 46.

Experimental distillation with lemongrass has also been made in one of the agricultural chemical experiment stations of Cochinchina[1]. These experiments showed that the oil content is much greater during the dry season, and that the upper third of the plant is much more aromatic than are the lower two-thirds. From thoroughly dried leaves that had lost 70 p. c. of their original weight, 8 to 8,5 p. c. of oil were obtained. Leaves distilled immediately after cutting yielded 2 p. c. in the rainy season, and 5,5 p. c. in the dry season.

According to a communication to the Imperial Institute[2], cultural experiments with lemongrass have been made in the Seychelles. Grass that had been imported a long time ago from Mauritius yielded 0,23 p. c. of oil, grass imported as recently as 1903 from Ceylon yielded 0,34 p. c. of oil.

According to R. F. Bacon[3], there is in the Philippines a lemongrass which, to judge by the oil obtained therefrom, may be regarded as *Andropogon citratus,* DC. It occurs all over the group of islands, either wild or as a garden plant. It grows abundantly in the uplands of the province of Benguet. However, it is cultivated to a slight extent only. In the language of the Tagali the oil grass is designated by the name given to it by its first investigator, the Spanish Jesuit Juan Eusebius Nuremberg, in 1635: *tanglat,* or more correctly *tañglad.* Other native designations are *salai* and *balyoco.* The Spanish name is *Paja de Meca.* The grass is not distilled for commercial purposes. Bacon correctly points out that under the present market conditions, the cultivation of lemongrass would not be remunerative in spite of quick and abundant returns. He, therefore, recommends it for intermediate cultivation only until other crops can yield a sufficient harvest. The distillation of a grass 5 months old, 2 days after it had been cut, yielded 0,2 p. c. of oil with the following properties: $d_{4^\circ}^{30^\circ}$ 0,894; $\alpha_{D30^\circ} + 8,1^\circ$; n_{D30° 1,4857; citral content 79 p. c.; complies with Schimmel's test *i. e.* soluble in 1 to 2 vols. and 10 vol. of 80 p. c. alcohol (apparently a con-

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[1] Bull. de la Chambre d'Agriculture de la Cochinchine **11** (1908), Nr. 98, p. 218; Report of Schimmel & Co. October **1908**, 82.

[2] Bull. Imp. Inst. **6** (1908), 108; Report of Schimmel & Co. October **1908**, 82.

[3] Philippine Journ. of Sc. 4 (1909), A, 111.

fusion with the test for citronella oil). The same plants cut again 4 months later yielded 0,2 p. c. of oil with the following constants: $d_{4^\circ}^{30^\circ}$ 0,8841; $\alpha_{D30^\circ} + 2{,}1^\circ$; n_{D30° 1,4765; citral content 77 p. c. Grass 7 months old, from another planting, yielded, when distilled immediately after having been cut, 0,21 p. c. of oil with the following constants: $d_{4^\circ}^{30^\circ}$ 0,891; $\alpha_{D30^\circ} + 7{,}76^\circ$; n_{D30° 1,4812; citral content 78 p. c. Basing his computations on the amount of grass harvested and assuming that these cuts can be made each year, Bacon points out that 240 to 300 kg. of oil per hectare per year can be expected. Inasmuch as the plant exhausts the soil, a transplanting must take place after three years.

Composition. Of the constituents of the West Indian lemongrass oil, the most important, the citral, only is known. Whether aldehydes other than citral are present has not yet been established, neither is it known what substances make the oil so difficultly soluble. When fractionated, the oil behaves very differently from the East Indian oil. According to the investigations of Umney and Bennett[1]) the former contains fewer low boiling substances than the latter. Whereas the East Indian oil began to distil at 210°, as much as 23 p. c. of the West Indian oil had passed over at this temperature. Furthermore, a comparative distillation under diminished pressure, in which the oils were resolved into fractions of 20 p. c. of the original oil, yielded appreciable differences of the respective fractions. Whereas the fractions of the West Indian oil were all inactive, those of the East Indian oil deviated between — 12 and — 2°.

Noteworthy is likewise the fact that the first 20 p. c. of the West Indian oil had a density of 0,821, as opposed to 0,882 of the East Indian oil.

This would seem to indicate an olefinic terpene. In harmony with this assumption is the behavior of the oil to dissolve in 2 vol. of 70 p. c. alcohol when freshly distilled, but to loose this property after a few days[2]). A similar behavior is revealed by oil of bay, in which case the loss of solubility is attributed to the polymerization of the myrcene contained therein.

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[1]) Chemist and Druggist **70** (1907), 138.

[2]) De Jong, Teysmannia **1907**, No. 8; Report of Schimmel & Co. Oct. **1908**, 81. — Watts and Tempany, West Indian Bulletin **9** (1908) 265; Report of Schimmel & Co. April **1909**, 63.

Properties. d_{15° 0,870 to 0,912; $\alpha_D - 1^\circ$ to $+0^\circ 12'$; n_{D20° 1,482 to 1,489. The solubility varies according to age and manner of storage. The old oils do not form a clear solution with 70 p.c. alcohol[1]); individual oils are soluble in several vol. of 80 p.c. alcohol, but the solution becomes turbid upon the addition of more alcohol. It is miscible with absolute alcohol in all proportions, but whereas some oils produce turbid solutions, others form clear solutions.

The citral content, determined according to the bisulphite method, varies between 53 and 83 p.c.

126. Root Oil of Cymbopogon citratus.

In Buitenzorg[2]) oils have been distilled both from the root tubers and the rhizomes of *Andropogon citratus* the properties of which are recorded in the following table:

	Oil from tubers	Oil from rhizomes
Yield	abt. 0,2 %	0,2 %
d_{26°	—	0,94
α_D	$-1^\circ 40'$	$-3^\circ 40'$
Citral content	82 %	11 %

127. Northern Bengal Lemongrass Oil.

An oil distilled by J. H. Burkill (Calcutta) in North Bengali had the properties of West Indian lemongrass oil, hence the plant was supposed to be *Cymbopogon citratus,* Stapf[3]). Later, however, the grass was identified as *Cymbopogon pendulus,* Stapf[4]).

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[1]) Only very fresh oils are soluble (see composition). The solubility is reduced after several days and after some time very turbid solutions only are obtained from which a part of the oil again separates. According to De Jong (Teysmannia 1907, No. 8; Report of Schimmel & Co. October 1908, 81) this change can not be attributed to oxidation for it has been observed in connection with oils that have been kept excluded from air. Several attempts made to prevent the change were unsuccessful. It was further observed that the change occurs rapidly when the oil is heated to 100°.

[2]) Jaarb. dep. Landb. in Ned.-Indië, Batavia, 1909, 64.

[3]) Report of Schimmel & Co. October 1909, 76.

[4]) *Ibidem* October 1911, 59.

The grass in question was obtained in the Jalpaiguri district (Northern Bengal). In part it was distilled on the spot (Sample I), in part in Calcutta (Sample II)[1]).

I. d_{15° 0,8954; $\alpha_D - 0^\circ 28'$; aldehyde content 90 p. c. (bisulphite method) and 84 p. c. (sulphite method).

II. d_{15° 0,8924; $\alpha_D - 0^\circ 49'$; aldehyde content 87 p. c. (bisulphite method) and 82 p. c. (sulphite method).

Neither of the oils was soluble in 70 p. c. alcohol, but dissolved in 0,9 vol. of 80 p. c. alcohol. The addition of more alcohol caused turbidity. Similar was their behavior toward 90 p. c. alcohol and even absolute alcohol. The solution which was clear at first became strongly opalescent upon dilution.

Burkill has also investigated the influence of the stage of development and of the time of harvest of the grass on the properties of the Northern Bengal oil[1]).

The oils were obtained from grass collected in the same region (Jalpaiguri district) at different periods. In July grass that was not yet in blossom was distilled immediately on the spot (Ia) and later in Calcutta (Ib). Two months later, in September, grass that had not yet reached the flowering stage was distilled (II). During the flowering period the flowers only were distilled (III), likewise the leaves only (IV). The data thus obtained, it was thought, would make it possible to draw conclusions as to the effect of different stages of vegetation on the properties of the oil. However, no remarkable differences were observable either between leaf and flower oil, or between the several leaf oils among themselves. The leaf oil is somewhat more dense and contains slightly more aldehyde than the flower oil, but the few observations at hand do not justify any final conclusion. The results are tabulated in the following table. (Page 209).

All of the above oils yielded a clear solution only in the beginning with even 90 p. c. alcohol. Upon dilution the solution became strongly opalescent.

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[1]) Report of Schimmel & Co. April 1910, 73.

No.	Origin, condition and time of harvest of the grass	$d_{15°}$	α_D	Aldehyde content	
				with $NaHSO_3$	with Na_2SO_3
	A. Non-flowering Jalpaiguri plants				
I.	July cut				
	a) Distilled in Jalpaiguri . . .	0,8954	$-0°28'$	90,0 %	84,0 %
	b) Distilled in Calcutta . . .	0,8924	$-0°49'$	87,0 %	82,0 %
II.	September cut				
	Distilled in Jalpaiguri	0,8925	$-0°53'$	85,5 %	83,0 %
	B. Flowering Jalpaiguri plants				
III.	Flowers only	0,8897	$-1°15'$	83,0 %	79,0 %
IV.	Leaves only	0,8916	$-1°5'$	86,0 %	81,0 %

B. T. Brooks[1]) described an oil closely related to lemongrass oil that was distilled in the Philippines from an unknown *Andropogon* species. It had the following constants: $d_{30°}^{30°}$ 0,8777; $\alpha \pm 0°$; $n_{D80°}$ 1,4868; and contained about 72 p. c. citral (m. p. of semicarbazone 155 to 160°) and 12 p. c. of geraniol that had been isolated with the aid of the calcium chloride compound.

128. Vetiver Oil.

Oleum Andropogonis muricati. — Vetiveröl. — Essence de Vétiver.

Origin and Production. Vetiver oil is obtained by the distillation of vetiver root. It is derived from *Vetiveria zizanioides,* Stapf (*Andropogon muricatus,* Retz.; *A. squarrosus,* Hack.; *Vetiveria muricata,* Griseb. a. o.)[2]), or vetiver grass, *Vettiver,* or known in Java as *Akar wangi,* in India as *Cus-Cus* or *Khas Khas,* a name that is probably of Hindostanic origin and signifies "aromatic root".

Since an early period the roots have been woven artistically into baskets, covers and mats. The latter are hung in doors and windows and in hot weather are frequently moistened with water, thus perfuming and cooling down the atmosphere.

Vetiver grass occurs both wild and cultivated and is highly prized on account of its roots which find manifold application. The wild plant occurs throughout India proper and Ceylon, more particularly along the shores of rivers and in rich marsh bottoms,

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[1]) Philippine Journ. of Sc. 6 (1911), A, 351.

[2]) Kew Bull. 1906, 346.

to an altitude of 600 m. Occasionally it is cultivated, *e. g.* in Rajputana and Chutia-Nagpur. In Malay territory vetiver occurs only as cultivated plant or having escaped cultivation. This also holds true of the West Indies[1]), Brazil[2]), Réunion and Java.

According to Bacon[3]) vetiver also occurs in the Philippines, where the natives designate the roots as *Moras* or *Raiz Moras.* The plant is further cultivated in Martinique[4]), the Seychelles, in Amani[5]) and in Momba.

The best varities of this species of grass are found in the neighborhood of Tutikorin, which up to this date is the most important port for the export of vetiver. In cultivating vetiver the tufts are torn apart and the individual plants set out in light soil. In the Philippines[4]) the hectare is said to yield 18 000 kg. of roots. The oil content of the roots increases up to the flowering period of the plant, hence it would seem rational to harvest and distil the roots within the first 3 months. Here also the plants are propagated by root division. The sowing of seed has not been attempted.

Cultural experiments made in Buitenzorg with the plant known as *Akar wangi,* the non-flowering variety of *Andropogon muricatus* occurring in Java[6]), have revealed that shade is apparently unfavorable to root development, whereas it is stimulated by repeated cutting of the plant.

The root is reddish and frequently rendered impure by a large amount of red sand. Frequently very pale roots are met with in commerce which yield but a very small amount of oil. It was formerly supposed[7]) that these roots had been partly exhausted by distillation. The opinion of G. Watt[8]), however, appears more rational, *viz.* that these roots have served as mats

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[1]) Dymock, Warden and Hooper, Pharmacographia indica. Part VI, p. 571, and Sawer, Odorographia. Vol. I, p. 309.

[2]) Peckolt, *Katalog zur National-Ausstellung in Rio* 1866. pp. 22 and 48. — Pharm. Rundschau 12 (1894), 110.

[3]) Philippine Journ. of Sc. 4 (1909) A, 118.

[4]) Report of Roure-Bertrand Fils, April 1908, 24.

[5]) Report of Schimmel & Co. April 1905, 84; April 1907, 102.

[6]) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 48.

[7]) First Edition of this treatise, p. 289.

[8]) G. Watt, The commercial products of India. London 1908, p. 1106.

and have frequently been sprinkled with water to cool off the houses, and that upon repeated drying much of the volatile oil has evaporated with the water.

The distillation of the oil is rendered difficult because of its sparing volatility, hence it is conducted mostly in Europe. In India the distillation is frequently carried out with sandalwood or sandalwood oil. This oil is but seldom exported. However, during recent decades considerable quantities of oil have been exported from Réunion. The oil distilled there differs somewhat from the oil distilled in Europe. This difference is due in part to the fresher condition of the root distilled in Réunion, partly to the method of distillation[1]).

In Europe the dry roots yield, according to their quality, from 0,4 to 1,0 p. c., rarely up to 2 p. c. of oil[2]).

From fresh, crushed Philippine roots Bacon[3]) obtained a yield of 1,09 p.c., from crushed, fresh roots only 0,3 p.c. of oil.

Properties. A distinction should be made between the viscid, dark yellow to dark brown, dense oils from dry roots and the less viscid and less dense oils from fresh roots. To the second class belongs *e. g.* the vetiver oil from Réunion. However, the odor of this oil is not as intense, neither is it as persistent as that of the European distilled oil, hence it is not as highly esteemed as the oil from the dry root. In consequence a lower price is paid therefor.

The properties of the oil distilled in Europe, hence from the dried roots, are as follows: d_{15° 1,015 to 1,04; $\alpha_D + 25$ to $+37^\circ$; n_{D20° 1,522 to 1,527; A. V. 27 to 65; E. V. 9,8 to 23; E. V. after acetylation 130 to 158; soluble in 1 to 2 vols. of 80 p.c. alcohol, additional alcohol causing turbidity.

In connection with Réunion oils the following constants have been observed: d_{15° 0,990 to 1,020; $\alpha_D + 22$ to $+37^\circ$; n_{D20° 1,515 to 1,527; A. V. 4,5 to 17; E. V. 5 to 20; E. V. after acetylation 124 to 145; soluble in 1 to 2 vols. of 80 p.c. alcohol, additional alcohol occasionally causing turbidity.

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[1]) E. Theulier, Bull. Soc. chim. III. **25** (1901), 454.

[2]) Report of Schimmel & Co. April **1907**, 102.

[3]) *Loc. cit.*

An oil obtained from the Fiji islands[1]) was dark green in color and revealed the following constants: $d_{15°}^{15°}$ 1,0298; S. V. 35,3; soluble in 80 p. c. alcohol, at first to a clear solution which becomes turbid after the addition of 25 vols. and more. Roots imported from the Seychelles yielded 0,482 p. c. of oil of which 0,072 p.c. were separated from the aqueous distillate. The examination of the oil obtained directly (0,41 p.c.) yielded the following results: $d_{15°}$ 1,0282; $\alpha_{D20°} + 27°$; A. V. 55,9; S. V. 67,3; E. V. 11,4; soluble in 1 vol. and more of 80 p. c. alcohol. The oil possessed a deep golden-brown color and was viscid. The oil separated from the aqueous distillate possessed similar properties, but had a somewhat fainter odor.

Composition. The statements recorded with regard to the composition of vetiver oil vary considerably and cannot always be harmonized. This is due in part to the difficulty of the investigation because of the high boiling point and viscid character of the oil. The confusion is further attributable to the circumstance that no well-defined crystalline derivatives have thus far been obtained from its constituents.

E. Theulier[2]) restricted his investigations to a comparison of the properties of two oils, one distilled at Grasse, the other in Réunion: *viz.* of the boiling temperatures under a pressure of 25 mm. and of the other properties of the corresponding fractions.

According to Franz Fritzsche & Co.[3]) vetiver oil is said to contain ketones which can be separated by means of their non-crystalline semicarbazones and oximes from the other constituents. These ketones (vetirone or vetiverone) are said to be mixtures of several isomers which boil at about 149 and 154° (10 mm.). $d_{15°}$ about 0,990. Their analysis revealed the empirical formula $C_{13}H_{22}O$. According to the investigations made by the same firm[4]), the oil contains in addition to the ketones two alcohols (vetirols or vetiverols) which can be isolated as the acid phthalic esters. The one boils between 150—155° (10 mm.),

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[1]) Bull. Imp. Inst. **10** (1912), 32.

[2]) Bull. Soc. chim. III. **25** (1901), 454.

[3]) Germ. Pat. 142415 (1902).

[4]) Germ. Pat. 142416 (1902).

d_{15° 0,980, and has the empirical formula $C_9H_{14}O$. The other alcohol has the formula $C_{11}H_{18}O$, boils between 174 and 176° (10 mm.), d_{15° 1,02.

P. Genvresse and G. Langlois¹) have shown the presence of two constituents in vetiver oil which are, however, of no importance so far as the odor is concerned. The two oils examined were obtained from Réunion and from Grasse. Both oils contained the same substances but in different proportion, the Réunion oil containing much more sesquiterpene than the other. The neutral Réunion oil had a specific gravity of 0,993 (20°) and an optical rotation of $+23° 43'$ (in alcoholic solution). The Grasse oil, which had an acid reaction, had a specific gravity of 1,012 (20°), and an optical rotation of $+27° 9'$. Upon steam distillation but $^1/_3$ of the total oil passed over and of this a part was relatively lighter than water, the other part heavier. The former consists principally of a sesquiterpene $C_{15}H_{24}$, vetivene, a colorless and odorless liquid boiling at 262 to 263° (740 mm.) or at 135° (15 mm.). It has a specific gravity of 0,932 (20°) and an optical rotation of $+18° 19'$. It absorbs 4 atoms of bromine, becoming blue, but does not solidify. The denser portion of the oil consists, in the main, of a sesquiterpene alcohol $C_{15}H_{26}O$, the vetivenol, a viscid, light yellow, odorless substance with the following physical constants: b. p. 169 to 170° (15 mm.), d_{20° 1,011; $\alpha_D + 53° 43'$ (in alcoholic solution). With acetic acid anhydride, the alcohol yields an acetate. When acted upon with anhydrous oxalic acid, vetivene, the sesquiterpene mentioned above, is produced. In addition to vetivenol, the distillation residue contains an acid $C_{15}H_{24}O_4$ or a mixture of acids. It is a viscid mass which becomes brown upon exposure to air and yields a soluble potassium salt. Genvresse and Langlois are of the opinion that the bearer of the odor of the oil is an ester of this acid with vetivenol, an ester that is readily saponifiable even with water. In connection herewith it should be mentioned that Schimmel & Co.²) have observed crystals of palmitate of zinc in a vetiver oil which had been kept for a long time in a zinc container. Hence the conclusion may be drawn that palmitic acid is a constituent of vetiver oil.

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¹) Compt. rend. **135** (1902), 1059.

²) Bericht von Schimmel & Co. April **1899**, 50.

Bacon[1]) also has studied the acids of vetiver oil. Upon saponification, 100 g. of oil yielded 19 g. of an acid mixture that possessed a fatty acid odor. After distillation in vacuum, 40 p. c. of a light yellow, viscid acid were obtained. It had the odor of oleic acid and boiled between 200 and 205° under 4 mm. pressure. The analysis of the sodium salt revealed the formula $C_{15}H_{24}O_2$.

As already pointed out, Genvresse and Langlois[2]) attribute the typical vetiver odor to the ester of the acid $C_{15}H_{24}O_4$ with vetivenol, an alcohol $C_{15}H_{26}O$. With this opinion Bacon could not agree, since the oils remaining after saponification revealed a strong vetiver odor. Upon fractionation of the saponified oil, the odor was observed in the middle and higher fractions (b. p. 137 to 140° and 140 to 145° under 12 to 15 mm. pressure), also in the semisolid, tar-like residue, but not in the lower fraction (b. p. 125 to 133°). From another sample of vetiver oil, Bacon obtained upon saponification, a large amount of benzoic acid.

According to the more recent investigations by F. W. Semmler, F. Risse and F. Schröter[2]), the formulæ assigned by Genvresse and Langlois to vetivenol and the acid are not correct. The former, it is claimed, has the composition $C_{15}H_{24}O$ and the latter the composition $C_{15}H_{22}O_2$.

The authors examined an oil distilled by Schimmel & Co., which had the following properties: d_{20° 1,0239; $\alpha_D + 31^\circ$; n_{D20° 1,52552. 400 g. were distilled under a pressure of 12 mm. and thus resolved into four fractions, *viz.:* —

A. b. p. 129 to 175°, 23 %,
B. b. p. 170 to 190°, 34 %,
C. b. p. 190 to 250°, 8 %,
D. b. p. 250 to 300°, 30 %.

By means of a second distillation, fraction D was resolved into two parts: —

a) b. p. 138 to 260° (13 mm.), 28 %,
b) b. p. 260 to 298° (13 mm.), 62 %.

According to analysis fraction D, b consisted of an ester $C_{30}H_{44}O_2$ *viz.* of the acid $C_{15}H_{22}O_2$ and the alcohol $C_{15}H_{24}O$. The free

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[1]) *Loc. cit.*

[2]) Berl. Berichte 45 (1912), 2347.

alcohol has the following properties: b. p. 170 to 174° (13 mm.); d_{20° 1,0209; $\alpha_D + 34^\circ 30'$; n_D 1,52437; mol. refr. found 65,94, computed for $C_{15}H_{24}O/^{=}$ 66,00. Hence vetivenol must be regarded as a tricyclic alcohol with a single double bond. The acid $C_{15}H_{22}O_2$ boils between 202 and 205° (13 mm.), is tricyclic and is named vetivenic acid by the authors. The boiling point of the methyl ester lies between 170 and 173° (18 mm.): d_{20° 1,0372; $\alpha_D + 42^\circ 12'$; n_D 1,50573; mol. refr. found 71,05; computed for $C_{16}H_{24}O_2/^{=}$ 71,31.

After several distillations in vacuum, fractions A and B yielded a fraction 173 to 180° (13 mm.), from which vetivenol could be removed by means of phthalic acid anhydride. It would seem therefore to be a primary alcohol. When reduced with hydrogen in the presence of platinum, vetivenol can be reduced to the tricyclic dihydrovetivenol, $C_{15}H_{26}O$: b. p. 176 to 179° (17 mm.); d_{20° 1,0055; $\alpha_D + 31^\circ$; n_D 1,51354. Vetivenol (tricycl.) yields an acetate b. p. 180 to 184° (19 mm.); d_{20° 1,0218; $\alpha_D + 28^\circ 48'$; n_D 1,50433; mol. refr. found 75,91, computed for $C_{17}H_{26}O_2/^{=}$ 75,61.

Upon saponification of fraction C, an oil resulted which, after repeated distillation, yielded a fraction with a boiling point of 178 to 185° (19 mm.); d_{20° 1,0137; $\alpha_D + 52^\circ 12'$; n_D 1,52822; mol. refr. found 66,81, computed for $C_{15}H_{24}O/^{=}$ 66,00, computed for $C_{15}H_{24}O/^{=}_{2}$ 67,71. Hence there is a mixture of di- and tricyclic vetivenol. The acid of fraction C proved to be vetivenic acid. Fractions A and B likewise contained a dicyclic primary vetivenol which is probably identical with that of fraction C. Tricyclic vetivenol was also contained in these fractions.

After repeated fractionation in vacuum, finally over sodium, two hydrocarbons were isolated from fraction A:

I. B. p. 123 to 130° (16 mm.); d_{20° 0,9355; $\alpha_D + 2^\circ 16'$; n_D 1,51126; mol. refr. found 65,32, computed for $C_{15}H_{24}/^{=}$ 64,45, computed for $C_{15}H_{24}/^{=}_{2}$ 66,15.

II. B. p. 137 to 140° (16 mm.); d_{20° 0,9321; $\alpha_D - 10^\circ 12'$; n_D 1,51896; mol. refr. found 66,42, computed for $C_{15}H_{24}/^{=}$ 64,45, computed for $C_{15}H_{24}/^{=}_{2}$ 66,15.

According to the molecular refractions, fraction I may be regarded as essentially a tricyclic hydrocarbon with one double bond, whereas fraction II may be a dicyclic hydrocarbon with two double bonds. These hydrocarbons are probably related to the vetivenols $C_{15}H_{24}O$ as the santalenes to the santalols and are to be differentiated as di- and tricyclic vetivenes.

The examination of a Réunion vetiver oil (d_{20° 0,9916 and 0,9982; $\alpha_D + 24^\circ 6'$ and $+31^\circ$; n_D 1,52429 and 1,52517) yielded somewhat different results. Of the high boiling vetivenol vetivenate little or scarcely appreciable amounts are present. Like the oil distilled by Schimmel & Co., the Réunion oil contains tricyclic and dicyclic vetivene. Tricyclic and dicyclic vetivenol also occur in this oil.

When acted upon with phosphorus trichloride in petroleum ether solution, the vetivenol from Réunion oil (b. p. 161 to 164° under 9 mm.) yields a chloride b. p. 140 to 147° (10 mm.) (d_{20° 0,9679; $\alpha_D - 24^\circ$; n_D 1,52640). When reduced with sodium and alcohol, an artificial vetivene resulted: b. p. 121 to 127° (9 mm.); d_{20° 0,9296; $\alpha_D - 25^\circ 48'$; n_D 1,51491; mol. refr. found 66,1, computed for $C_{15}H_{24}/^{=}_{2}$ 66,15. Semmler, however, obtained different results when he reduced, with sodium and alcohol, the chloride which had likewise been prepared with the aid of phosphorus pentachloride, but had not been rectified in vacuum. After the resulting hydrocarbon had been distilled over sodium and then shaken for a longer period with a 3 p.c. permanganate solution, it revealed the following properties: b. p. 123 to 129° (10 mm.); d_{20° 0,9288; $\alpha_D + 6^\circ 12'$; n_D 1,50682; mol. refr. found 63,88, computed for $C_{15}H_{24}/^{=}$ 64,45. To what extent, if any, the artificial vetivenes are identical with the natural ones, will have to be revealed by further investigations.

The reduction of the crude vetivenol from the Réunion oil with hydrogen in the presence of finely divided platinum, apparently yielded tricyclic dihydrovetivenol and dicyclic tetrahydrovetivenol. In small part the vetivenol was thereby reduced to a hydrocarbon.

In the aqueous distillate of vetiver oil the presence of methyl alcohol, furfurol and diacetyl (monophenylhydrazone, m. p. 133 to 134°; hydrazoxime, m. p. 158°; dimethylbishydrazimethylene, m. p. 158°; trimethylglyoxaline) has been proven¹).

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¹) Report of Schimmel & Co. April 1900, 45.

Citronella Oils.

Botanical Origin. Citronella oil is distilled from the grass of *Cymbopogon Nardus,* Rendle. The name *Nardus* is due to the mistaken identity, by various botanists, of this plant with the *Nardus Indica* of the Ancients. Linné originally named the plant *Andropogon Nardus.* The designation *Cymbopogon Nardus* has recently been reintroduced by O. Stapf[1]). Others have associated this grass with *Calamus aromaticus*[2]) of antiquity. Nicolaus Grimm, who lived as physician in Colombo toward the close of the 17. century, named it *Arundo Indica odorata.* He knew that it grew abundantly in the vicinity of Colombo and that a volatile oil was distilled therefrom. Subsequently citronella grass was frequently confounded with lemon grass.

With the exception of Ceylon, where the grass is reported to occur wild also[3]), citronella grass is found in the cultivated state only. It is cultivated primarily in the southern part of Ceylon, in the peninsula of Malacca and in Java. These countries supply the citronella grass of commerce. In recent years attempts at cultivation have been made in the West Indies, in the Seychelles and the South Sea islands. In tropical East Africa the grass is said to occur frequently[4]).

The managrass of Ceylon, *Cymbopogon confertiflorus,* Stapf of Ceylon is regarded as the mother plant of the citronella grasses.

For the purpose of distilling the commercial oil, two varieties of citronella grass are cultivated, *Maha Pengiri (Maha Pangiri)*[5]) and *Lena batu (Lana Batu).* The first kind is also known as "old citronella grass" or "Winter's grass". It is cultivated prin-

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[1]) The Oil Grasses of India and Ceylon. Kew Bull. **1906**, 297; Report of Schimmel & Co. April **1907**, 20.

[2]) According to Royle, this name applies to palmarosa grass or *Cymbopogon Martini,* Stapf. Hence he suggested the name *Andropogon Calamus aromaticus* (comp. Stapf *loc. cit.* p. 336).

[3]) J. F. Jowitt, Annals of the Royal Botanic Gardens, Peradeniya, Vol. IV, pt. IV, December **1908**, p. 185.

[4]) A. Moller, Berichte d. deutsch. pharm. Ges. 7 (1897), 501.

[5]) *Maha* means large and *Pangiri* signifies the nebulæ of oil particles that result when orange or lemon peels are pressed.

cipally in Java, also in the Malacca peninsula. In Ceylon it was cultivated only temporarily by Winter, a well-known distiller of citronella oil of Baddagama, hence the name. According to Jowitt[1]) this grass occurs wild in Ceylon and constitutes a variety distinct from the managrass. Probably by crossing[2]) of the two the third variety, the lena batu grass, has resulted. According to Stapf's observations, the *Maha Pengiri* and *Lenabatu* can not be distinguished morphologically. However, the habits of the two plants are different as are also the two volatile oils. For this reason the two varieties are distinguished botanically: the *Maha Pengiri* variety is known as *Cymbopogon Winterianus,* Jowitt (*Andropogon Nardus Java,* de Jong), the *Lena batu* variety as *C. Nardus,* Rendle, *lena-batu* (*A. Nardus Ceylon,* de Jong).

The maha pengiri grass is distilled but little in Ceylon. It yields the Java citronella oil.

The lena batu variety, also known as "new citronella grass" supplies the bulk of the Ceylon citronella grass and yields the ordinary Ceylon citronella oil of commerce.

129. Ceylon Citronella Oil.

Cultivation. Valuable statements concerning the citronella oil industry are contained in a paper by B. Samaraweera[3]) which was read by A. Jayasuriya at a meeting of the Agricultural Society of Ceylon. The maha pengiri grass (comp. p. 217) affords a good yield of oil rich in aromatic substances. However, it demands a rich soil, much care, and must be transplanted frequently. The lena batu affords a smaller yield of less aromatic oil, but flourishes on poorer soil and requires no transplanting. Inasmuch as the bulk of the Ceylon oil is obtained from lenabatu, this explains why the Ceylon citronella oil possesses less commercial value than the Java and Singapore citronella oils. A change in this respect can be brought about only when maha pengiri is cultivated in Ceylon.

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[1]) *Loc. cit.*

[2]) Comp. also Bull. Imp. Inst. **10** (1912), 299.

[3]) Oil, Paint and Drug Reporter **70** (1906), 25. — The Times of Ceylon April 3rd 1906; Report of Schimmel & Co. October **1906**, 16; April **1907**, 27.

Fig. 26.

A Field of Maha Pengiri-Grass in Ceylon.

Care should be exercised not to set the plants too close; about 15000 plants per acre[1]). The soil should be well drained and fertilized, and more attention should be paid to the removal of weeds. Because of the difficulty of obtaining cheap labor during the rice harvest, citronella plantations are in danger of being ruined entirely or in part. Hence farmers are advised to introduce mowing machines for the purpose of reducing the cost of production. The freshly cut grass, however, is not used for distillation, for it yields an oil with an unpleasant odor; but the well dried grass which yields an oil with an agreeable odor. During the process of drying, fermentation and decay must be carefully avoided. Four or only three cuts are made annually on the plantations. The latter practice is preferable. The yield of oil increases up to the third year and averages about 71 lbs. 3 oz. annually per acre. After the third year the yield of oil decreases continuously although the appearance of the grass is very good.

The meteorological conditions exert a great influence on the citronella grass. Moderate altitudes afford a good oil and a larger yield than the same grass affords at higher altitudes.

In Ceylon the cultivation of the grass is carried on exclusively in the Southern Province[2]), more particularly in the region between the Gin Ganga to the Northwest and the Walawi Ganga to the East. The grass is cultivated on the slopes of the hills. The individual tufts of grass grow, at irregular intervals, to a height of 1 m. According to reliable dealers, somewhat between 40000 and 50000 acres are cultivated with citronella grass.

Provided the formation of seeds is prevented by regular harvests, the plants demand little or no care. If not harvested regularly, the tufts grow too dense, become yellow within and decay. Generally two periods for harvest are distinguished. The first and principal season occurs in the months of July and August, the second during the months of December to February. The yield per acre for the summer campaign is estimated at from 16 to 20 bottles (of 22 oz.) per acre and from 5 to 10 bottles for the winter campaign. Exact statements cannot be made

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[1]) 1 acre = 40,467 Are.

[2]) Comp. Bericht von Schimmel & Co. October 1889, 11.

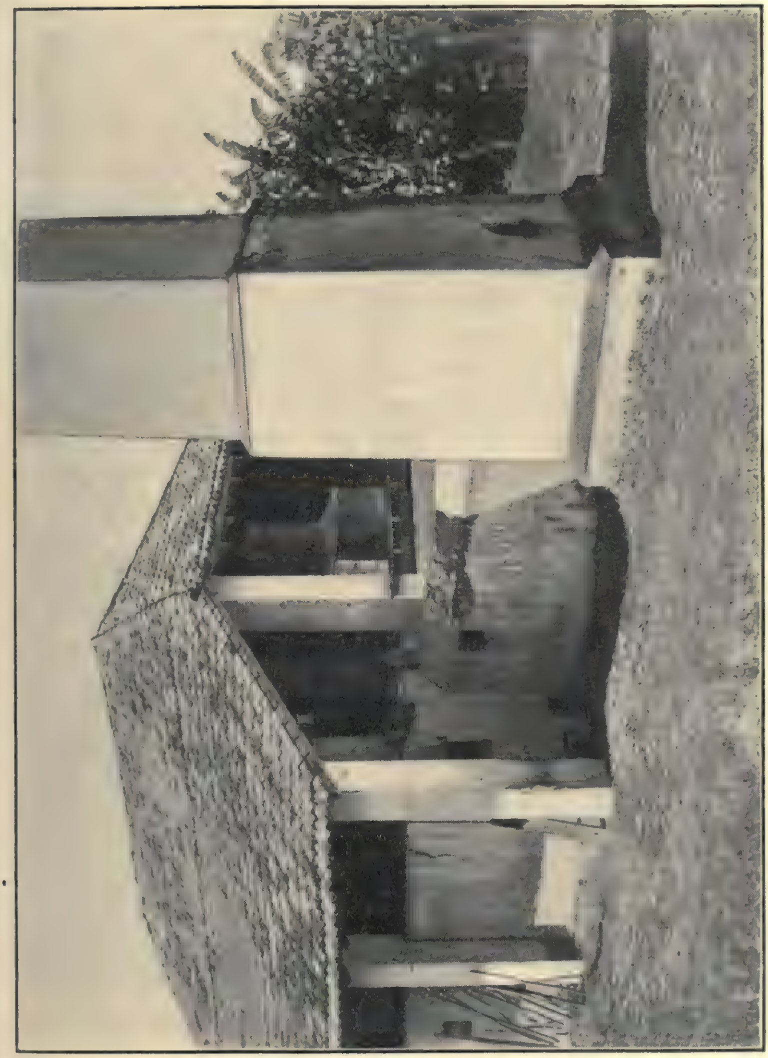

Fig. 27.

Citronella Oil Distillery Plant in Ceylon.

since the yield naturally depends on the weather, on the age of the plants, and the location of the plantation. Thus *e. g.* even favorable conditions of weather and soil will not prevent the diminution of the oil output with the advance of age. When a field has reached the age of 15 years, a replanting is necessary if it is to be worked profitably.

Production. The distilleries are mostly located at the foot of a chain of hills where an abundance of water of low temperature may be had.

As becomes apparent from the description which follows, the construction is by no means primitive. Indeed it is remarkable to note the advancement achieved by the natives, for such are the majority of distillers. Under a long roof that affords protection against the sun there is mounted, on a solid foundation, a boiler provided with safety valve and water gauge. Beside it, on a slight elevation, are placed two iron, cylindrical stills, 6 to 7 ft. high and 3 to 4 ft. in diameter with a common interchangeable helmet. Next to these is the condenser, consisting of a wooden vat and resting on a water basin, sunk into the earth, which accommodates the coil. The container which acts as receiver is still lower in a cellar and kept under lock and key. The entire outfit is illustrated by the accompanying plans (figs. 28 and 29, p. 223).

The method of distillation is that of direct steam distillation without the addition of water. The warm water of the upper condenser is used to feed the boiler, whereas the subterranean basin, through which the coil also makes several turns, serves to effect complete condensation. It is noteworthy that the unseparated distillate as it leaves the condenser is collected in the container behind lock and key. Within certain intervals the owner visits his several plants to skim the oil. The aqueous distillate is allowed to run off whenever the capacity of the receiver demands it.

Dried grass only is distilled. One charge requires about 6 hours to be exhausted.

As fuel the exhausted grass is used after it has been dried in the sun. Inasmuch as the Southern Province is poor in wood for fuel, the campaign comes to an end with the rainy season, since the exhausted grass can no longer be dried.

An apparatus 7 ft. high and 4 $^1/_2$ ft. in diameter yields about 16 to 20 flasks of 22 oz. each, hence 360 to 440 oz. per day.

Elevation.

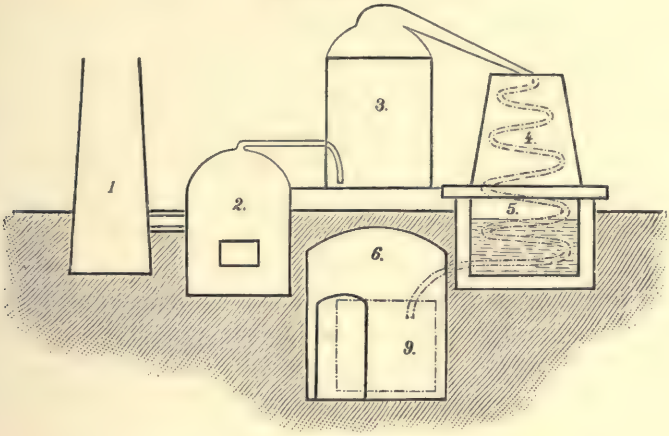

Fig. 28.

Floor-plan.

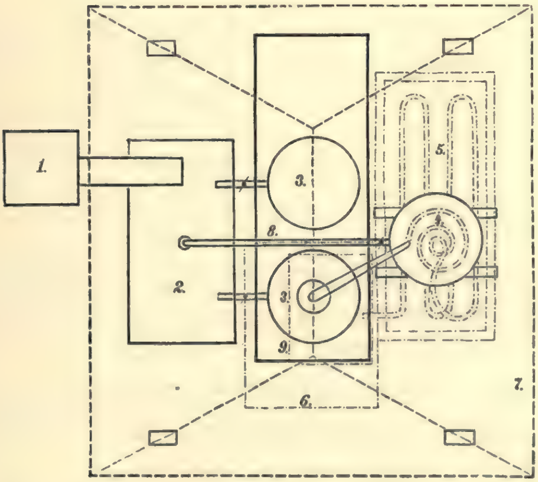

Fig. 29.

1. Chimney. 2. Boiler. 3. Stills. 4. Condenser. 5. Water basin (condenser). 6. Locked cellar for the storage of the distillate. 7. Roof. 8. Water supply pipe for boiler. 9. Basin for the storage of the distillate.

The grass is never weighed. The still being charged the distillation is begun. Hence more exact figures are not available.

In addition to the steam distillation outfit described above, apparatus involving direct heat are said to be used in a few districts. However, the bulk of the citronella oil is nowadays obtained by steam distillation. Wherever direct heat is employed, water must naturally be added to the grass. It remains to be stated that the grass is not specially dried previous to distillation. However, it is never moist when placed into the still since several hours elapse between the time of cutting and the time of distillation. At a temperature of about 65 to 70° C. in the sun this suffices to remove a large part of the moisture.

The districts in which citronella oil is distilled are graphically outlined on the accompanying map. The number of distilleries in operation in Ceylon is estimated at between 500 and 600.

According to the estimate of N. Wickremaratne[1]), the acre, when cut four times, yields a total of 18000 lbs. of grass per annum and, if the grass be in good condition, this yields 68 lbs. of oil.

Statistics. The exports of citronella oil from Ceylon are recorded in the following table.

1905	1282471 lbs.
1906	1107655 „
1907	1230159 „
1908	1276965 „
1909	1512084 „
1910	1747934 „
1911	1524275 „

The exports of oil from Ceylon from 1892 to 1912 and the variations in price during this period are graphically represented by the accompanying curve.

Composition. Ceylon citronella oil is a very complex mixture of hydrocarbons and oxygenated constituents. Of terpenes it contains about 10 to 15 p. c.

Fraction 157 to 164° contains *camphene*[2]). When hydrogen chloride is passed into an ethereal solution of this fraction, there is obtained, in addition to liquid products, a solid chloride

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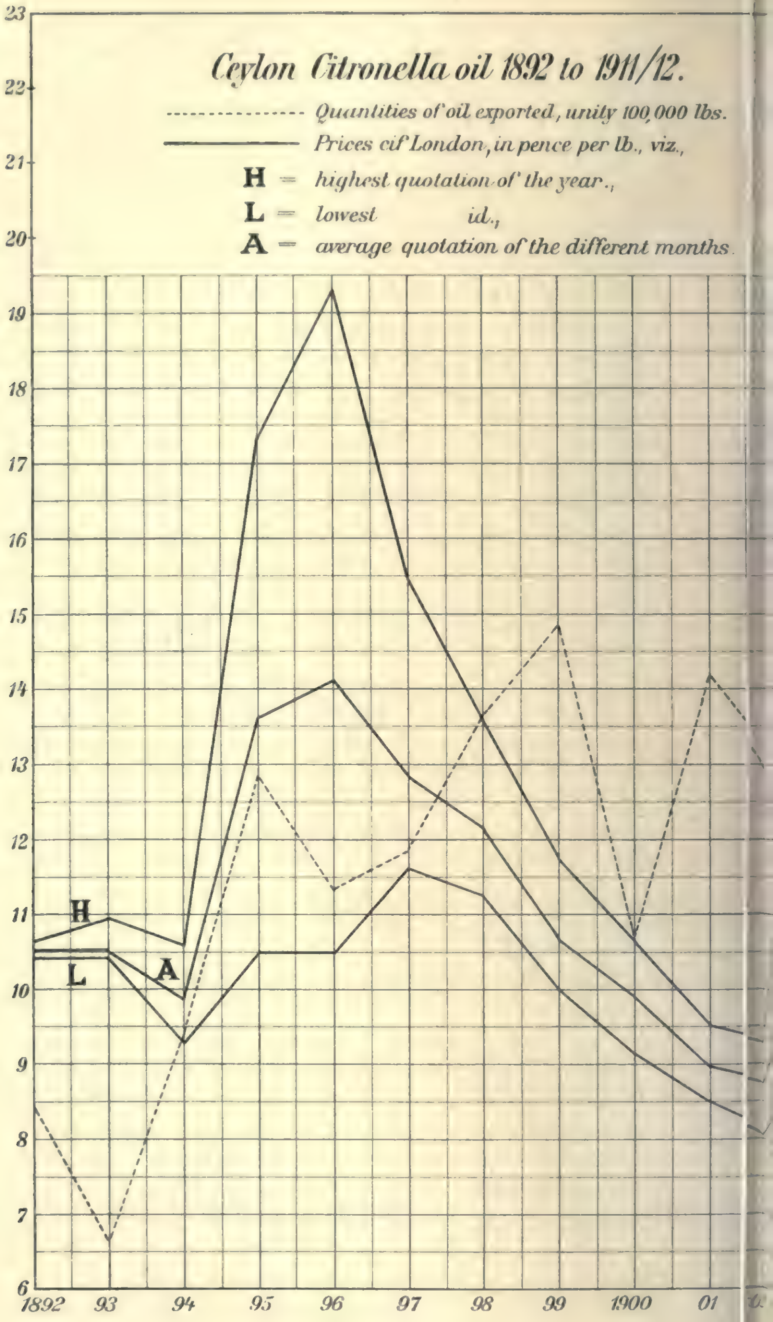
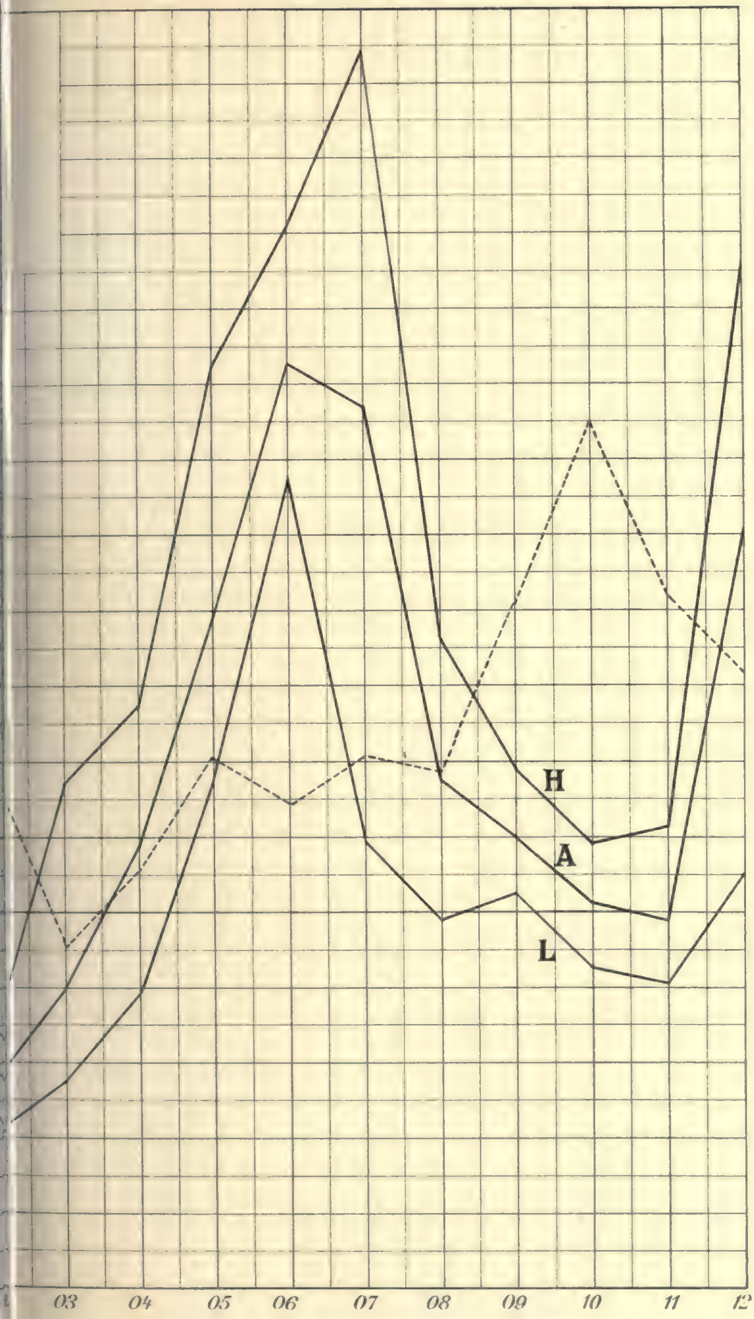
[1]) Tropical Agriculturist April 1911; Chemist and Druggist 79 (1911), 443.

[2]) Bertram and Walbaum, Journ. f. prakt. Chem. II. 49 (1894), 16.



Ceylon Citronella oil 1892 to 1911/12.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from which camphene can be obtained quantitatively by heating it to 100° with water under pressure. When the same fraction is heated with glacial acetic acid and sulphuric acid, *iso*borneol (m. p. 212°) results¹). If fraction 158 to 162° is oxidized with mercuric acetate²), a mercury compound is formed which, when decomposed with sulphuretted hydrogen, yields solid camphene³). Somewhat later Schimmel & Co.⁴) succeeded in isolating solid camphene directly from the oil. Fraction 160 to 163° as well as fraction 164 to 168°, when oxidized with permanganate in alkaline solution, yielded camphene-camphoric acid melting at 142°. That portion of the oil which was not changed by the oxidation, when distilled with steam, solidified in the condenser. After purification by means of alcohol it revealed all of the properties of ordinary camphene. It melted at 49 to 50°; $[\alpha]_D - 173° 22'$ in 10,2 p. c. chloroform solution. Inasmuch as the lower fractions contain neither α- nor β-pinene nor sabinene, it must be assumed that they contain considerable amounts of another terpene. This is probably an isomeric camphene which, under certain conditions, may be converted into derivatives of the ordinary camphene.

Of other terpenes, the presence of *dipentene* has been demonstrated (m. p. of tetrabromide 124⁵) to 125°⁶)), also that of l-*limonene*⁴) (tetrabromide; m. p. of nitrolbenzylamine 92 to 93°). In the course of a fractionation, terpene mixtures of very low specific gravity have been observed. This would seem to indicate the presence of a new terpene, the isolation of which, however, has not yet been successful.

Of oxygenated constituents, *methylheptenone* (m. p. of semicarbazone 134 to 135°), of which traces occur in the lower fractions, should be mentioned.

Citronellal is largely responsible for the odor of citronella oil, hence may be regarded as its principal constituent. It is an aldehyde of the formula $C_{10}H_{18}O$. It first attracted the

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¹) Report of Schimmel & Co. October **1899**, 13.

²) L. Balbiano and V. Paolini, Berl. Berichte **35** (1902), 2995.

³) Report of Schimmel & Co. April **1903**, 84.

⁴) *Ibidem* April **1912**, 40.

⁵) Bertram and Walbaum, Journ. f. prakt. Chem. II. **49** (1894), 16.

⁶) Report of Schimmel & Co. October **1899**, 18.

attention of the investigators, though contained in the oil to the extent of from 6 to 10 p. c. only. Because of the instability of this aldehyde, the ideas concerning its composition have undergone several changes in the course of time.

J. H. Gladstone[1]) found the "citronellol", as he called the substance, to boil between 199 and 205° and assigned to it the formula $C_{10}H_{16}O$. C. R. A. Wright[2]) assigned to it the boiling point of 210°, and the formula $C_{10}H_{18}O$. By shaking out the aldehyde with alkali bisulphite and regenerating it with acid, Kremers[3]) obtained a product that had no constant boiling point whatever, which he regarded as heptaldehyde. Schimmel & Co.[4]) designated as "citronellone" the substance which they regenerated from the acid sodium sulphite addition product with soda and which boiled between 205 and 210°. However, they left undecided whether the substance in question was a ketone or an aldehyde. Dodge[5]) favored the idea that it was an aldehyde but supplied no proof for the aldehyde nature of the "citronella aldehyde" as he called it. This was supplied by Semmler[6]) who oxidized the "citronellone" to an acid with the same number of carbon atoms, the citronellic acid, $C_{10}H_{18}O_2$. Hence this substance is now more rationally designated "citronellal", which name indicates its chemical character. The citronellal of citronella oil is dextrogyrate. For properties and derivatives see vol. I, p. 414.

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[1]) Journ. chem. Soc. **25** (1872), 1. — Pharmaceutical Journ. III. **2** (1872), 746; Jahresb. f. Chemie **1872**, 815.

[2]) Pharmaceutical Journ. III. **5** (1874), 233. Both Gladstone and Wright give *Andropogon Schœnanthus* as the botanical source of citronella oil. From their records, however, it becomes apparent that they worked with citronella oil and not with the oil of *A. Schœnanthus*. However, the „*Untersuchung des Öls von Andropogon Iwarancusa*" of Stenhouse (Liebig's Annalen **50** [1844], 157), which is designated East Indian grass oil by him was, in all probability, not palmarosa oil, but citronella oil. Comp. „*Über Palmarosaöl*" by E. Gildemeister and K. Stephan. Arch. der Pharm. **234** (1896), 323.

[3]) Proceed. Americ. pharm. Ass. **35** (1887), 571; Chem. Zentralbl. **1888**, 898.

[4]) Bericht von Schimmel & Co. October **1888**, 17.

[5]) Dodge proposed the correct formula $C_{10}H_{18}O$. Americ. chem. Journ. **11** (1889), 456; Chem. Zentralbl. **1890**, I. 127.

[6]) Berl. Berichte **26** (1893), 2254.

The Citronella-oil districts on CEYLON.

Scale 1 : 740000.

Simultaneously with citronellal there passes over during the fractional distillation a substance that solidifies in the receiver and that has been identified as l-*borneol*[1]) (m. p. of phenylurethane 138°). In addition there occurs a substance with linalool-like odor which upon oxidation yields citral (m. p. of citrylidene cyanacetic acid 120 to 121°) but which, contrary to an opinion previously expressed[2]), does not appear to be linalool.

In a fraction 218 to 230°, from which the borneol had been removed as completely as possible, the presence of small amounts of *nerol* (m. p. of tetrabromide 116 to 118°) has been demonstrated[3]). The next fraction which constitutes an appreciable portion of the oil, consists of *geraniol*[4]). This alcohol can be separated by treating this fraction with calcium chloride and decomposition of the purified calcium chloride geraniol with water. Further distillation yields an oil that consists of a mixture of esters of d-*citronellol* and geraniol. Citronellol (m. p. of the silver salt of the acid phthalate 125 to 126°) does not occur as such but as *acetate* and probably also as n-*butyrate*. Geraniol occurs as acetate[3]).

The highest boiling fractions contain *methyleugenol*[5]) which was identified by its oxidation to veratric acid (m. p. 179°) with potassium permanganate and by its conversion into methyl*iso*eugenol (m. p. of dibromide 102°).

If the highest boiling fractions referred to are shaken repeatedly with 70 p. c. alcohol in order to remove the methyleugenol and if the residual oil is redistilled, there finally result two fractions which consist chiefly of *sesquiterpenes*[6]). The lower boiling fraction of the two, which, however, was not perfectly free from oxygen, had the following properties: b. p. 157° (15 mm.); d_{15° 0,8643; $\alpha_D + 1^\circ 28'$; n_{D15° 1,51849. Under ordinary pressure this substance boiled between 270 and 280°, however, with considerable decomposition. When shaken with dilute permanganate solution in the cold, carbonic acid, oxalic acid and

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[1]) Report of Schimmel & Co. April 1912, 47.

[2]) *Ibidem* October 1899, 21.

[3]) *Ibidem* April 1912, 47.

[4]) *Ibidem* October 1893, 15.

[5]) *Ibidem* October 1898, 11; October 1899, 24.

[6]) *Ibidem* October 1899, 24.

a glycol-like substance, insoluble in water, resulted. The odor of the sesquiterpene is peculiar and reminds of cedarwood. Hydration with glacial acetic acid-sulphuric acid (0,1 p.c.) mixture yielded a product the saponification value of which was not higher than 43,6. Inasmuch as it appeared greatly resinified it did not invite further investigation. When exposed to the air for but a day, resinification took place and a syrupy liquid resulted that was not soluble in even 10 vols. of 95 p. c. alcohol.

The entire behavior and the low specific gravity of the sesquiterpene suggest an *aliphatic* sesquiterpene (see vol. I, p. 328).

From the higher fraction of the two, careful fractionation under diminished pressure yielded a *second sesquiterpene* with the following properties: b. p. 272 to 275° under 760 mm., 170 to 172° under 16 mm. pressure; d_{15° 0,912; $\alpha_D + 5^\circ 50'$. Owing to the slight difference in the boiling point, it was not possible to free this substance entirely from the light sesquiterpene.

Finally, it may be mentioned that Schimmel & Co. made an observation that seems to indicate the presence of *thujyl alcohol*. When the fraction rich in the substance with a linalool-like odor (see p. 227) was oxidized with chromic acid, there resulted, in addition to citral, a thujone-like substance that yielded a semicarbazone melting between 179 and 182°. (As to the melting point of the thujone semicarbazones, see vol. I, p. 463.) The attempt to oxidize fraction 202 to 210°, which had the odor of thujyl alcohol with permanganate to thujaketonic acid was unsuccessful[1]).

Properties. As to their physical properties, the oils of the two citronella grasses differ considerably from each other. The Ceylon citronella oil (Lena batu oil), which constitutes the bulk of the commercial oil, is a yellow to yellowish-brown liquid that is occasionally colored green by copper. Frequently oils that were brown originally become green upon exposure to the air. This change does not take place if the oil has previously been shaken with dilute acids[2]). The odor of the oil is peculiar and very persistent. Frequently it is characterized as being balmlike, but this comparison is not correct since balm has the odor of citral and not of citronellal, the principal bearer of the citro-

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[1]) Report of Schimmel & Co. April 1912, 47.

[2]) Umney, Pharmaceutical Journ. III. 21 (1891), 922.

nella odor. The specific gravity lies between 0,900 and 0,920 and only in exceptional cases does the density of pure oils drop as low as 0,898; $\alpha_D - 7$ to $-22°$; $n_{D20°}$ 1,479 to 1,494; the so-called total geraniol content (geraniol + citronellal[1])) of good oils is not below 57 p.c. With 1 to 2 vols. of 80 p.c. alcohol the oil yields a clear solution which remains clear upon the addition of more alcohol up to 10 vols., or shows a slight opalescence only. But even in the latter case oily drops never separate upon prolonged standing in stoppered containers.

Citronella oil is not characterized by a definite saponification value, since the citronellal is slowly decomposed by prolonged boiling with the alkali.

Examination. The quality of citronella oil is best ascertained by the quantitative determination of the acetylizable constituents, *viz.* geraniol, nerol, citronellol, borneol and citronellal which, for this purpose, are designated by the collective name of total geraniol. The value of the oil increases with the content of these constituents. The designation "total geraniol" as applied to citronella oil is naturally not quite correct. Not only do other alcohols enter into the reaction, but the citronellal is thereby converted quantitatively into *iso*pulegol acetate. Moreover, the original esters of the oil are included in the determination. Nevertheless this expression has become quite common and, for the sake of simplicity, may as well be retained in actual practice. The method of determination is given in detail in the first volume of this work (p. 578). Inasmuch, however, as comparable results of the so-called total geraniol depend so much on a rigid observation of details, the directions are herewith repeated.

A mixture of 10 cc. each of citronella oil and acetic acid anhydride, to which 2 g of fused sodium acetate and a few boiling chips have been added, are heated in an acetylation flask on a sandbath so as to maintain uniform boiling for 2 hours. Upon cooling some water is added to the contents of the flask and the latter heated in a water bath for $^1/_4$ hour with occasional shaking so as to hydrate the excess of acetic acid anhydride. The oil is then separated by means of a separating funnel and washed with water, or better still with a solution of sodium

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[1]) Comp. Report of Schimmel & Co. October 1912, 47.

chloride until the reaction is neutral. The acetylated oil is dried with anhydrous sodium sulphate, 1,5 to 2,0 g. of this dried oil are saponified with 20 cc. of half-normal potassium hydroxide, any traces of free acid having previously been carefully neutralized. The saponification should last at least one hour, the acetylation, however, 2 hours, for otherwise results are obtained that are from 1 to 5 p. c. too low or even more[1]). For similar reasons a longer period of acetylation should be avoided. This method has been tested by Schimmel & Co. in connection with mixtures of known geraniol and citronellal content.

For the separate determination of the primary alcohols referred to here as geraniol Schimmel & Co.[2]) have worked out a method that is based on the different behavior of geraniol and citronellal toward phthalic acid anhydride. Whereas the former readily reacts with phthalic acid anhydride forming acid esters, citronellal does not undergo a change. The method is carried out in the following manner: In an acetylizing flask about 2 g. of phthalic acid anhydride, 2 g. of the oil to be examined and 2 cc. of benzene are heated for 2 hours in a water bath. The reaction mixture, having been allowed to cool, is shaken with 60 cc. of aqueous half-normal potassium hydroxide solution for 10 minutes. For this purpose the flask is closed with a glass stopper. At the end of 10 minutes all of the acid anhydride is converted into neutral potassium phthalate and the acid geraniol ester into its potassium salt. The excess of alkali is now titrated back with half-normal sulphuric acid. If from the amount of alkali equivalent to the amount of phthalic acid anhydride used, the amount of alkali actually used is deducted, the difference is the equivalent of the geraniol that has combined with phthalic acid. From this the percentage of geraniol can be computed. When applied by Schimmel & Co. to several Ceylon oils, this method yielded between 29,6 and 34,4 p. c. geraniol.

Inasmuch as citronella oil contains several alcohols in addition to geraniol, partly free partly as ester, which react when the oil is acetylated but not when it is treated with phthalic acid

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[1]) Report of Schimmel & Co. April **1910**, 154. Comp. also A. W. K. de Jong, *Andropogon Nardus* Java. Teysmannia **1908**, 1.

[2]) Report of Schimmel & Co. October **1899**, 24. Comp. also *ibidem* October **1912**, 43.

anhydride, it becomes apparent that the citronellal content is not equal to the difference between the geraniol content and the so-called total geraniol content, but must be determined by a special method. For this purpose several methods have been proposed. Of these the method of J. Dupont and L. Labaune[1]) should first be mentioned. It depends on the conversion of the citronellal into its oxime, the subsequent acetylation of the oil and the determination of the ester value of the acetylated oil. When the oximated oil is heated with acetic acid anhydride, the citronelloxime is converted into citronellonitrile. This is stable toward alkali even when heated, hence upon saponification the amount of ester only is determined. The method is as follows: 10 g of citronella oil are first shaken with a hydroxylamine solution[2]) for 2 hours at ordinary temperature (15 to 18°). The oximated oil is dried and then acetylated. The ester number of the acetylated oil reveals the content of alcohol $C_{10}H_{18}O$. By subtracting this from the so-called total geraniol content the amount of citronellal is ascertained. Inasmuch as the molecular weights of citronellal (154) and citronella nitrile (151) are in close approximation, the change which the citronellal has undergone can be ignored in the computation.

Applying this "method of oximating" to Ceylon citronella oil, Dupont and Labaune found 17,2 p. c. of citronellal, Schimmel & Co.[3]) found 6,5 and 6,7 p. c. in two oils.

For the citronellal assay, C. Kleber[4]) suggests a method originally applied to the citral assay in lemon oil, according to which the aldehyde is allowed to react with phenylhydrazine. He suggests the following details: 5 g. of Ceylon oil or 2 g. of Java oil are weighed accurately in a flask, 20 cc. of a freshly prepared 5 p. c. alcoholic solution of phenylhydrazine are added,

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[1]) Report of Roure-Bertrand Fils April 1912, 3. The authors recommend their method for the direct determination of geraniol. As a matter of fact all of the alcohols contained in the citronella oil are included in the estimation. Hence the determination of the so-called total geraniol enables the analyst to inform himself with regard to the citronellal content.

[2]) Hydroxylamine solution: 10 g. of hydroxylamine hydrochloride and 12 g. of potassium carbonate are dissolved each in 25 g. of water, the solutions are mixed and filtered.

[3]) Report of Schimmel & Co. October 1912, 43.

[4]) Americ. Perfumer 6 (1912), 284; Report of Schimmel & Co. April 1912, 75.

the flask stoppered and set aside for about 1/2 hour at 35°. Then as much half-normal hydrogen chloride is added as is necessary for the neutralization of the phenylhydrazine solution used. This is previously ascertained with a blank. The mixture is transferred to a separating funnel, the flask rinsed with 20 cc. of water and the entire mixture shaken thoroughly. As soon as the two layers have separated, the lower layer is drawn off into an Erlenmeyer flask, the residue washed with 5 cc. of water and the total contents of the Erlenmeyer flask are titrated with half-normal sodium hydroxide. Ethyl orange is used as indicator, titration being stopped when the brownish color, which precedes the rose color, has been reached. Since each cc. of half-normal sodium hydroxide corresponds to 0,077 of citronellal, the citronellal content of the oil can be readily computed from the consumption of the soda solution.

Schimmel & Co. carry out the method somewhat differently: 1 g. of Ceylon oil or 0,5 g. of Java oil (weighed exactly) are mixed with 10 cc. of freshly prepared 2 p. c. alcoholic phenylhydrazine solution and set aside for 1 hour[1]) in a 50 cc. flask provided with a glass stopper. 20 cc. of tenth-normal hydrogen chloride are then added and the mixture gently shaken. 10 cc. of benzene[2]) having been added, the mixture is shaken thoroughly and transferred to a separating funnel. After having stood for a short time, the 30 cc. of acid liquid, which separate readily, are drawn off and filtered through a small filter.

20 cc. of this filtrate, to which 10 drops of ethyl orange (1:2000) have been added, are titrated with tenth-normal potassium hydroxide until a distinct yellow color is attained. From this result the amount of tenth-normal potassium hydroxide requisite for 30 cc. of filtrate is computed. In order to ascertain the strength of the phenylhydrazine solution, the same test is conducted on a blank. If for the actual experiment *a* cc. and for the blank *b* cc. of tenth normal potassium hydroxide

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[1]) According to the experience which Schimmel & Co. have thus far had with this method, it seems desirable to prolong the period of contact to 1 1/2 hrs. Report of Schimmel & Co. October 1912, 40.

[2]) The reason for shaking out with benzene is to clarify the solution which has become turbid upon the addition of hydrochloric acid. This enables a better observation of the changes in color when titrating.

are used, then the citronellal equivalent of the amount of oil used (5 grams) is equal to $a—b$ cc. tenth-normal potassium hydroxide. Since 1 cc. of tenth-normal potassium hydroxide corresponds to 0,0154 g of citronellal, the percentage of citronellal in the oil results from the following formula.

$$\frac{(a-b)\cdot 1{,}54}{s}$$

Kleber records a citronellal content of from 7 to 9 p. c. for Ceylon oil, Schimmel & Co. found 7,5 and 10 p. c.

The citronellal content of citronella oil can likewise be ascertained according to the method suggested by V. Boulez[1]). However, as pointed out by Schimmel & Co., this method is applicable, only when the aldehyde content is not too high. Hence it is applicable to the Ceylon oil only. In an Erlenmeyer flask 25 or 50 g. of oil are shaken with 100 or 200 g. of a bisulphite solution previously saturated with normal sulphite and the mixture set aside for 2 to 3 hours until all of the aldehyde has combined. 100 or 200 g. of water are then added, the flask connected with a reflux condenser, and the mixture heated in a water bath until a complete separation has taken place between the oily layer and the aldehyde sulphonate solution. The oil is separated by means of a separating funnel and weighed. The loss in weight represents the citronellal content of the original oil. By means of acetylation of the non-dissolved portion of the oil the alcohol content can be ascertained. This method is not applicable to Java oil since, in consequence of the high citronellal content, the amount of non-aldehyde oil dissolved in the bisulphite solution becomes so great as to yield results that are too high[2]).

In a Ceylon citronella oil Boulez found 18 p. c. of citronellal whereas Schimmel & Co. found only 6,0 and 7,0 p. c. in two oils. It is noteworthy that the results found by Dupont and Labaune, also by Boulez on the one hand, and those found by Schimmel & Co. on the other hand differ materially from each other.

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[1]) Bull. Soc. chim. IV. **11** (1912), 915. Report of Schimmel & Co. October **1912**, 44.

[2]) Report of Schimmel & Co. October **1912**, 45.

Whether these differences are due to the method or are due to the differences in the Ceylon citronella oil cannot be decided until the methods have been applied more extensively.

The formylation method as applied to citronellal (vol. I, p. 580) does not yield satisfactory results[1]), hence cannot be recommended.

Although the total geraniol assay leads to the best valuation of citronella oil, its application on the part of the non-expert is too difficult, hence it cannot be universally applied in commerce. For this reason the solubility test, which has come to be known as "Schimmel's Test"[2]) has become common. This test can be applied readily without special skill and is useful as a rapid test that throws light on the approximate nature of the oil. According to this test the oil is to be soluble in 1 to 2 vols. of 80 p. c. alcohol at 20°. The solution should remain clear when the amount of alcohol is increased to 10 vols. or should at most become slightly opalescent, but never separate oil even after standing for several hous. While adding the alcohol, violent shaking should be avoided, for otherwise such oil as has not gone into solution may be so finely suspended that a separation takes place only after prolonged standing, thus interfering with the observation.

This test is directed primarily against adulteration with fatty oils or petroleum, both of which are insoluble in 80 p. c. alcohol. In the case of citronella oil, petroleum has been a favorite adulterant.

Citronella oil adulterated with fatty oil does not form a clear solution with 80 p. c. alcohol. Adulterated with petroleum, the oil mostly yields a clear solution with 1 to 2 parts of 80 p. c. alcohol, but this solution becomes turbid upon the addition of more solvent. Moreover, fatty oil is apt to settle to the bottom, whereas petroleum rises to the surface. The exact proof of such adulteration is described on pp. 613 and 614 of the first volume.

For the detection of smaller amounts of petroleum, the presence of which is not revealed by the test just described,

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[1]) Report of Schimmel & Co. October 1912, 43.

[2]) Bericht von Schimmel & Co. October 1889, 22. Report April 1896, 16.

Schimmel & Co.[1]) have recommended their modified, more rigid Schimmel's test. This consists in adding 5 p. c. of Russian or American[2]) petroleum to the oil and subsequently testing it with 80 p. c. alcohol. Even when thus modified, pure citronella oil yields a clear solution with 1 to 2 vols. of 80 p. c. alcohol which remains clear also when the amount of solvent is increased to 10 vol. At most the solution reveals a slight opalescence but should not separate oily drops upon standing.

Naturally, this sort of test affords but a general criterion as to the quality of an oil and leaves much to be desired. However, it has the advantage of being readily performed and may be expected to continue in practice in spite of the enemies it has made. Up to the present time at least, it has not been possible to replace this test by one equally simple and better. An attempt in this direction was made several years ago by M. K. Bamber[3]). He published directions for a test for which it was not only claimed that it was better than Schimmel's test, but also afforded the means of ascertaining the amount of adulterant insoluble in alcohol. The technique of the test known as "Bamber's Test" is as follows:

In a glass cylinder provided with the necessary graduation, a mixture of 2 cc. of pure, acid-free cocoanut oil and 2 cc. of citronella oil is shaken for a minute with 20 cc. of alcohol of 83 p. c. by weight ($d_{15^\circ}^{30^\circ}$ 0,8273) at 29 to 30°. It is then centrifuged for $^1/_2$ to 1 minute. According to Bamber, pure citronella oil is completely dissolved in the alcohol, wheras the cocoanut oil remains behind quantitatively. If the citronella oil contains an adulterant insoluble in alcohol, this likewise is separated. Hence the volume for the cocoanut oil is increased and from the increase the amount of adulterant becomes apparent.

Schimmel & Co.[4]) have tested this method as to its practicability and have found that, whereas it may render good service for the qualitative testing of citronella oil, it fails as a quantitative test. Moreover it becomes apparent that unadulterated oils do not always comply with this test. This certainly is a

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[1]) Report of Schimmel & Co. April **1904**, 29; April **1910**, 40.

[2]) *Ibidem* April **1911**, 47.

[3]) Proceed. chem. Soc. **19** (1903), 292.

[4]) Report of Schimmel & Co. April **1904**, 29.

disadvantage. It should be added further that Bamber's test demands greater exactness on the part of the operator than does Schimmel's test and that the apparatus is more complex. As a result, Bamber's test has not been generally adopted.

Adulterations. As already pointed out, Ceylon citronella oil is adulterated principally with fatty oil and petroleum. Occasionally an oil is met with to which alcohol has been added. The addition of alcohol is indicated by a lowering of the specific gravity and can be shown by the reduction in volume when shaken with water. Inasmuch as alcohol is included in the geraniol assay when the oil is acetylated, its presence causes the total geraniol content to be seemingly increased. The true total geraniol content is ascertained only when the oil has been shaken repeatedly with water before it is acetylated. Details for the detection of alcohol will be found on p. 612 of the first volume of this treatise. The terpenes from lemon oil have also been observed as adulterant¹).

130. Java Citronella Oil.

Cultivation. The necessary information concerning the botanical origin of the Javanese citronella grass has already been recorded on p. 217. Its cultivation has been discussed by S. Smith²) who had visited one of the large plantations. If the grass has been planted on good fertile soil and if rain has been abundant, it will grow rapidly and yield a good harvest. Cut four times, the yield is about 4,8 tons per acre. Assuming an oil content of 0,5 p. c., 10 acres will yield 4,8 cwt. of oil at a value of £ 46 16 s. After a period of 12 years the grass must be replanted.

As in the case of lemongrass³), de Jong⁴) studied the oil content of Java citronella grass *(Sereh wangi)* in the different stages of growth in order to ascertain the best time for the

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¹) Report of Schimmel & Co. October 1905, 20.

²) Agricultural News 5, 335; Kew. Bull. 1906, 363; Report of Schimmel & Co. April 1907, 29.

³) See p. 204.

⁴) Teysmannia 1908; Report of Schimmel & Co. April 1909, 36.

distillation of the oil. The result was the same as with lemon grass: the oil content diminishes with the age of the leaf; the sheaths and roots contain much less oil than do the leaves. In this instance also, de Jong regards as the best time for cutting when four to five leaves have developed. Noteworthy is the higher oil content of the citronella grass as compared with lemongrass, three to four times as much oil being obtained throughout. So far as the properties of the oils, obtained from leaves differing in age, are concerned, the angle of rotation as well as the total geraniol content revealed but slight differences. The optical rotation varies without regularity: values of $-2° 7'$ to $-7° 36'$ were observed for oils from leaves of different age. Passing from the youngest to the oldest leaf, an increase of the total geraniol content is first noticeable, later a reverse: the lowest value observed was 85,5 p. c., the highest 93,3 p. c. The oils examined by de Jong were soluble in three parts of 80 p. c. alcohol. The addition of more than four parts of solvent caused turbidity.

According to A. J. Ultée[1]), a various of oil grasses, but particularly citronella grass, have been cultivated in the Botanical Garden of Salatiga (Southeast of Buitenzorg, Java). Inasmuch as Salatiga is located at a much higher altitude than is Buitenzorg, it seemed desirable to Ultée to ascertain whether this difference in altitude has any effect on the composition of the oil. Upon distillation he obtained 0,66 p. c. of an almost colorless oil which possessed the following constants: $d_{29°}$ 0,8721; $\alpha_D - 3° 15'$; total geraniol 92,75 p. c.; soluble in 1,5 vols. and more of 80 p. c. alcohol. This oil differed principally from the Buitenzorg oils by a better solubility. According to de Jong, the latter yielded a clear solution only with three parts of 80 p. c. alcohol, which became turbid again upon the addition of more than four parts of solvent. Inasmuch as Ultée had obtained only 0,66 p. c. of oil whereas the yield in Buitenzorg ranged from 0,5 to 0,9 p. c., experiments were made in Salatiga to ascertain whether the oil content could be increased by fertilizing. Of four experimental fields, three were supplied with different mixtures of artificial

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[1]) Cultuurgids, Orgaan van het Algemeen-Proefstation op Java **11** (1909), 404; Report of Schimmel & Co. April **1910**, 41.

fertilizer. At the end of 10 weeks the grass was cut and equal amounts from each field distilled in like manner. The yields obtained varied between 0,6 and 0,65 p. c. thus showing that the oil content is not influenced by fertilizers.

The Report of the Royal Botanical Gardens of Ceylon for 1904 contains an interesting communication[1] regarding the experimental cultivation of the *Maha pangiri* variety of citronella grass. From a one acre field, planted in 1902, the following amounts were harvested:

in March 1904	10809 $^{1}/_{4}$ lbs.	Yield of oil abt. 48 lbs.
„ August 1904	8511 „	„ „ „ „ 36 „
Total 1904	19320 $^{1}/_{4}$ lbs.	Yield of oil abt. 84 lbs.

Hence 1 lb. of pure citronella oil was obtained from an average of 230 lbs. of grass. Another field yielded 16038 lbs. of grass per acre within 6 months, which in turn yielded 60 lbs. of oil. A third field, planted in June, yielded in December 9765 lbs. of fresh grass per acre which in turn yielded 49 $^{1}/_{2}$ lbs. of oil.

Production. In connection with a trip in the Malay peninsula, made by Carle[2] at the request of the "Directeur de l'Agriculture en Cochinchine" he also made a report on the cultivation of citronella grass *(Maha pangiri)* and the production of the oil in the district of Johore. The equipment described by Carle was arranged in a shed built on the steep slope of a hill. A boiler that had the capacity to run a 20 horse power engine, furnished the steam for both the still and the pump that supplied the water for condensation. The outfit included two stills each of which had a capacity of 150 kg. of citronella grass. The condenser consisted of a box with a capacity of 2 cbm., the inside of which was lined with zinc. It contained a condensing tube, the lower end of which projected from the side over a Florentine flask which received the oil. Both stills were operated at the same time. The distillation of 300 kg. citronella grass, which lasts about 2 hours, yields about 2 kg. oil = 0,67 p. c. It is estimated that

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[1] Report of Schimmel & Co. October **1905**, 18.

[2] Bulletin de la Chambre d'Agriculture de la Cochinchine **10** (1907), September number, p. 18; Report of Schimmel & Co. April **1908**, 32.

Fig. 30.

Citronella grass Plantation and Distillery in Java.

1 hectare yields annually about 25,000 to 30,000 kg. of citronella grass which, in turn, yields 180 to 200 l of oil. At a price of 3 frs. pro kg., the gross income amounts to from 500 to 600 frs. Deducting 350 to 380 frs. for expenses, 150 to 200 frs. remain as net profit.

Another, somewhat larger distillery within the neighborhood of Singapore was likewise visited by Carle[1]). The plant was arranged similarly to that in Johore. Of stills there were 16 arranged in two batteries, one of which was used exclusively for the distillation of citronella oil, the other for the distillation of patchouli oil. A boiler, sufficient to run a 30 horse power engine, supplied the steam necessary for the alternate operation of the one or other battery, and to run the pump which supplied the condensation water. The capacity of the stills was the same as in Johore. The distillation of a charge of 150 kg. also lasted 2 hours. The average yield of citronella oil amounts to 0,65 to 0,7 p. c. The very fertile soil admits of five cuttings annually and yields about 40000 kg. citronella grass (280 l citronella oil). The cost of cultivation and operation amounts to about 500 frs., hence the net profits are as high as 340 frs.

Composition. The composition of Java citronella oil is similar to that of the Ceylon oil. The principal constituents, *citronellal, geraniol* and *citronellol,* are the same in both[2]). However, the percentage of these constituents, so important in perfumery, is greater in the Java oil. Hence it possesses a much more intensive odor than does the Ceylon oil. The citronellol of the Java oil is the dextrogyrate modification[3]). The *methyleugenol*[4]) content of the Java oil is very low, amounting to less than 1 p.c., whereas the Ceylon oil contains more than 8 p.c. *citral*[5]) (m. p. of naphthocinchoninic acid 197 to 198°) is also a constituent of the Java citronella oil, being present to the extent of

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[1]) Bulletin de la Chambre d'Agriculture de la Cochinchine **10** (1907), September number, p. 36; Report of Schimmel & Co. April **1908**, 32.

[2]) Report of Schimmel & Co. April **1900**, 12.

[3]) *Ibidem* April **1902**, 21.

[4]) *Ibidem* April **1900**, 13.

[5]) *Ibidem* April **1910**, 29.

about 0,2 p. c. Whether the hydrocarbons of the two oils are the same has not yet been ascertained.

According to J. Dupont and L. Labaune[1]), *iso*amyl alcohol and *iso*valeric aldehyde are contained in Java citronella oil, but the investigators do not report the methods of identification employed.

Properties. The Java or Singapore citronella oil is characterized by a much finer odor and hence constitutes the more valuable commercial article. It is colorless to slightly yellow, has a specific gravity of 0,885 to 0,901 at 15°, and reveals a slight lævorotation, as a rule not exceeding 3°. In recent years slight dextrorotation (α_D up to $+1^\circ 47'$ has also been observed but in very exceptional cases only[2])). The index of refraction n_{D20° fluctuates between 1,465 and 1,472. The oil forms a clear solution with 1 to 2 vols. and more of 80 p. c. alcohol. Rarely does opalescence set in upon dilution.

The amount of acetylizable constituents (socalled total geraniol) is much greater than in Ceylon citronella oil, being not less than 85 p. c. in good oils. In order to enable proper comparison, the acetylation must be conducted under like conditions as described under Ceylon citronella oil (p. 229). The separate determination of geraniol and citral can be carried out as with the Ceylon oil. Using the phthalic acid anhydride method, Schimmel & Co.[3]) found 26,6 to 38,2 p. c. of geraniol in several Java citronella oils. In an oil containing 83,8 p. c. of total geraniol and 26,6 p. c. geraniol, the phenylhydrazine method yielded, according to the length of the reaction period, 36,4 and 41,3 p. c. of citronellal whereas the oxime method yielded 46,6 and 43,5 p. c.[4]). The formylation method, applied to several other oils yielded 23 to 35 p. c. which results, however, may be regarded as too low.

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[1]) Berichte von Roure-Bertrand Fils April 1912, 8.

[2]) Report of Schimmel & Co. April 1908, 32. — Jaarb. dep. landb. in Ned.-Indië, Batavia 1907, 67.

[3]) Report of Schimmel & Co. April 1900, 12; October 1912, 43.

[4]) *Ibidem* October 1912, 47.

131. Citronella Oils from different Sources.

It is but natural that the commercial importance of a citronella oil has led to numerous attempts at the cultivation of citronella grass. Judging from the properties of the oils obtained, these experiments have been made principally with the *Maha Pengiri* grass.

In the first place reference may here be had to the experiments made in the German colonies in the South Sea, more particularly in German New Guinea. As becomes apparent from the examination of two samples by Schimmel & Co., the oils there distilled resemble the Java citronella oil: $d_{15°}$ 0,8819; α_D — 0° 46′; $n_{D20°}$ 1,46278; total geraniol content 85,9 p. c.; and $d_{15°}$ 0,8964; α_D — 1° 20′; total geraniol content 78 p. c. These favorable results, it is reported, have already lead to the production of oil on a large scale[1]), but commerce has not yet taken cognisance thereof.

Another oil, the equal of Java oil, is being distilled in the Malay peninsula. It is described by B. J. Eaton[2]). It was faintly yellow in color and dissolved in 1 vol. and more of 80 p. c. alcohol. $d_{15,5°}$ 0,8890. The total geraniol content amounted to 82,4 p. c. of which 27,7 p. c. was geraniol and 54,7 p. c. (?) citronellal.

The same holds true of an oil obtained from Jamaica. It had the following properties: $d_{15°}$ 0,8947; α_D — 4° 16′; $n_{D20°}$ 1,47098; total geraniol 86,4 p. c.; soluble in 1,2 vol. and more of 80 p. c. alcohol, the diluted solution showing slight opalescence upon standing.

According to the Imperial Institute in London[3]) attempts at the cultivation of Ceylon citronella grass have been made since 1903 in the Seychelles. An oil equal to the Ceylon oil has been obtained. A trial distillation yielded 0,39 p. c.: $d_{15°}$ 0,910; α_D — 12° 49′.

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[1]) P. Preuß, Berichte d. deutsch. pharm. Ges. **19** (1909), 25.

[2]) Agric. Bull. of the Straits and Fed. Malay States **1909**, No. 4, p. 142; Chemist and Druggist **75** (1909), 21.

[3]) Bull. Imp. Inst. **6** (1908), 109.

132. Mana-grass Oil.

Origin. According to O. Stapf[1]), mana-grass is in all probability the mother plant of the citronella-grass. There are two varieties, the *Cymbopogon Nardus* var. *Linnæi (typicus)* and *C. Nardus* var. *confertiflorus.* The native of Ceylon makes further distinctions, all of which have been referred by Stapf to the two varieties mentioned. However, the oils of these two grasses have no peculiar characteristics. Both vary irregularly in yield and in properties, which differences are probably due to differences in cultivation, fertilization, and the season in which the oils are distilled.

Production. In Bandarawela, Ceylon, J. F. Jowitt[1]) has made experiments as to the cultivation and distillation of both varieties. The oils obtained were examined in the Imperial Institute, London, by S. S. Pickles[1]). The yield fluctuated between 0,06 and 0,45 p.c., the grasses distilled in May giving a specially low yield, those distilled in subsequent months mostly higher yields.

Properties. 1. Oil from *C. Nardus* var. *Linnæi:* d_{15° 0,894 to 0,926; $\alpha_D + 4^\circ 54'$ to $-6^\circ 32'$; total geraniol 43,5 to 64,7 p.c. 2. Oil from *C. Nardus* var. *confertiflorus:* d_{15° 0,900 to 0,929; $\alpha_D + 12^\circ 12'$ to $-2^\circ 11'$; total geraniol 39,1 to 64,2 p.c.

These oils were light to dark yellow in color. With few exceptions their odor was agreeably citronella-like, but mostly somewhat pungent. With 1 to 1,4 vol. of 80 p.c. alcohol they yielded clear solutions, which became more or less distinctly opalescent upon the addition of 10 vols. of solvent. In two cases a light turbidity resulted, but in one case only the solution remained clear upon dilution. In addition to the "total geraniol" content, that of geraniol alone was determined separately according to the phthalic acid anhydride method. These determinations revealed fluctuations as great as were observed in the other properties of the two grass oils.

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[1]) J. F. Jowitt, Cymbopogon Grass Oils in Ceylon. Circulars and Agricultural Journal of the Royal Botanic Gardens, Ceylon. 5 (1910), No. 12, p. 115. Comp. also S. S. Pickles, Bull. Imp. Inst. 8 (1910), 144.

133. Java "lemon olie".

For the sake of completeness, reference may here be made to an oil of which samples have repeatedly been sent to Schimmel & Co.[1]) under the designation of *"Java lemon olie."* As to its botanical origin nothing could be ascertained. However, the plant yielding the oil appears to be a species of *Andropogon,* presumably a wild mana-grass (see above), for the oils seemed to resemble citronella oil though their odor was somewhat different. The constants observed were within the following limits: d_{15° 0,8809 to 0,8914; $\alpha_D + 10^\circ 6'$ to $+ 14^\circ 52'$; n_{D20° 1,46466 to 1,46684; total geraniol 49,1 to 50,9 p.c. The oils were readily soluble in 80 p.c. alcohol (abt. 1 vol.), but upon dilution the solution invariably became turbid.

Of special interest is the occurrence of l-*citronellal* which thus far has not been observed in any other volatile oil. The aldehyde, separated from an oil with bisulphite solution, had the following properties: b.p. 205 to 208°; d_{15° 0,8567; $\alpha_D - 3^\circ$; n_{D20° 1,44791; m.p. of semicarbazone 74°. Other constituents are *cineol* and probably *limonene* or a mixture of limonene and *dipentene.*

134. Camel-grass Oil.

Origin. Camel-grass, *Cymbopogon Schœnanthus,* Spreng. (*Andropogon Schœnanthus,* L.; *A. laniger,* Desf.; *A. Iwarancusa* subsp. *laniger,* Hook. f.)[2]), has been known since early times and has found numerous applications for medicinal and cosmetic purposes. In the older pharmacopœias and herbals it is mentioned as *Herba Schœnanthi.* However, other names were also used, such as *Juncus odoratus* and *Fœnum*[3]) or *Palea camelorum.* The common Arabic name is Izkhir. As a characteristic desert plant that can get along with a minimum of water, it occurs throughout North Africa and Arabia. It also occurs in the Persian province Kirman, where it is met with at altitudes of 2000 m. and more, furthermore in southwest Afghanistan and

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[1]) Report of Schimmel & Co. April **1903**, 22.

[2]) O. Stapf, Kew Bull. **1906**, 303.

[3]) Flückiger and Hanbury, Pharmacographia II. Edit., p. 728.

northwest Beluchistan as far as the Punjab. In the desert it is the principal food for camels. Upon distillation of the dried grass, as sold in the Indian bazaars, Dymock[1]) obtained 1 p.c. of oil.

Properties and Composition. Dymock observed the sp. gr. of 0,905 at 29,5° and an optical rotation of $\alpha_D - 4°$. Schimmel & Co.[2]) observed the sp. gr. of 0,915 at 15° and an angle of rotation $\alpha_D + 34° 38'$. The odor of camel-grass reminds one of that of elemi oil, an observation readily explained by the presence of *phellandrene*[2]). When distilled, the oil passes over between 170 and 250°.

135. Delft-grass Oil.

Delft-grass, *Cymbopogon polyneuros,* Stapf (*Andropogon polyneuros,* Steud.; *A. versicolor,* Nees; *A. Schœnanthus* var. *versicolor,* Hack.; *A. nardoides β minor,* Nees ex Steud.)[3]), which is characterized by its anise- or fennel-like odor, occurs in the southwestern part of India proper, more particularly in the Nilgiris where it replaces *C. Martini.* It also occurs in Ceylon, mostly at higher altitudes (up to 1500 m.); furthermore in the island of Delft in Adam's Straits, hence the name "Delft-grass". It constitutes a good fodder for horses. The oil was first distilled in 1902 in Ootakamund with a yield of 0,25 p.c. According to a report from the Imperial Institute[4]) four samples of oil were distilled later by Jowitt in Bandarawela, Ceylon, from this species of grass. The yields varied from 0,20 to 0,34. The properties of these oils were determined by S. S. Pickles, of London. The distillates had a yellowish to reddish-brown color and a peculiar sweetish odor, very different from that of citronella and lemongrass oils: $d_{15°}$ 0,936 to 0,951; $\alpha_D + 30° 53'$ to $+ 55° 15'$. Each of the four oils was soluble in 1 vol. of 80 p.c. alcohol, but the solutions became opalescent upon the addition of 10 vols. The amount of acetylizable constituents (total geraniol) varied from 38,7 to 51,8 p.c. computed as $C_{10}H_{18}O$, but no tests

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[1]) Dymock, Warden and Hooper, Pharmacographia indica, Part VI, p. 564.

[2]) Report of Schimmel & Co. April 1892, 59.

[3]) O. Stapf, Kew Bull. 1906, 345.

[4]) Bull. Imp. Inst. 8 (1910), 144; 10 (1912), 30.

were made as to whether the oils contained alcohols or not. Further statements concerning the composition of the oils are wanting.

136. Oil of Cymbopogon coloratus.

Cymbopogon coloratus, Stapf (*Andropogon coloratus,* Nees; *A. Nardus* var. *coloratus,* Hook. f.), occurs in the Tinnevelly district to the Anamalai mountains, also in the province of Karnatik (Madras Presidency). It belongs to the lemongrasses of the Malabar districts. It differs from *C. flexuosus* by being much smaller[1]).

In the Fiji islands an oil has been distilled from this grass[2]), the yield of which was not ascertained. It had the odor of a mixture of lemongrass oil and Java citronella oil. Its density was 0,920. It contained 42 p.c. of constituents that reacted with bisulphite, also 15 p.c. of geraniol. It yielded a clear solution with 70 p.c. alcohol. In the Fiji islands this oil is known as "lemongrass oil." Somewhat later[3]) three other distillates were described. All had an odor reminding one simultaneously of citronella and lemongrass oils. The color varied from golden yellow to brown, the rectified oil was lighter in color. Further investigation of the crude oils led to the following results: d_{15° 0,9155 to 0,920; $\alpha_D - 7°43'$ to $-8°40'$; geraniol 15,6 p.c.; citronellal 45,7 to 49,5 p.c.; constituents reacting with bisulphite 42,0 to 43,5 p.c. With 1 vol. of 80 p.c. alcohol, the oils yielded clear solutions; in 70 p.c. alcohol they were either insoluble or the 1:3 clear solution became turbid upon the addition of more alcohol. The rectified oil showed like solubility and was further characterized by the following constants: d_{15° 0,9111; $\alpha_D - 10°42'$; constituents reacting with bisulphite 42 p.c.

137. Oil of Cymbopogon cæsius.

Kamakshi grass[4]) derived from *Cymbopogon cæsius,* Stapf (*Andropogon cæsius, α* et *β,* Nees; *A. Schœnanthus* var. *cæsius,*

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[1]) O. Stapf, Kew Bull. **1906**, 321.

[2]) Bull. Imp. Inst. **8** (1910), 145.

[3]) *Ibidem* **10** (1912), 27.

[4]) O. Stapf, Kew Bull. **1906**, 341.

Hack.), is closely related to *C. Martini* yet differs distinctly from the latter. Only where both species grow side by side hybrids may be found. *C. cæsius* grows over the larger part of the Karnatik where it is rather common. In the southeast of India proper it replaces *C. Martini.*

A note regarding this oil is found in the Administration Report of the Government Botanic Gardens and Parks, the Nilgiris, for 1901, p. 5. The grass subjected to distillation was obtained from Arni, in the northern Arcot district, Madras Presidency, where it occurs abundantly. The yield of oil from the freshly cut grass in December amounted to 0,431 p.c. Another lot of dried grass which was distilled in April yielded 0,711 p.c. of oil. The properties of the oil are not recorded.

138. Oil of Cymbopogon sennaarensis.

From the Soudan the Imperial Institute in London received an oil said to be derived from *Cymbopogon Iwarancusa*[1]). A more careful investigation revealed the source to be *Cymbopogon sennaarensis,* Chiov.[2]). The herb, with a pennyroyal-like odor, yielded upon distillation 1,005 p.c. of an oil of the following properties: d_{15° 0,9383; $\alpha_{D20^\circ} + 34^\circ 14'$; total alcohols 17,3 p.c.; 26 to 27 p.c. of the constituents reacted with sodium bisulphite. The principal constituent of the oil is a ketone which resembles pulegone as to odor and other properties. It also contains a strongly dextrogyrate terpene and other high boiling constituents.

139. Oil of Andropogon odoratus.

Andropogon odoratus, Lisb.[3]), a grass which is used as a domestic remedy by the natives of the coast of western India, yields upon distillation as much oil as does the palmarosa-grass.

Properties. According to Dymock[4]), the oil has a sherry color, a specific gravity of 0,931 at 31° and an optical rotation of $\alpha_D - 22,75^\circ$.

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[1]) Bull. Imp. Inst. **8** (1910), 145.

[2]) *Ibidem* **10** (1912), 31.

[3]) O. Stapf, Kew Bull. **1906**, 349.

[4]) Dymock, Warden and Hooper, Pharmacographia indica, Part VI, p. 571.

An oil distilled from fresh grass had an odor resembling that of pine needle oil, specific gravity 0,915 and an optical rotation of $-23^\circ 10'$[1]).

An oil distilled in Java, probably from *Andropogon odoratus* (author's name not given), was obtained with a yield of 0,35 p.c.: d_{26° 0,914; $\alpha_D - 31^\circ 10'$[2]).

140. Oil of Andropogon Schœnanthus subspec. nervatus.

From the *"Kolonialwirtschaftliches Komitee"* in Berlin, Schimmel & Co.[3]), received a small lot of grass obtained from the Sudan, which Dr. Giessler, Custodian at the Botanical Institute in Leipzig, recognized as *Andropogon Schœnanthus* subspec. *nervatus,* Hack. From it 1,9 p.c. of a brownish oil were obtained which showed some similarity with the common gingergrass oils but which could not compete with them because of its faint odor. Its constants were as follows: d_{15° 0,9405; $\alpha_D + 26^\circ 22'$; n_{D20° 1,49469; A. V. 4,6; E. V. 9,3; E. V. after acetylation 99,1; soluble in 0,5 and more vol. of 80 p.c. alcohol. From the diluted solution paraffin separated.

141. Oil of Andropogon intermedius.

In the Botanical Institute at Buitenzorg[4]) an oil was distilled from *Andropogon intermedius* (R. Br.?) which had a specific gravity of 0,889 (26°) and an optical rotation of $\alpha_D - 21^\circ 52'$.

Another sample, distilled at the same place[5]) (yield 0,03 p.c.), had a specific gravity d_{26° 0,919; $\alpha_D - 15^\circ 30'$.

142. Andropogon Oils of unknown species.

An oil obtained from an *Andropogon* species cultivated in the Botanical Garden of Buitenzorg (Java) has been examined by Schimmel & Co.[6]). As to appearance and odor it resembled

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[1]) Report of Schimmel & Co. April **1892**, 59.

[2]) Jaarb. dep. landb. in Ned.-Indië, Batavia **1910**, 49.

[3]) Report of Schimmel & Co. April **1911**, 19; October **1911**, 20.

[4]) Jaarb. dep. landb. in Ned.-Indië, Batavia **1907**, 67.

[5]) *Ibidem* **1910**, 48.

[6]) Report of Schimmel & Co. October **1908**, 72.

palmarosa oil, but had a much lower geraniol content: d_{15° 0,9411; α_D — 3° 16′; A. V. 1,9; E. V. 24,9; E. V. after acetylation 144,5 corresponding to 44,6 p.c. of total geraniol. In alcohol the oil was but imperfectly soluble: the clear solution obtained with 2,3 vols. of 70 p.c. alcohol became turbid upon the addition of more solvent; even with 90 p.c. alcohol the dilute solution was turbid. This poor solubility as well as the very high specific gravity are probably attributable to resinification, for the oil rectified with water vapor formed a clear solution with 1 vol. and more of 70 p.c. alcohol.

Apparently the oil mentioned in the annual report of Buitenzorg for 1906, p. 46, was obtained from the same species of *Andropogon:* d_{20° 0,991 (!); α_{D26° — 2° 50′; S. V. 18,7; S. V. after acetylation 157.

Schimmel & Co.[1]) have examined a second oil from Buitenzorg which was obtained from a new, also unknown species of *Andropogon,* probably from the same plant mentioned in the report[2]) of the botanical institute there. The oil was light yellow in color. Its odor was peculiar, reminding one simultaneously of fatty aldehydes and geraniol or methylheptenone: d_{15° 0,9961; α_D — 2°; n_{D20° 1,51236; A. V. 3,6; E. V. 7,3; soluble in 1 vol. of 80 p.c. alcohol, the solution becoming turbid upon the addition of 3 vol. and more of solvent. The oil reacted with sodium bisulphite. Decomposed with soda solution, the addition product yielded a fatty aldehyde, which is possibly identical with decylic aldehyde, but which could not be further investigated as the amount of oil was too small.

143. Mumuta Oil.

From Samoa, Schimmel & Co.[3]) obtained the tuberous roots of the mumuta grass, an *Andropogon* species, from which they obtained upon steam distillation 1,05 p.c. of a brown volatile oil, the odor of which reminded one of vetiver oil. Its constants

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[1]) Report of Schimmel & Co. April 1909, 19.

[2]) Footnote 4, p. 248.

[3]) Report of Schimmel & Co. October 1908, 136. Comp. also O. Thiele, Chem. Ztg. 31 (1907), 629.

were: d_{15° 0,9845; $\alpha_D + 41^\circ 50'$; n_{D20° 1,51505; A.V. 0,9; E.V. 13,8; E.V. after acetylation 65,2; insoluble in 10 vols. of 80 p.c. alcohol; soluble in 1 vol. and more of 85 p.c. alcohol and in all proportions in 90 p.c. alcohol.

Family: PALMÆ.

144. Oil of Saw Palmetto.

Origin. Oil of saw palmetto is obtained from the berries of *Sabal serrulata,* R. et Sch., which grows in the southern United States, more particularly in Florida. Apparently it was first obtained by C. C. Sherrard[1]) from the chloroform extract with a yield of 0,54 p.c., and Coblentz[2]) obtained it by steam distillation in 1895. However, J. U. Lloyd[3]) had obtained considerable quantities as early as 1890.

Production. The oil is obtained by distillation from the fresh berries with a yield of about 1,2 p.c. Dry berries yield no oil[4]). It can also be obtained by expression of the fruits. The oil collects on the surface of the juice and is readily separated. (P. L. Sherman and C. H. Briggs)[5]).

Properties. The odor of the distilled oil is at first pleasant, but later it becomes disagreeable. The oil obtained by Lloyd in 1890 had a specific gravity in 1900 of 0,8682 at 20°. After distillation under reduced pressure it had the following properties: b. p. 60 to 170° (18 mm.); $d\frac{20^\circ}{20^\circ}$ 0,8679; n_{D20° 1,41233; $\alpha_D \pm 0^\circ$. (Schreiner)[4]).

Two oils (d 0,8651 and 0,8775), separated from the expressed juice, yielded upon distillation with water vapor 4 to 5 p.c. of a brownish colored oil with a density of 0,8650 and 0,8653 respectively.

Composition. Sherman and Briggs[6]) examined an oil which had been obtained by expression of berries preserved in alcohol.

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[1]) Proceed. Americ. Pharm. Ass. **42** (1894), 312.

[2]) Proceed. New Jersey Pharm. Ass. **1895**, 63.

[3]) Private communication to Prof. Kremers.

[4]) O. Schreiner, Pharm. Review **18** (1900), 220.

[5]) Pharmaceutical Archives **2** (1899), 101.

[6]) *Loc. cit.*

It boiled between 70 and 270° (16 mm.) and consisted to the extent of 63 p.c. of free fatty acids (*capronic, caprylic, caprinic, lauric, palmitic* and *oleic* acids) and of about 37 p.c. of the *ethyl esters* of these acids. The oil from the pulp of the berries contained no glycerides. These as well as stearic acid were found in the oil obtained from the seeds. The fruity odor of the oil is due to the esters.

Inasmuch as the saw palmetto oil contains considerable free acids, the assumption seems plausible that the ethyl esters are formed while the berries are stored in alcohol[1]). This assumption is supported by the observation that dry berries contain no volatile oil.

145. Volatile Cocoa-nut Oil.

Origin and Production. In order to render palatable the crude expressed cocoa nut oil of *Cocos nucifera*, L. (family *Palmæ*) it must be deprived of its malodorous constituents, principally fatty acids, and treated with high tension steam. In addition to fatty oil carried over mechanically, the distillate contains a disagreeably smelling volatile oil which has been examined by A. Haller and A. Lassieur[2]).

Properties. In a 200 mm. tube the oil deviated $+0°28'$. It contained 0,7 p.c. acids computed as capronic acid, and 12 p.c. alcohols, computed as methylnonyl carbinol, also traces of an aldehyde.

Composition. By treatment with phthalic acid anhydride, the alcohols were separated from the other constituents. This alcohol mixture yielded two fractions: (I) b. p. 190 to 195°, and (II) b. p. 228 to 233°.

Fraction I is a liquid with a strong odor and the following properties: $d_{4°}^{25°}$ 0,823; $\alpha_D + 2°$; $n_{D21°}$ 1,4249; mol. refr. 44,8, computed for $C_9H_{20}O$ 45,0. The analyses likewise agreed with the formula $C_9H_{20}O$. Upon oxidation with chromic acid mixture, methylheptyl ketone resulted. Hence the alcohol was d-*methylheptyl carbinol*, $CH_3CH(OH)C_7H_{15}$, the optical antipode of which

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[1]) Schreiner, *loc. cit.*

[2]) Compt. rend. **150** (1910), 1013; **151** (1910), 697.

occurs in oil of rue. The differences in the degree of rotation (methylheptyl carbinol from oil of rue deviates — 7° 28′) are probably due to inversion caused by the treatment with phthalic acid anhydride.

Fraction II contained an alcohol of the following properties: $d_{4°}^{23°}$ 0,827; $\alpha_D + 1° 10'$; $n_{D23°}$ 1,4336; mol. refr. 54,1, computed for $C_{11}H_{24}O$ 54,2. The analyses suggested the formula $C_{11}H_{24}O$. Upon oxidation with chromic acid mixture a ketone (m. p. of semicarbazone 120 to 122°) was obtained. Hence the alcohol $C_{11}H_{24}O$ is d-*methylnonyl carbinol,* $CH_3CH(OH)C_9H_{19}$, and the semicarbazone, methylnonyl ketone semicarbazone. Of this alcohol the optical antipode ($\alpha_D - 6° 12'$) likewise occurs in oil of rue.

Of non-alcoholic constituents the following were identified: *methylheptyl ketone* (m. p. of semicarbazone 119 to 120°), *methyl*-n-*nonyl ketone* (m. p. of oxime 44 to 45°, of semicarbazone 122°), and *methylundecyl ketone.* Regenerated from its semicarbazone (m. p. 121 to 122°), the latter-named body constitutes a white mass melting at 29°. Its properties agree well with those of the synthetic product (m. p. 28°; b. p. 263°)¹).

Haller and Lassieur are of the opinion that the ketones and alcohols found in the volatile oil of the cocoanut result from the action of an enzyme on an unknown substance.

Family: ARACEÆ.

146. Calamus Oil.

Oleum Calami. — Calmusöl. — Essence de Calamus (acore).

Origin and Production. The root of *Acorus Calamus,* L. (family *Araceæ*), which occurs well-nigh throughout Europe, Asia and North America, contains cells, both in the outer tissues of the bark and in the basal tissues of the interior part, which are filled with a volatile oil.

Upon steam distillation the fresh root which contains 70 to 75 p. c. of water, yields about 0,8 p. c., the unpeeled dry root about 1,5 to 3,5 p. c. of volatile oil. Calamus peels (the root

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¹) Krafft, Berl. Berichte **12** (1879), 1667.

bark) as well as the peeled root afford, when dried and distilled by themselves, smaller yields than the unpeeled dried root. This is due to the fact that the thin strips resulting from peeling lose more volatile oil because of volatilization and resinification than does the entire root. A calamus oil of inferior quality and deviating somewhat from the ordinary in its properties is distilled in Galicia.

Composition. In the earlier days of chemical investigations, calamus oil was examined repeatedly but without much success[1]). A. Kurbatow[2]) established the presence of 5 p. c. of a terpene which boiled between 158 and 159° and yielded with dry hydrogen chloride a compound melting at 63°. It may be assumed that the terpene is pinene, although the hydrochloride of this melts at 125°.

The higher boiling portions of this oil have been examined by H. Thoms and R. Beckstrœm[3]). The principal material used by them consisted of a fraction 272 to 340°: d_{20° 1,0254; α_D —0,34°. When treated with a 2 p. c. soda solution, n-*heptylic acid* (m. p. of amide 96°), *palmitic acid* (m. p. 32°) and an unsaturated acid were isolated; when shaken with a 2 p. c. potassium hydroxide solution, *eugenol* (m. p. of benzoyleugenol 70,5 to 71°) was isolated.

The oil was then shaken with bisulphite solution, from which a liquid with a characteristic calamus-like odor was isolated. Upon standing there crystallized long needles of *asarylic aldehyde* (m. p. 114°; m. p. of oxime 137°) or 2,4,5-trimethoxybenzaldehyde.

The free acids, phenols and aldehydes having been removed, the oil was saponified. In the saponification liquid *palmitic* and *acetic acids* were found. After fractionation of the oil a substance $C_{15}H_{26}O_2$ melting at 128° crystallized out. It is identical

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[1]) T. Martius, Liebig's Annalen 4 (1832), 264 and 266. — Schnedermann, *ibidem* 41 (1842), 374. — J. H. Gladstone, Journ. chem. Soc. 17 (1864), 1 ff.; Jahrb. f. Chem. 1863, 546, 547.

[2]) Berl. Berichte 6 (1873), 1210. — Liebig's Annalen 173 (1874), 4. The older references should be accepted with caution. Some of them, *e. g.* that of Gladstone *(loc. cit.)*, refer to adulterated oils.

[3]) Berl. Berichte 34 (1901), 1021; 35 (1902), 3187. — Berichte d. deutsch. pharm. Ges. 12 (1902), 257.

with the *calamus camphor* previously found by Schimmel & Co.[1]) and also by H. von Soden and W. Rojahn[2]), in calamus oil. Thoms and Beckstrœm designate this substance *calameone.*

Calameone constitutes shiny crystals of the bisphenoid (rhombic-hemihedric) class of the rhombic system; $[\alpha]_{D26^\circ} - 8{,}94^\circ$ in 5,04 p.c. alcoholic solution. When acted upon by bromine, calameone yields derivatives $C_{15}H_{21}Br$, $C_{15}H_{20}Br_2$ and $C_{15}H_{18}Br_4$. With hydrogen chloride it yields an addition product melting at 119°. Its benzoate melts at 155°. When heated with 50 p.c. sulphuric acid, calameone yields a hydrocarbon $C_{15}H_{22}$, *calamene.* When treated with bromine, this yields a compound $C_{15}H_{21}Br$; with hydrogen chloride a chlorhydrate melting at 108°; when oxidized with permanganate an acid melting at 196° in addition to acetic and oxalic acids.

When oxidized with potassium permanganate at ordinary temperature calameone is oxidized to calameonic acid, a monobasic acid $C_{15}H_{24}O_4 + H_2O$ which contains a molecule of water of crystallization and melts at 153°. Heated to its melting point, it becomes anhydrous and then melts at 138°.

Inasmuch as calameone is neither an alcohol, aldehyde, ketone, acid, nor a phenol ether, its oxygen atom must be combined with two carbon atoms within a cycle. Hence its constitution is analogous to cineol.

From the mother-liquor of the crystals, Thoms and Beckstrœm obtained considerable amounts of a second, well crystallizable constituent which melted at 61° and revealed itself as *asarone.*

The constitution of calameone led to the supposition that, like cineol, it might combine with phosphoric or arsenic acids. This, however, proved not to be the case. When fraction 150 to 155° (10 mm.) was treated with a 90 p.c. arsenic acid, Thoms and Beckstrœm obtained a white, plastic mass. This proved to be an arsenic compound which, when treated with water, yielded a substance melting at 173 to 184° and which, judging by elementary analysis and molecular weight determination, must be regarded as a polymer of asarone. By way of control, the same substance with like properties was obtained by the action of

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[1]) Report of Schimmel & Co. October 1899, 8.

[2]) Pharm. Ztg. 46 (1901), 243.

90 p.c. arsenic acid on pure asarone. This compound, designated *parasarone,* is not oxidizable to asarylic aldehyde. Distilled in a vacuum, it is largely reconverted into asarone.

In addition to the substances enumerated, calamus oil contains two hydrocarbons $C_{15}H_{24}$. The one obtained from the middle fraction boils at 146° (19 mm.), has a sp. gr. d_{18° 0,9330 and is dextrogyrate, $[\alpha]_{D18^\circ} + 34{,}83^\circ$. The hydrocarbon from the higher fractions (b.p. 151° under 22 mm.; d_{12° 0,9336) is lævogyrate, $[\alpha]_{D22^\circ} - 13{,}38^\circ$. Solid derivatives of these hydrocarbons have not been obtained thus far but only liquid chlorhydrogen addition products.

According to Kurbatow[1]), a sesquiterpene $C_{15}H_{24}$ (d_{14°0,932) is contained in fraction 250 to 255° which, after having been treated with sodium boils at 255 to 258° and does not combine with hydrogen chloride. At a still higher temperature a blue fraction distils over[2]).

Properties. Calamus oil is a somewhat viscid oil of yellowish to brownish-yellow color with a camphor-like, aromatic odor, and a corresponding bitter, burning, spicy taste. d_{15° 0,959 to 0,970; $\alpha_D + 9$ to $+ 31^\circ$; n_{D20° 1,5028 to 1,5078; A. V. up to 2,5; S. V. 6 to 20; E. V. after acetylation 32 to 50; methyl value (2 determinations)[3]) 15,3 to 16. In 90 p.c. alcohol calamus oil is miscible in well-nigh all proportions. In dilute alcohol, however, it does not dissolve readily. Of 80 p.c. alcohol 15 vols. are required, of 50 p.c. alcohol about 1000 vols. to produce a clear solution.

Japanese Calamus Oil. According to the investigations of Y. Asahina[4]) the Japanese calamus plant appears to be identical with the European *Acorus Calamus,* L. According to Holmes[5]), however, it is not impossible that the Japanese plant may be *Acorus spurius,* Schott, which occurs commonly in Japan and the rhizome of which differs but little from that of *Acorus Calamus,* L. The yield of oil amounts to as much as 5 p.c.

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[1]) *Loc. cit.*

[2]) Flückiger, Pharmakognosie. 1891, p. 352.

[3]) R. Beckstrœm, Berichte d. deutsch. pharm. Ges. 12 (1902), 266.

[4]) Apotheker Ztg. 21 (1906), 987.

[5]) Pharmaceutical Journ. III. 10 (1879), 102.

The properties of the Japanese oil are: d_{15° 0,973 to 0,992; $\alpha_D + 7^\circ 20'$ to $+ 25^\circ 20'$; soluble in 1 vol. of 90 p.c. alcohol, in 6 to 10 vols. of 80 p.c. and in about 500 vols. of 50 p.c. alcohol[1]). S.V. up to 3,9; E.V. after acetylation 17,0 (1 determination); methoxyl content 9,3 p.c. (1 determination)[2]).

According to Asahina[2]), the bulk of the oil distils over between 250 and 280°. A careful investigation revealed the absence of a terpene $C_{10}H_{16}$. The presence of *methyleugenol* was ascertained since the principal fraction yielded veratric acid upon oxidation. Inasmuch as the fraction was strongly optically active, and contained much more carbon than the formula of methyleugenol calls for, and since the oil assumed a green color upon the addition of acetic acid and sulphuric acid, Asahina infers the presence of a sesquiterpene.

Javanese Calamus Oil. A calamus oil distilled by Dr. Carthaus in Java has been examined at the Botanical Institute at Buitenzorg[3]). It gave the following constants; d_{26° 1,06; $\alpha_D + 0^\circ 52'$; S. V. 9.

Two similar oils from the same source have been described by Schimmel & Co.[4]). The constants of the one were: d_{15° 1,0783; $\alpha_D + 0^\circ 53'$; n_{D20° 1,55043; E. V. 12; those of the other d_{15° 1,0771; $\alpha_D + 0^\circ 51'$; n_{D20° 1,55065. From the common calamus oil these oils differ by their higher specific gravity, their lower rotation and their larger index of refraction. The Javanese oils were soluble in 1 to 1,5 vol. of 70 p.c. alcohol with the separation of small amounts of paraffin.

147. Oil of Calamus Herb.

The fresh green parts of *Acorus Calamus,* L. yield upon distillation with water an oil closely resembling that from the root: d_{15° 0,964; $\alpha_D + 20^\circ 44'$[5]).

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[1]) Schimmel's Bericht April 1889, 7.

[2]) Apotheker Ztg. 21 (1906), 987.

[3]) Jaarb. dep. landb. in Ned.-Indië, Batavia 1907, 67.

[4]) Report of Schimmel & Co. April 1909, 22.

[5]) *Ibidem* April 1897, Table in the appendix p. 6.

Family: LILIACEÆ.

148. Sabadilla Seed Oil.

The volatile oil of sabadilla seed[1]) is obtained by distillation of either the comminuted seed of *Sabadilla officinalis,* Br. *(Schœnocaulon officinale,* A. Gray, family *Liliaceæ)* or of the benzin extract of the fat which results as a by-product in the manufacture of veratrine. The yield from fresh seeds amounts to about 0,32 p. c., from old seeds that have been stored for a long time it is much less. The specific gravity of the oil lies between 0,902 and 0,928. Upon distillation most of the oil passes over between 190 and 250°, however, the esters present undergo considerable decomposition.

After saponification, the bulk of the oil distills between 220 and 250°; $[\alpha]_j - 9°10'$. From the saponification liquor *hydroxymyristic acid,* $C_{14}H_{28}O_3$, m. p. 51°, and *veratric acid,* $C_9H_{10}O_4$, m. p. 179 to 180°, were obtained. Presumably these acids are present in the original oil as methyl and ethyl esters. In addition some of the lower aliphatic aldehydes were found.

149. Oil of Aloe.

The aloe plant owes its faint but characteristic odor to a very small amount of volatile oil.

Upon the distillation of 500 lbs. of Barbadoes aloes (from *Aloe vulgaris,* Lam.; *A. barbadensis,* Mill.; *A. vera,* L., family *Liliaceæ*), T. & H. Smith & Co., London, obtained 2 fld. dr. of aloe oil. It is a light yellow, mobile liquid, sp. gr. 0,863, and boils between 266 and 271°[2]).

150. Xanthorrhœa Resin Oil.

Upon distillation of the Australian yellow xanthorrhœa resin (acaroid resin, or yellow grass tree gum) from *Xanthorrhœa hastilis,* R. Br. (family *Liliaceæ*) Schimmel & Co.[3]) obtained

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[1]) E. Opitz, Arch. der Pharm. **229** (1891), 265.

[2]) Pharmaceutical Journ. III. **10** (1880), 613.

[3]) Report of Schimmel & Co. October **1897**, 60.

0,37 p. c. of a yellow oil with a storax-like odor: $d_{15°}$ 0,937; α_D —3° 14′; S. V. 4,9; E. V. 69,4. The free acid was isolated by shaking with dilute sodium hydroxide solution and identified as *cinnamic acid* by means of its melting point, 133°. From the saponification liquor, cinnamic acid was likewise separated to a fairly considerable extent, for 200 g. of oil yielded about 40 g. of cinnamic acid recrystallized from water.

The saponified oil boiled between 145 and 240°. From the lower distillates a fraction 145 to 150° with the properties of *styrene* was obtained (m. p. of styrene dibromide 74 to 75°).

From the red acaroid resin, which is obtained from *Xanthorrhœa australis,* R. Br. and several other species of *Xanthorrhœa,* 0,33 p. c. of a reddish-brown oil were obtained[1]) that had a pleasant odor reminding of tolu and Peru balsams: $d_{20°}$ 0,9600; α_D inactive; S. V. 47,6; E. V. 37,5. It contained *cinnamic acid,* free as well as ester, also *styrene.*

151. Garlic Oil.

Upon distillation of the entire garlic plant, *Allium sativum,* L., (family *Liliaceæ*) 0,005 to 0,009 p. c. of a volatile oil[2]) are obtained. It has a yellow color and possesses an intense, very unpleasant garlic odor: $d_{15°}$ 1,046 to 1,057; α_D inactive.

As the result of a chemical investigation made in 1844, T. Wertheim[3]) arrived at the conclusion that garlic oil consists principally of allyl sulphide $(C_8H_5)_2S$. For nearly 50 years this was the prevailing opinion and without re-examination it found its way into all of the text books.

When Semmler[4]) in 1892 re-examined the oil, it was found that garlic oil does not contain a trace of allyl sulphide[5]). In addition to carbon and hydrogen, the analysis of the oil revealed

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[1]) H. Hænsel, Chem. Zentralbl. **1908**, I. 1837.

[2]) Schimmel's Bericht October **1889**, 52; Report of Schimmel & Co. October **1890**, 33.

[3]) Liebig's Annalen **51** (1844), 289.

[4]) Arch. der Pharm. **230** (1892), 434.

[5]) This also disposes of the statement that other oils, such as the oils of *Thlaspi arvense,* L. and *Alliaria officinalis,* L. contain garlic oil or allylsulphide.

the presence of sulphur[1]), whereas oxygen and nitrogen were wanting.

Inasmuch as the oil is decomposed by distillation under ordinary pressure it had to be distilled under diminished pressure. Under 16 mm. pressure it distilled over between 65 and 125°. Semmler isolated the following substances:

1. A *disulphide* $C_6H_{12}S_2$ (abt. 6 p.c.) which boils between 66 and 69° under 16 mm. pressure, and which presumably is an *allyl-propyl disulphide,* $C_3H_5S \cdot SC_3H_7$;
2. A *disulphide* $C_6H_{10}S_2$ (60 p.c.) constitutes the bulk of the oil and is the bearer of the pure garlic odor. B. p. 79 to 81° (16 mm.); $d_{14,8°}$ 1,0237. Its constitution is probably $C_3H_5S \cdot SC_3H_5$;
3. A substance $C_6H_{10}S_3$ (20 p.c.). B. p. 112 to 122° (16 mm.); $d_{15°}$ 1,0845; constitutional formula $C_3H_5 \cdot S \cdot S \cdot S \cdot C_3H_5$.

The distillation residue reveals an even higher sulphur content and probably has the composition $C_6H_{10}S_4$.

Inasmuch as allyl sulphide boils at 36 to 38° under 15,5 mm. pressure, and since the lowest fraction of garlic oil boils at 60 to 65°, the presence of allyl sulphide in the oil is excluded.

Neither was there a sesquiterpene in the oil examined by Semmler[2]).

152. Onion Oil.

The common onion, *Allium Cepa,* L., owes its pungent, persistent odor to a volatile oil which, when distilled from the entire plant, is obtained with a yield of 0,046 p. c.[3]).

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[1]) An interesting compilation of the occurrence of sulphur-containing oils of the vegetable kingdom has been published by C. Hartwich (Apotheker Ztg. 17 [1902], 339). This list not only includes the oils in which the presence of sulphur has been proved but also those the garlic-like odor of which leads to the supposition of its presence.

[2]) According to Parry (The chemistry of essential oils. London 2nd ed. 1903, p. 191) the statement in the Jahresber. d. Chem. 1876, 398 that Beckett and Wright [Journ. chem. Soc. 1 (1876), 1] found a sesquiterpene in garlic oil is due to an error in translation, since oil of cloves was translated as *"Knoblauchöl"* (oil of garlic).

[3]) Schimmel's Bericht April 1889, 44.

It is dark brown in color and rather viscid. $d_{8,7^\circ}$ 1,0410[1]), or d_{19° 1,036[2]); $\alpha_D - 5^\circ$.

An oil obtained by H. Hænsel[3]) from common onions (0,015 p. c.) was concrete; d_{35° 0,9960; $\alpha_D - 3^\circ 40'$; soluble with difficulty in ordinary solvents.

Oil of onion[4]) is decomposed when distilled under ordinary pressure; under 10 mm. pressure it passes over almost completely between 64 and 125°.

According to Semmler[1]), the principal constituent is a disulphide $C_6H_{12}S_2$ (b. p. 75 to 83° under 10 mm.; d_{12° 1,0234), which upon reduction with zinc dust is changed to a substance $C_6H_{12}S$ (b. p. 130°). Nascent hydrogen reduces it to the disulphide $C_6H_{14}S_2$ (b. p. 68 to 69° under 10 mm.).

Onion oil also contains a higher sulphide with the same radicles which zinc dust reduces to $C_6H_{12}S$. Finally, the oil contains still another sulphur-containing substance which, probably is identical with one of the higher boiling constituents of asafetida oil.

Neither allyl sulphide nor terpenes are contained in oil of onion any more than in garlic oil.

153. Oil of Allium ursinum.

All parts of *Allium ursinum,* L. (Ger. *Bärlauch*), leaves, flowers and bulb have a most penetrating, garlic-like odor.

Upon distillation of the entire plant, 0,007 p. c. of a strongly refractory oil of dark-brown color was obtained. Its odor, which somewhat resembles that of garlic, is yet quite different therefrom. The taste is burning and pungent; d_{18° 1,015.

The oil distils over almost completely between 95 and 106°. According to Semmler[5]), it consists principally of *vinyl sulphide*

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[1]) Semmler, Arch. der Pharm. **230** (1892), 443.

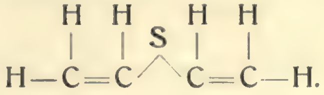
[2]) Schimmel's Bericht April 1889, 44.

[3]) Apotheker Ztg. **18** (1903), 268.

[4]) In the freshly expressed juice, W. D. Kooper (Zeitschr. Untersuch. d. Nahrungs- u. Genußm. **19** [1910], 569) found *hydrogen sulphocyanide* and *allylthiocyanate.* The presence of formaldehyde, acetaldehyde or acrolein could not be detected.

[5]) Liebig's Annalen **241** (1887), 90.

$(C_2H_3)_2S$ (b. p. 101°; d 0,9125). The constitution of *vinyl sulphide* is expressed by the following structural formula



In addition, this oil contains polysulphides of vinyl, also a very small amount of a mercaptan, and an aldehyde that has not been further investigated.

154. Oil of Hyacinth.

A volatile oil has been prepared by Spalteholz[1]), of Haarlem, from the hyacinth *(Hyacinthus orientalis,* L., family *Liliaceæ).* Immediately after picking, the flowers were transferred to zinc containers and brought into contact for a few minutes with benzene, which had been purified by freezing. The benzene was drawn off and the flowers washed a second time with the solvent, 381 kg. of flowers being treated in this way with 200 *l.* of benzene. Under diminished pressure the solution was concentrated to 2 *l.* at a temperature of 30°. The fats and waxes were then precipitated with dilute alcohol, the solution filtered and concentrated still further in vacuo. The resulting oil (60,5 g. = 0,016 p.c.) as such, had a disagreeable and pungent odor and only after considerable dilution did it develop the natural hyacinth odor.

Spalteholz identified *hydrogen sulphide* in the aqueous solution of potassium hydroxide with which the oil had been shaken. 10 g. of this oil were turned over to Enklaar for a chemical examination for which he used 7,7 g. He first removed fatty oil and resin from the crude product by exposing the petroleum ether solution thereof to —20°. Thus he obtained 3,6 g. of a pure oil which, upon distillation under 10 mm. pressure, was resolved into three fractions: I. b. p. up to 90° 0,6 g.; II. 92 to 94° 1,3 g.; III. 94 to 150° 1,7 g.

Fraction I contained a very volatile substance with an unpleasant odor, that was not farther investigated. In fraction II Enklaar found a hitherto unknown substance which consisted of carbon, hydrogen and oxygen, and which revealed the following constants: b. p. 205 to 206° (760 mm.), 92 to 94° (10 mm.);

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[1]) C. J. Enklaar, Chem. Weekblad 7 (1910), 1.

d_{15° 0,907; $\alpha_D + 1^\circ 52'$; n_{D16° 1,4914. Fraction III contained *benzyl benzoate* and probably *benzyl alcohol,* also *cinnamic alcohol* as ester. The benzoic acid, regenerated from the alkaline saponification liquor, possessed a distinct odor of *vanillin.* In addition, this fraction contained a nitrogen-free basic substance which fluoresced, had a narcotic odor and was colored red by acids and yellow by alkalies. As to its properties it reminded one of oxonium compounds. The presence of anthranilic acid methyl ester and methylanthranilic acid ester could not be proved; for, when heating with trinitrobenzene, which forms difficultly soluble addition products with these substances, only a reddish coloration resulted.

The hyacinth wax crystallizes from alcohol in colorless laminæ which persistently retain the odor of the flowers.

155. Oil of Asparagus Root.

From the dry roots of asparagus, *Asparagus officinalis,* L. (family *Liliaceæ*), H. Hænsel[1]) obtained 0,0108 p. c. of a dark brown oil of an intensely acid odor. d_{23° 0,8777; A.V. 33; E.V. 68. It contained *palmitic acid.*

156. Lily of the Valley Leaf Oil.

Upon distillation with water vapor, the leaves of *Convallaria majalis,* L. (family *Liliaceæ*), yield 0,058 p. c. of a greenish-brown oil which has a pleasant odor[2]) and melts at 40,5°. It begins to boil at 120°. After expressing the liquid, white shiny crystals that melt at 61°, and have the composition $C_{20}H_4O_5$ (?) are obtained.

Family: AMARYLLIDACEÆ.

157. Oil of Buphane disticha.

According to F. Tutin[3]), the alcoholic extract of the bulb of *Buphane disticha,* Herb., a South African *Amaryllidacea,* yields a small amount of volatile oil containing *furfurol,* and an acid with the odor of valerian.

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[1]) Chem. Zentralbl. **1909**, II. 1557.

[2]) H. Hænsel, Chem. Zentralbl. **1901**, II. 419.

[3]) Journ. chem. Soc. **99** (1911), 1241.

158. Tuberose Oil.

Origin and Production. The fragrant flowers of *Polianthes tuberosa,* L. (family *Amaryllidaceæ*), which is native to Central America and which is cultivated extensively in southern France[1]), yield upon distillation no essential oil but a product of an unpleasant odor. In order to obtain the perfume as completely as possible, it is necessary to apply the enfleurage process (see vol. I, p. 258) which has been used in southern France for a long time. According to A. Hesse[2]), to whom we are indebted for very interesting comparative experiments, 1000 kg. of tuberose blossoms yielded 801 g. of volatile oil to the fat used in the enfleurage process. The flowers removed from the fat yielded, upon extraction and subsequent distillation with steam, an additional 78 g. of oil. The direct extraction (see vol. I, p. 247) of the same amount of flowers yielded only 56 g., and at the beginning of the flower harvest only 36 g. of oil. To this, however, there should be added 10 g. of oil obtained from subsequent distillation of the extracted flowers. Hence enfleurage yields 13 times as much oil as the extraction method. It may be assumed, therefore, that during the period of enfleurage the tuberose blossoms develop 12 times the amount of volatile oil originally contained in the flowers.

Properties. The oil obtained by Hesse from tuberose flowers by means of the extraction method with petroleum ether had the following properties: d_{15° 1,007; $\alpha_D - 3^\circ 45'$; A.V. 22; S.V. 224; it contained 1,13 p.c. of anthranilic acid methyl ester. An oil obtained from the enfleurage fat, that had been obtained at different times, revealed the following properties: d_{15° 1,009 to 1,035; α_D (1 determination) $-2^\circ 30'$; A.V. (1 determination) 32,7; S.V. 243 to 280; methyl anthranilate content 3,2 to 5,4 p.c. The oil referred to above obtained by extraction and steam distillation of the waste flowers of the enfleurage process, showed the following constants: d_{15° 1,043; $\alpha_D - 3^\circ 21'$; S.V. 225,4; methyl anthranilate content 2 p.c.

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[1]) Comp. L. Mazuyer, *Production et culture de Tubéreuse.* Journ. Parfum. et Savonn. 21 (1908), 195.

[2]) Berl. Berichte 36 (1903), 1459.

Composition. The oil from the flowers of tuberose was first examined by A. Verley[1]). He isolated from the oil about 10 p. c. of a substance which he designated *tuberone,* and which he supposed to be a ketone of the formula $C_{13}H_{20}O$. Schimmel & Co.[2]) tried in vain to isolate a ketone from the corresponding fraction of an oil obtained from a floral extract *(Essence concrète).* Upon oxidation of this oil which, because of its fluorescence, was supposed to contain anthranilic acid methyl ester with permanganate, a readily volatile oil remained unattacked. Upon saponification this yielded benzoic acid (m. p. 122°; analysis of silver salt), hence it was regarded as methylbenzoate.

Hesse[3]), who worked with larger amounts, succeeded in definitely demonstrating the presence of *methyl anthranilate,* and isolated the stable ester of benzoic acid by oxidation with potassium permanganate solution.

The mixture of esters not attacked by the potassium permanganate distilled between 199 and 240°. Upon saponification benzoic acid and benzyl alcohol could be isolated. Hence a part of the ester mixture may be regarded as *benzyl benzoate.* The presence of methyl benzoate, which Schimmel & Co. suspected in this mixture, is questioned by Hesse who is of the opinion that, if it is present at all, the quantity is infinitesimal.

Nevertheless it is remarkable that the mixture of esters resulting upon oxidation is relatively so volatile. Hesse records the boiling temperature of the first half of the mixture as from below 199 to 240°, and that of the other half as above 240°. The boiling point of benzyl benzoate, however, is 324°. It follows that lower boiling esters must be present and therefore the presence of *methylbenzoate* (b. p. 199 to 200°) is not at all improbable.

Moreover by treating the oil with phthalic anhydride, Hesse isolated an alcohol which, judging from its boiling temperature, *viz.,* 206 to 214°, and its other constants consists chiefly of *benzyl alcohol.* Hence this alcohol also occurs in the free state in the oil of tuberose flowers.

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[1]) Bull. Soc. chim. III. 21 (1899), 307.

[2]) Report of Schimmel & Co. April 1903, 74.

[3]) *Loc. cit.*

In the oil from the pomade, Hesse demonstrated the occurrence of *methyl salicylate* which could not be detected in the oil obtained by extraction.

Family: IRIDACEÆ.

159. Saffron Oil.

Upon distillation with water in a current of carbon dioxide, R. Kayser[1]) obtained from saffron, the stigmata of *Crocus sativus*, L. (family *Iridaceæ*), a small amount of a limpid oil which possessed a faintly yellow color and an intense saffron odor. It absorbed oxygen from the air very readily, becoming viscid and brownish in color. Elementary analysis yielded figures corresponding with the terpene formula $C_{10}H_{16}$.

The same oil resulted when the aqueous solution of the bitter principle of saffron, picrocrocin, was heated. Kayser assumes that in this case the picrocrocin is hydrolyzed to crocose and saffron terpene.

$$\underset{\text{Picrocrocin}}{C_{38}H_{66}O_{17}} + \underset{\text{Water}}{H_2O} = \underset{\text{Crocose}}{3C_6H_{12}O_6} + \underset{\text{Terpene}}{2C_{10}H_{16}}$$

According to A. Hilger[2]), scarcely any volatile oil is obtained when saffron is distilled with water vapor. Only after the addition of sulphuric acid is such an oil obtained. The pigment of saffron is thereby decomposed into glucose and volatile oil. The latter consists of terpene and a substance $C_{10}H_{18}O$. In the low boiling fractions *pinene* and *cineol* were found.

160. Oil of Orris.

Oleum Iridis. — Irisöl. — Essence d'Iris concrète. Beurre de Violettes.

Origin and Production. Of the genus *Iris* (Ger. *Schwertlilie*), belonging to the family *Iridaceæ*, three species contain a fragrant

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[1]) Berl. Berichte **17** (1884), 2228.

[2]) Chem. Ztg. **23** (1899), 854; Chem. Zentralbl. **1900**, II. 576. For the older literature on crocus oil see: Dehne, Crell's Chem. Journ. **3** (1780), 11. — Aschoff, Berl. Jahrb. **1818**, 51. — Henry, Journ. de Pharm. **7** (1821), 400. — B. Quadrat, Journ. f. prakt. Chem. **56** (1852), 68. — B. Weiss, *ibidem* **101** (1867), 65. — W. W. Stoddart, Pharmaceutical Journ. III. **7** (1876), 238.

volatile oil in their rhizomes, *viz., Iris germanica,* L., *Iris pallida,* Lam. and *Iris florentina,* L.

For commercial purposes, the first two species[1]), are more particularly cultivated, principally in the province of Florence. The cultivation is carried on chiefly in the municipalities Greve, Dicomano, Pelago, Regello, Bagno a Ripoli, Pontassieve, Galluzzo, S. Casciano in Val di Pesa and Montespertoli. The very best root is cultivated in the villages S. Polo and Castellina belonging to the municipality of Greve. Cultivations to no mean extent have also developed in provinces bordering upon that of Florence, *viz.* in Arezzo, Castelfranco di Sopra and Lore Ciuffenna, all in the province of Arezzo; in Grosseto in the province of like name; in Faenza, province of Ravenna; and in Terni, province of Perugia. As to quality, the product of these provinces corresponds to that of Florence.

Iris is planted on hills or the slopes of hills, never in the valley, mostly in open, sunny spaces in the woods, or in narrow strips between vineyards, and rarely in extensive fields. It flourishes particularly in stony, very dry soil[2]). As a rule the root is harvested after three years. However, when prices are high, it is frequently cut after 2 years. The freshly cut rhizomes are first placed in water in order to facilitate the removal of the skin. They are then spread out on terraces and dried, a process requiring about a fortnight. When dry, the rhizomes are turned in a lathe to the so-called "orris root" (Ger. *Veilchenwurzeln*) which are given to children when teething. Rosaries are also made therefrom in large numbers. Orris powder is used in the making of sachets. The unsightly rhizomes, fragments and waste from peeling and cutting, enter commerce as crude material for the distillation of orris oil.

The principal places of export of Italian or Florentine orris root are Leghorn, Verona, and Trieste.

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[1]) According to H. Blin (Parfum. moderne **3** [1910], 13) the variety "Clio" of *Iris pallida* is principally cultivated.

[2]) For a more detailed account on the cultivation see U. Somma, Staz. sperim. agrar. ital. **34** (1901), 417. — G. L. Mazuyer, Americ. Perfumer **6** (1911), 31. — Daily Consular and Trade Report June 1st 1911; Report of Schimmel & Co. October **1911**, 65.

For the purpose of distillation the Florentine drug is used almost exclusively. Of inferior quality and but rarely used for distillation is the Veronese drug derived from *Iris germanica.* Still poorer is the Moroccan or Mogador orris root, which also is obtained from *Iris germanica.* It is darker in color and has but a faint odor. In order to impart a lighter color to the root, it is occasionally bleached with sulphurous acid, thus rendering it unfit for the distillation of the volatile oil.

Now and then Indian roots have¹) entered the London market. Their inferior quality was probably due to improper methods of collecting and treatment. Hence they have so far been found unfit for purposes of distillation.

Upon steam distillation, orris root yields but 0,1 to 0,2 p.c. of volatile oil. The distillation is tedious and difficult because of the strong frothing, largely due to the high starch content of the root. In order to facilitate the distillation, the addition of sulphuric acid has been recommended, whereby the orris starch is partly converted into sugar. This process, however, has not come into general use since it impairs the odor of the oil.

Composition. The bulk of the oil of orris, about 85 p.c. thereof, consists of the completely odorless *myristic acid*²). The substance which imparts to it the violet-like odor is the *irone,* a ketone of the formula $C_{13}H_{20}O$³). In addition to these two substances the oil contains very small amounts of *myristic acid methyl ester,* and of *oleic acid* and its esters.

In order to obtain the irone from the orris oil, the myristic acid, according to Tiemann and Krüger³), is first removed by means of dilute potassium hydroxide. This solution is shaken out with ether and the ether extract distilled with water vapor.

In the residue there remains iregenin, iridic acid, and esters of myristic and oleic acid, whereas myristic acid methyl ester, oleic acid and one of its esters together with irone distil over.

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¹) Report of Schimmel & Co. October **1896**, 55.

²) F. A. Flückiger, Arch. der Pharm. **208** (1876), 481. Of the older references compare Vogel, Journ. de Pharm. III. **1** (1815), 483, Trommsdorff's Journ. der Pharm. **24**, II. (1815), 64, Dumas, Journ. de Pharm. II. **21** (1835), 191 and Liebig's Annalen **15** (1835), 158.

³) Berl. Berichte **26** (1893), 2675.

During the second steam distillation of the first distillate the irone passes over first, and can thus be separated to a certain extent from the other constituents.

For the purpose of rectification the irone is converted into its phenylhydrazone by means of phenylhydrazine, and regenerated by means of sulphuric acid. In order to obtain an entirely pure irone, the crystalline irone oxime is prepared and this again decomposed with dilute acid.

According to Tiemann and Krüger, irone has the specific gravity of 0,939 at 20°; it boils at 144° (16 mm.); and in a 100 mm. tube it deviates the ray of polarized light about 40° to the right. In water it is wellnigh insoluble, but readily soluble in alcohol, ether, chloroform, benzene and ligroin. For its constitution, constants and derivatives see vol. I, p. 469.

The odor of irone is pungent, and in the concentrated condition apparently totally different from that of the violet. However, the violet-like odor becomes very distinct when the irone is dissolved in a large amount of alcohol, and the alcohol allowed to evaporate.

An investigation undertaken in the laboratory of Schimmel & Co.[1]) was made primarily with reference to the constituents of orris oil which are more volatile than irone, i. e. to the malodorous first distillate which is removed in the preparation of the liquid orris oil. The oil used (about 100 g.) passed over between 40 and 92° (5 mm.). It was of a golden-yellow color and had an unpleasant basic odor reminding one somewhat of *skatol*. Fraction 160 to 170°, obtained after repeated fractionation, contained *furfurol* (red coloration with solution of aniline hydrochloride in aniline). Both odor and other properties of the next higher fraction, b. p. 171 to 173°, indicated the presence of a *terpene* which, however, could not be further characterized (d_{15° 0,8611; $\alpha_D + 10^\circ 40'$).

When fraction 45 to 46° (10 mm.) was treated with bisulphite solution, there resulted a solid compound. Upon decomposition this yielded an aldehyde which, upon oxidation, yielded benzoic acid melting at 122 to 123°, hence it was *benzaldehyde*.

The fraction distilling at about 60° (5 mm.) yielded a small amount of semicarbazone (m.p. 100 to 101°) of n-*decylic aldehyde*.

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[1]) Report of Schimmel & Co., April 1907, 76.

Fraction 65 to 90° (4 mm.) likewise reacted with sodium bisulphite. The aldehyde regenerated from the pure bisulphite compound distilled at 80° (5 mm.). The combustion of its semicarbazone (m. p. 167 to 168°) yielded results pointing to the semicarbazone of nonylic aldehyde. In accord therewith was also the molecular weight determination according to Beckmann's method: found 192,5, computed 199. Oxidation with moist silver oxide yielded an oily substance which had the odor of a fatty acid, and which, when subjected to a low temperature, congealed to laminar crystals which, however, melted at little over 0°. In vacuum it boiled at 128° (4 mm.); under atmospheric pressure at 253 to 254°. The analysis of the silver salt, which was unstable toward light, indicated nonylic acid. The zinc salt of the acid, regenerated from the silver salt, melted at 127 to 128°, the copper salt slightly above 200°. Hence the aldehyde in question may be regarded as *nonylic aldehyde* which, upon oxidation, passes into a nonylic acid, the properties and salt of which show a close correspondence with those of pelargonic acid.

An oil obtained by fractional distillation from the fractions devoid of aldehydes and which boiled between 73 and 75° (4 mm.), yielded, upon exposure to low temperature, considerable amounts of laminar crystals of *naphthalene* (elementary analysis; m. p. 80 to 80,5°).

Fraction 65 to 71° (4 mm.) contained a ketone of mint-like odor. The analysis of the semicarbazone, melting at 217 to 218°, indicated a *ketone* of the formula $C_{10}H_{18}O$. In addition the oil contained traces of a *base*, a *phenol*, and an *alcohol* that reacted with phthalic acid.

Finally, it was ascertained that oleic aldehyde which, according to Tiemann and Krüger, is contained in the orris oil obtained by extraction, is not a constituent of the distilled oil. Heretofore, oleic aldehyde $C_{18}H_{34}O$ was not known in chemical literature. For the sake of comparison, this aldehyde was prepared by the distillation of a mixture of oleate of calcium and formate of calcium. Purified through its bisulphite compound, it had the following properties: b.p. 168 to 169° (3 to 4 mm.); $d_{15°}$ 0,8513; $n_{D20°}$ 1,45571. Its odor is rather faint and resembles that of the higher fatty aldehydes. When cooled, the aldehyde congeals to a wax-like mass. Its semicarbazone melts at 87 to 89°.

For the examination of the highest boiling portions of orris oil, fraction 140 to 180° (3 to 4 mm.) was used. With bisulphite no addition product resulted, hence oleic aldehyde is not a component of the distilled orris oil.

In the aqueous distillate resulting upon cohobation, the presence of the following substances was ascertained[1]: *acetaldehyde* (b. p. 51—57°; reduction of ammoniacal silver solution), *methyl alcohol* (m. p. of oxalic acid dimethyl ester 54°), *diacetyl* (m.p. of osazone 242°) and *furfurol* (m.p. of semicarbazone 197°).

Properties. At ordinary temperature orris oil constitutes a yellowish-white or yellow mass of a fairly hard consistence, which possesses a strong odor reminding one of orris root. It melts at about 40 to 50° to a yellow or yellowish-brown liquid[2].

Oil of orris root is slightly dextrogyrate. Its acid value, about 204 to 236, corresponds to an 83 to 96 p.c. content of myristic acid. Its ester value is from 2 to 10.

The so-called liquid oil of orris[3]) prepared by Schimmel & Co., which contains only the pleasantly smelling constituents of the oil, has the following constants: d_{15° 0,93 to 0,94; $\alpha_D + 14$ to $+ 30°$; n_{D20° about 1,495; A. V. 1 to 8; E. V. 20 to 40; soluble in 1 to 1,5 vol. and more of 80 p.c. alcohol.

Adulteration. In commerce a liquid or semi-liquid orris oil is occasionally met with, which is obtained by the distillation of orris roots with cedar oil or other oils; more often it is merely such a mixture of oils with a little oil of orris.

One of these oils had the following properties[4]: $d_{15,5^\circ}$ 0,9489; $\alpha_D - 28,25°$; congealing point —5°. Another oil[5] had the following properties: d_{15° 0,9452; $\alpha_D - 21° 14'$; insoluble in 80 p.c. alcohol. As became apparent from the lævorotation, a strongly lævorotatory oil such as oil of cedar or oil of gurjun balsam had evidently been added.

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[1] Report of Schimmel & Co., October 1908, 98.

[2] In order to avoid superheating that may prove detrimental, the oil is melted by placing the bottle in warm water of about 60°.

[3] Report of Schimmel & Co. April 1901, 44.

[4] *Ibidem* April 1900, 33.

[5] *Ibidem* April 1908, 79.

Some years ago, a mixture of 97,5 parts of acetanilide with 2,5 parts of orris oil was sold as "irisol" at enormous prices.

Statistics. The export[1] of orris root from Leghorn for the last 10 years is given in the following table:

From	September	1902	to	August	1903	840	tons,
„	„	1903	„	„	1904	820	„
„	„	1904	„	„	1905	500	„
„	„	1905	„	„	1906	920	„
„	„	1906	„	„	1907	550	„
„	„	1907	„	„	1908	525	„
„	„	1908	„	„	1909	755	„
„	„	1909	„	„	1910	760	„
„	„	1910	„	„	1911	560	„
„	„	1911	„	„	1912	690	„

161. Oil of Iris versicolor.

The oil of the North American *Iris versicolor*, L. was prepared from the dry root by F. B. Power and A. H. Salway[2]) with a yield of 0,025 p.c. It is yellow, of a somewhat unpleasant pungent odor: $d_{20^\circ}^{20^\circ}$ 0,9410; $\alpha \pm 0$. Of its constituents *furfurol* only was identified.

Family: ZINGIBERACEÆ.

162. Turmeric Oil.

Origin and Production. The curcuma plant, *Curcuma longa*, L. (family *Zingiberaceæ*), is indigenous to southern Asia and is cultivated in India, also in southern and eastern China because of the yellow pigment contained in the roots. Upon distillation with water vapor these roots yield 3 to 5,5 p.c. of a volatile oil.

Properties. Turmeric oil is an orange-yellow, slightly fluorescing liquid, the odor of which reminds one faintly of curcuma, and the specific gravity of which fluctuates between 0,942 and 0,961. The optical rotation of the oil varies. An oil distilled

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[1]) Report of Schimmel & Co. October 1912, 87.

[2]) Americ. Journ. Pharm. 83 (1911), 2.

from old roots of unknown source had $\alpha_D + 22°2'$; an oil from Madras roots, — 23°. When the optical rotation was re-determined after 7 and 4 years, respectively, the first showed $\alpha_D + 34°15'$; the second, — 18°55'. Hence in both oils a decided increase of the dextro rotation was noticeable. A.V. 1,6 to 3,1; E.V. 7,8 to 16; E.V. after acetylation 30 to 53. With $^1/_2$ to 1 vol. of 90 p.c. alcohol it yields a clear solution which occasionally becomes milky upon the addition of more alcohol.

A turmeric oil distilled in the Philippines by F. Bacon¹) with a yield of 2,4 p.c. was soluble in all proportions in 75 p.c. or stronger alcohol; $d_{30°}^{30°}$ 0,930; $\alpha_{D30°}$ 8,6° (+?); $n_{D30°}$ 1,5030; E.V. 81.

Composition. According to Bolley, Suida and Daube²), turmeric oil begins to boil at about 220°, and boils actively at 250°; later, decomposition sets in. Upon the addition of ammonium sulphide to fraction 230 to 250°, crystals separated which the investigators regarded as carvone hydrosulphide. F.A. Flückiger³), however, obtained no hydrogen sulphide compound with any of the fractions, which proves the absence of carvone.

From roots exhausted with water and redried J. Kachler⁴) obtained by extraction with carbon disulphide 8 p.c. of a viscid oil which could not be saponified.

C. L. Jackson and A. E. Menke⁵), also Jackson and W. H. Warren⁶) examined an oil not obtained by steam distillation but by extraction with ligroin. Hence their product was always contaminated with petroleum hydrocarbons. After repeated fractionation *in vacuo,* they isolated, as principal constituent, an alcohol which they named *turmerol* and to which, according to analysis, either the formula $C_{13}H_{18}O$ or $C_{14}H_{20}O$ should be assigned. Turmerol has the following properties: b.p. 158 to 163° (11 to 12 mm.); $d_{4°}^{24°}$ 0,9561; $[\alpha]_D + 24,58°$. Hydrogen chloride or phosphorus trichloride converted it into a chloride, and sodium into a sodium derivative. The latter reacted with *iso*butyl iodide

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¹) Philippine Journ. of Sc. **5** (1910), A, 262.

²) Journ. f. prakt. Chem. **103** (1868), 474.

³) Berl. Berichte **9** (1876), 470.

⁴) *Ibidem* **3** (1870), 713.

⁵) Americ. chem. Journ. **4** (1882), 368; Pharmaceutical Journ. III. **13** (1883), 839; Chem. Zentralbl. **1883**, 438.

⁶) Americ. chem. Journ. **18** (1896), 111; Chem. Zentralbl. **1896**, I. 757.

with the formation of an ether. Upon oxidation with dilute nitric acid, paratoluic acid resulted (m.p. 178°); with potassium permanganate, terephthalic acid.

When oxidized with chromic acid the products are very different. Thus Ivanow-Gajevsky[1]) obtained valeric and capronic acids from fraction 280 to 290°.

The latest investigations have been carried out by H. Rupe[2]) together with E. Luksch[3]), A. Steinbach and J. Bürgin. They failed to obtain turmerol in a pure state, neither were they successful in preparing the sodium compound and ether, nor the chloride described by Jackson. In all instances the curcumone, to be described later, could be isolated after treatment with sodium, hydrogen chloride, or phosphorus trichloride. This curcumone, however, is not contained in the original oil. If the principal fraction of turmeric oil which, after repeated fractionation distils between 155 and 158° (11 mm.), is treated with acid or alkali, there results a ketone $C_{13}H_{18}O$, the *curcumone,* an isomer of turmerol. For the preparation of this compound the oil itself may be used as starting point. 100 g. of curcuma oil are heated for 3 hours with an equal volume of alcohol and 30 p.c. potassium hydroxide solution in a flask connected with a reflux condenser. After cooling, the mixture is diluted with water and extracted 3 to 4 times with ether. The ethereal solution is washed with dilute phosphoric acid and dried over potassa. The crude ketone, boiling between 115 and 130° (10 mm.), is purified by means of the bisulphite addition product.

Curcumone is a colorless, not perfectly limpid oil with a penetrating, ginger-like odor, and has the following constants: b.p. 119 to 122° (8 to 11 mm.); $d_{20°}$ 0,9566; $[\alpha]_{D20°} + 80{,}55°$; n_D 1,50526; mol. refr. found 58,98, calculated 58,93. Of derivatives the following have been prepared: the oxime (b.p. 159° under 11 mm.), phenylhydrazone (m.p. 92°), *p*-bromophenylhydrazone (m.p. 71°), benzylidene curcumone (m.p. 106°), piperonal curcumone (m.p. 113°), and the condensation product with anisic aldehyde (m.p. 77 to 78°).

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[1]) Berl. Berichte **5** (1872), 1102.

[2]) *Ibidem* **40** (1907), 4909; **42** (1909), 2515; **44** (1911), 584, 1218.

[3]) E. Luksch, *Über Curcumaöl.* Inaug. Dissert., Basel 1906.

Upon oxidation of curcumone with potassium permanganate there resulted terephthalic acid (m.p. of the methyl ester 140°), *p*-tolylmethyl ketone (m. p. of semicarbazone 204 to 205° when heated very slowly), and *p*-acetyl benzoic acid (m.p. of benzylidene compound 232 to 233°). With hypobromous acid there resulted, in addition to bromoform, an acid which was volatile with water vapor and which was purified by means of its calcium salt. It revealed the following constants: m.p. 33 to 34°; b.p. 168 to 170° (12 mm.); $[\alpha]_{D20^\circ} + 31{,}15^\circ$ (9,9 p.c. alcoholic solution). The acid named *curcumic acid* has the composition $C_{12}H_{16}O_2$ and results from the curcumone $C_{13}H_{18}O$ upon oxidation of the $COCH_3$ group to COOH. The synthesis of γ-methyl-γ-*p*-tolyl butyric acid and of *p*-tolylmethyl ethyl acetic acid have shown the non-identity of these two acids with curcumic acid.

In the residue obtained after steam distillation of curcumic acid there was contained a small amount of an acid which, after regeneration from its calcium salt, crystallized in large, shiny needles melting at 150 to 151°. It is probably a hydroxycurcumic acid. When heated with permanganate solution it yields terephthalic acid.

When curcumic acid is oxidized with potassium permanganate, there results *p*-totyl methyl ketone, which is volatile with water vapor (m.p. of semicarbazone 204 to 205°). In the residue left after the steam distillation, the presence of a dicarboxylic acid, $C_{12}H_{14}O_4$, was established, melting at 226 to 228°.

The lowest fractions of turmeric oil contained *d*-α-phellandrene[1]) (m.p. of nitrite 108°)[2]).

163. Zedoary Oil.

Oleum Zedoariæ. — Zitwerwurzelöl. — Essence de Zédoaire.

Origin and Production. The rhizomes of *Curcuma Zedoaria,* Roscoe *(Curcuma Zerumbet,* Roxb., family *Zingiberaceæ)* enter commerce primarily from Ceylon via Bombay. The plant has long been cultivated in Ceylon because the leaves are a favorite vegetable with the natives[3]).

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[1]) Report of Schimmel & Co. October 1890, 28.

[2]) Luksch, *loc. cit.*

[3]) Flückiger, *Pharmakognosie* p. 369. — Dymock, Materia medica of Western India. Bombay and London 1885, p. 772.

Upon distillation the dry rhizome yields 1 to 1 ½ p.c. of oil. R. F. Bacon[1]) obtained but 0,1 p.c., presumably from fresh root grown in the neighborhood of Manila.

Properties. Oil of zedoary is a somewhat viscid, oily liquid. In thin layers its color is greenish, in thick layers reflected light shows a greenish-black color, whereas transmitted light is reddish. Its odor reminds one of that of ginger oil, but differs therefrom by a camphor-like odor due to cineol. d_{15° 0,982 to 1,01; $\alpha_D + 8$ to $+ 17^\circ$; n_{D20° 1,50233 to 1,50556; A.V. 0,3 to 2,4; E.V. 16 to 21; E.V. after acetylation 56 to 66; soluble in 1½ to 2 vols. of 80 p.c. alcohol.

Composition. The lowest boiling fractions, which constitute but a small portion of the oil, contain *cineol* (hydrogen bromide addition product)[2]).

Crystals that had separated from "heavy zedoary oil" were observed by H. Hænsel[3]). They melted at 142,5°; d_{15° 1,0322; $\alpha_{D20^\circ} + 20^\circ$; combustion C 76,3 p.c., H 9,8 p.c., O 13,9 p.c.; in alcoholic solution the body was found to be strongly dextrorotatory. It was neither acid, aldehyde nor ketone.

From fraction 140 to 166° (7 mm.) Bacon[4]) isolated a sesquiterpene alcohol of a strong, rather pleasant odor, which imparts to zedoary oil its characteristic aroma. It is conspicuous by its decided capacity to crystallize. From the alcoholic solution crystals several centimetres long were frequently obtained. They melted at 67°; the boiling point could not be ascertained, since the alcohol sublimes below its boiling temperature; $d_{30^\circ}^{30^\circ}$ 1,01; $\alpha_D \pm 0$. Concentrated sulphuric acid produces first a red color, then carbonization takes place. Concentrated nitric acid produces a solid substance which is colorless and odorless, and which dissolves in 10 p.c. sodium hydroxide solution with a red color, from which solution acids again precipitate it. If to the petroleum ether solution phosphorus pentachloride be added, no reaction takes place, until a drop of concentrated formic acid has been added, when a hard resin is formed.

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[1]) Philippine Journ. of Sc. 5 (1910), A, 261.

[2]) Report of Schimmel & Co. October 1890, 66.

[3]) Jahresb. f. Pharm. 1900, 338. — Pharm. Ztg. 44 (1899), 752.

[4]) Philippine Journ. of Sc. 5 (1910), A, 261.

164. Oil of Hedychium.

The oil from the flowers of *Hedychium coronarium,* L. var. *maximum,* Eichler (family *Zingiberaceæ*), which is cultivated in Java, has a pleasant and delicate, but faint odor. Sp.gr. 0,869; $\alpha_D - 0° 28'$ [1]).

From the blossoms of plants grown in Brazil, Th. Peckolt [2]) obtained 0,023 to 0,029 p.c. of oil; $d_{15°}$ 0,869.

165. Oil of Kæmpferia rotunda.

The *Rhizoma Zedoariæ rotundæ* of the apothecary shops was formerly obtained from *Kæmpferia rotunda,* L. (family *Zingiberaceæ*). Upon distillation the root yields 0,2 p.c. of an oil [3]) of a light yellow color and an unpleasant odor which at first reminds one of camphor, later of tarragon oil. The specific gravity of the fresh oil fluctuates between 0,886 and 0,894 [3]) at 26°. An oil which apparently was old had a specific gravity of 0,945 [4]) at 15° and $\alpha_D + 13° 4'$ to 14°. When distilled, one-half distilled below 200°, the other half mostly at 240° [3]). The oil contains *cineol* [4]).

166. Oil of Kæmpferia Galanga.

Kæmpferia Galanga, L., is cultivated by the natives of Java for medicinal and culinary purposes. Its rhizome contains a volatile oil which has been examined by P. van Romburgh [5]). Upon distillation of the root, which is known as *Kentjoer* or *Tjekoer,* with water vapor, there was obtained at first an oil which floated on the aqueous distillate, whereas the later distillate sank, and in fact, solidified to a crystalline mass. Re-crystallized from alcohol, large, transparent, glossy crystals, m. p. 50°, were obtained, which consisted of the *ethyl ester* of p-*methoxycinnamic acid.*

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[1]) Report of Schimmel & Co. April 1894, 59.

[2]) Pharm. Rundsch. (New York) 11 (1893), 287.

[3]) Verslag van 's Lands Plantentuin, Buitenzorg 1893, 55.

[4]) Report of Schimmel & Co. April 1894, 58.

[5]) On the crystallized constituent of the essential oil of *Kæmpferia Galanga,* L. Koninklijke Akademie van Wetenschapen te Amsterdam. Reprinted from: Proceedings of the Meeting of Saturday May 26th, 1900.

In fraction 155 to 165° (30 mm.) of the liquid oil, van Romburgh[1]) found *cinnamic acid ethyl ester.* This substance, which constitutes about one-fourth of the oil, was separated only with difficulty from another substance of almost the same boiling point. The separation was finally accomplished by means of 80 p.c. alcohol in which the bulk of the ester was soluble. The remaining portion was purified by boiling with potassium hydroxide, treating with bromine-in-chloroform solution, and shaking with concentrated sulphuric acid. In this manner an inactive, colorless and odorless liquid was obtained (b. p. 267,5° under 738 mm. pressure; d_{26° 0,766) which upon cooling congealed completely. By means of elementary analysis and molecular weight determination, the formula $C_{15}H_{32}$ was established. The only known hydrocarbon of this formula is the *pentadecane* described by Krafft. The properties of the two substances are in such close agreement that their identity cannot be doubted. More than one half of the liquid kæmpferia oil consists of this paraffin.

Another oil from Java had d_{25° 1,0174; α_{D25° —16°; n_{D25° 1,54284. It was soluble in 1 vol. of 80 p.c. alcohol, the addition of more solvent producing a decided opalescence.

167. Oil of Galangal.

Oleum Galangæ. — Galgantöl. — Essence de Galanga.

Origin and Production. *Alpinia officinarum,* Hance, of the family *Zingiberaceæ,* is originally indigenous to the Chinese island of Hai-nan, where it is now cultivated, also on the opposite island of Leitschou, and the neighboring coast and in Siam. It is official in the German Pharmacopœia as *Rhizoma Galangæ.* Upon distillation of the comminuted root 0,5 to 1 p.c. of volatile oil is obtained.

Properties. Galangal oil is a greenish-yellow, not very limpid oil with a camphoraceous odor and a taste which is at first bitter, and later, somewhat cooling.

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[1]) On some further constituents of the essential oil of *Kæmpferia Galanga,* L. Koninklijke Akademie van Wetenschappen te Amsterdam. May 1902, 618.

The specific gravity lies between 0,915 and 0,921; the angle of rotation between —1° 30′ and —5° 30′; $n_{D20°}$ 1,476 to 1,482; A. V. up to 2; E. V. after acetylation 40 to 45. It is miscible with one half and more vol. of 90 p.c. alcohol; of 80 p.c. alcohol 10 to 25 vol. are required to form a clear solution.

Composition. According to Schindelmeiser[1]), the lowest fraction consists of d-*α-pinene* (nitrosochloride, nitrolpiperidide). *Cineol* (hydrobromide[2])) is another constituent to which the oil owes its camphor-like odor. Upon shaking the oil with sodium hydroxide solution, P. K. Horst[3]) isolated about 75 p.c. of *eugenol* (m.p. of benzoyleugenol 69 to 70,5°). From fraction 230 to 240° ($d_{20°}$ 0,932; $\alpha_{D20°}$ —27° 21′; $n_{D20°}$ 1,4922) Schindelmeiser[4]) obtained a viscid hydrochloride which boiled at 145 to 150° (10 mm.), congealed when cooled, and after repeated crystallization from alcohol and water melted at 51°. A chlorine determination revealed the formula $C_{15}H_{24} \cdot 2HCl$. Inasmuch as heretofore no sesquiterpene dihydrochloride of the above melting point has been observed, the hydrocarbon in question appears to be a new one. In the higher boiling fractions (b.p. 274 to 276°) the presence of *cadinene* is suspected.

168. Oil of Alpinia Galanga.

The rhizome of *Alpinia Galanga,* Willd., which formerly entered commerce as *Rhizoma s. Radix Galangæ majoris,* yields upon distillation 0,04 p.c. (fresh root) of oil. An oil obtained from A. J. Ultée in Salatiga, Java, had a lemon-yellow color and a peculiar, decidedly spicy odor. Upon examination in the laboratory of Schimmel & Co.[5]), it revealed the following properties: $d_{15°}$ 0,9847; α_D + 4° 20′; $n_{D20°}$ 1,51638; A.V. 1,8; E.V. 145,6; soluble in 1 vol. of 80 p.c. alcohol, the addition of 3 vol. of solvent producing opalescence.

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[1]) Chem. Ztg. **26** (1902), 308.

[2]) Schimmel's Bericht April **1890**, 21.

[3]) Pharm. Zeitschr. f. Rußland **39** (1900), 378.

[4]) Chem. Ztg. **26** (1902), 308.

[5]) Report of Schimmel & Co. October **1910**, 148.

A second oil examined by Ultée[1]) himself had the following properties: d_{29° 0,968; $\alpha_{27,50^\circ}$ abt. + 6°. The oil contained 48 p.c. of *cinnamic acid methyl ester* (m.p. 34°). The *cineol* content (b.p. of the cineol 175 to 177°; m.p. of the iodol derivative 112°) was about 20 to 30 p.c. In addition a hydrocarbon with a turpentine-like odor (b.p. 151 to 161°; d_{25° 0,8566; α_{27° + 14,90°), presumably d-*pinene,* also *camphor* (m.p. 170 to 175°) were found.

From the leaves of *Alpinia Galanga* an oil can also be obtained, though in but small percentages. It probably contains cinnamic acid methyl ester, since upon saponification it yielded cinnamic acid[1]).

169. Oil of Alpinia malaccensis.

The fresh rhizome of *Alpinia malaccensis,* Roscoe *(Ladja goah),* which grows wild in Java, yields upon distillation about 0,25 p.c. of oil of a pleasant odor. Its specific gravity fluctuates between 1,039 and 1,047 at 27°. In a 200 mm. tube, it deviates polarized light between 0,25 and 1,5° to the right.

When cooled slightly, the bulk of the oil solidifies, handsome, long needles being formed. As their investigation has shown, these crystals consist of *cinnamic acid methyl ester.*

An oil which congealed at 25,5° had a S.V. of 279,5 = 80,5 p.c. of methyl cinnamate. It formed a clear solution with 1 vol. of 80 p.c. alcohol[2]). Another oil had the following properties: d_{15° 1,0493; $\alpha_D - 0°20'$; n_{D20° 1,54768; congealing point 19,6°; A.V. 1,8; E.V. 256,0 = 74,1 p.c. methyl cinnamate; soluble in 1 vol. of 80 p.c. alcohol, the addition of 2 vol. and more of alcohol causing the separation of paraffin. (Observation in the laboratory of Schimmel & Co.).

The oil from the leaves was likewise prepared and examined by P. van Romburgh[3]). From 700 kilos of fresh leaves 1100 cc. = 0,16 p.c. of oil were obtained: d_{26° 1,02; α_D + 6,5°. When the oil was treated with sodium hydroxide solution, about 25 p.c.

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[1]) Mededeelingen van het Algemeen-Proefstation op Java te Salatiga II. Serie No. 45; (Reprint from Cultuurgids **1910**, II. No. 8); Report of Schimmel & Co. April **1911**, 19.

[2]) P. van Romburgh, Koninklijke Akademie van Wetenschappen te Amsterdam **1898**, 550.

[3]) *Ibidem* **1900**, 445.

thereof remained unattacked. A volatile liquid was obtained, which distilled for the most part between 160 and 170°. This substance can also be separated by steam distillation from the 75 p.c. of methyl cinnamate which remains behind in a fairly pure state and crystallizes well upon cooling.

Fraction 158 to 160° (d_{26° 0,857; $\alpha_D + 21^\circ 50'$) consists of d-*α-pinene* (m. p. of nitrosochloride 108°; of nitrolpiperidide 118 to 119°).

170. Oil of Alpinia nutans.

The root of *Alpinia nutans,* Roscoe, contains a volatile oil[1]): d_{29° 0,95. When distilled, a large part thereof passes over below 230°. From fraction 255 to 265°, saponification with methyl alcoholic potassium hydroxide yielded an acid melting at 134°, presumably *cinnamic acid.*

171. Ginger Oil.

Oleum Zingiberis. — Ingweröl. — Essence de Gingembre.

Origin and Production. The original home of *Zingiber officinale,* Roscoe (*Amomum Zingiber,* L.), is southern Asia. On account of its spicy rhizome, it is cultivated there as well as in the islands of the South Asiatic archipelago, in Japan, the West Indies and Africa. Arranged according to the amounts shipped[2]), ginger is exported from the following countries: China, India, Japan, Jamaica, Sierra Leone. Concerning its cultivation in East Africa, which has been undertaken recently, Prof. Dr. Zimmermann[3]) makes the following statement:

Ginger makes rather high demands on the fertility of the soil, which must not be too firm, neither too marshy. A sandy clay containing lime is best adapted for the cultivation of ginger. New plants are started exclusively from cuttings of the rhizomes. These are stored in a dry place, and shortly before planting, are cut into pieces, each of which is 3 to 5 cm. long and must contain at least one bud. The arrangement of the fields is like

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[1]) Verslag 's Lands Plantentuin te Buitenzorg **1897**, 36.

[2]) For statistical data concerning the commerce in ginger see Bull. Imp. Inst. **10** (1912), 118; Report of Schimmel & Co. October **1912**, 66.

[3]) Mitteilungen aus dem Biologisch-Landwirtschaftlichen Institut Amani July 2nd 1904. No. 28. Reprint from the Usambara Post.

that of the potato field; the ridges should preferably have a width of 30 cm., the furrows one of 70 cm. The cuttings of the rhizome are planted in the ridges at a distance of from 25 to 30 cm. in holes 7 to 10 cm. deep. These holes should be well filled up with earth, for the roots that lie in cavities are said to rot easily.

The harvest begins when the overground portion has dried, *i. e.* as a rule after 9 to 11 months. The rhizomes are dug up, carefully washed, and all roots removed. From this stage onward, the treatment varies according to whether the ginger is to be dried or preserved. With regard to the dried rhizome, a further distinction is made between peeled or white ginger, and unpeeled or black ginger.

If the ginger is to be peeled, only a very thin layer of skin should be removed, for the aromatic constituents are deposited just beneath the epidermis. As soon as peeled, the rhizomes are again placed in pure water, where they remain over night, after which they are dried. Since great stress has been laid on a white color for peeled ginger, attempts to improve thereon by means of chlorinated lime and gypsum have been made. Such practices, however, are to be discouraged.

The unpeeled ginger is dried immediately after careful cleaning.

The output of a ginger field averages about 1100 to 1700 kg. per hectare; in exceptional cases 2200 kg. per hectare are harvested. The ginger plants greatly exhaust the soil, so that repeated cultivation in the same field is possible only with much fertilization.

When distilled, dried ginger yields on the average 2 to 3 p.c. of volatile oil. Some varieties yield less. Thus *e. g.* a Japanese ginger yielded but 1,23 p.c., a Jamaica ginger 1,072 p.c.[1]) and a Cochin ginger 1,5 p.c.[2]).

Properties. Ginger oil has the aromatic, not very strong, but persistent odor of ginger, without, however, possessing its pungent taste. It is greenish-yellow in color and somewhat viscid. d_{15° 0,877 to 0,886. However, individual oils, both lighter

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[1]) H. Hænsel, Pharm. Ztg. **48** (1903), 58.

[2]) H. Hænsel, Apotheker Ztg. **20** (1905), 396.

and heavier have been observed; $\alpha_D - 28$ to $-50°$, but oils with lower angles appear to occur; A. V. up to 2; E. V. 0 to 15; E. V. after acetylation 33 to 42. Ginger oil is difficultly soluble in alcohol: of 95 p.c. alcohol up to 7 vols. are required and even then the solution is not always clear; even in 90 p.c. alcohol some of the oils are not completely soluble no matter how many volumes are used.

An oil obtained from Japanese root differed from that commonly distilled from the African and Jamaica drug. However, it could not be regarded as a perfectly normal oil, since it had resulted from a trial distillation of but a few kilograms of ginger. It had the high specific gravity of 0,894. Contrary to the commonly observed lævorotation, it was dextrogyrate, $\alpha_D + 9° 40'$. It was soluble in even 2 vols. of 90 p.c. alcohol and showed no reaction for phellandrene.

Another oil prepared in Japan[1]) revealed properties which did not differ from those of the ordinary oils: $d_{15°}$ 0,883; $\alpha_D - 26° 52'$. With sodium nitrite and glacial acetic acid it gave a very distinct reaction for phellandrene.

An oil distilled in the Philippines with a yield of 0,072 p.c. (presumably from fresh root) revealed the following properties as determined by R. F. Bacon[2]): $d_{30°}^{30°}$ 0,8850; $\alpha_{D30°}$ 5,9° (+ ?); $n_{D30°}$ 1,4830; S. V. 14. The oil was light yellow in color and soluble in twice its volume and more of 90 p.c. alcohol.

Composition[3]). The lower boiling fractions of ginger oil contain terpenes. The angle of rotation of fraction 155 to 165° is opposite to that of the oil itself, *viz.*, $+ 63° 13'$. This fraction contains d-*camphene*[4]). When treated with acetic acid and sulphuric acid there results an acetate, which upon saponification yields *iso*borneol (m. p. 212°; m. p. of bromal derivative 71°). The fraction boiling about 170° contains *β-phellandrene*[4]) (m. p. of nitrite 102°).

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[1]) Report of Schimmel & Co. October 1893, 50.

[2]) Philippine Journ. of Sc. 5 (1910), A, 259.

[3]) The older investigations threw no light on the chemical composition of the oil. Papousek, Sitzungsberichte der Akademie der Wissenschaften zu Wien 9 (1852), 315; Liebig's Annalen 84 (1852), 352. — J. C. Thresh, Pharmaceutical Journ. III. 12 (1881), 243.

[4]) Bertram and Walbaum, Journ. f. prakt. Chem. II. 49 (1894), 18.

So far as the aroma is concerned, an important part of the oil are three oxygenated constituents observed by Schimmel & Co.[1]), *viz., cineol, citral* and *borneol.* Fraction 170 to 175°, distilled under ordinary pressure, yielded, upon the addition of iodol, considerable amounts of the iodol addition product of cineol (m. p. 112°).

A fraction boiling between 90 and 105° (5 mm.) became solid and on being drawn off yielded crystals of a borneol-like odor which, after recrystallization from petroleum ether, melted at 204°. Additional amounts of borneol as well as a small amount of an alcohol, with the odor of geraniol, were obtained by treating the liquid drained from the borneol referred to above, with phthalic acid anhydride in benzene solution. The alcohols obtained from the acid phthalic acid esters upon saponification with alcoholic potassium hydroxide, remained liquid in part. Hence, in addition to borneol, there must have been present another alcohol, possibly *geraniol.* After re-crystallization from light petroleum, the free bornylphthalic acid melted at 164°. Fractions 90 to 122° (5 mm.) also contained citral, which was separated as a solid addition compound by shaking with a concentrated solution of sodium bisulphite. Regenerated with soda solution, it was converted into citryl-β-naphthocinchoninic acid melting at 179°.

Upon fractionation of the saponified ginger oil, H. von Soden and W. Rojahn[2]) obtained a new sesquiterpene, the *zingiberene,* which has the following properties: d_{15° 0,872; $\alpha_D - 69^\circ$. Under atmospheric pressure it distils at 269 to 270° with slight decomposition; under 14 mm., at 134°. Elementary analysis yielded results agreeing with the formula $C_{15}H_{24}$.

O. Schreiner and E. Kremers[3]) prepared several characteristic derivatives of zingiberene which have been described in Vol. I, p. 329.

From the first fraction of ginger oil v. Soden and Rojahn isolated an aldehyde with the aid of bisulphite. However, the amount was too small for a more minute examination.

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[1]) Report of Schimmel & Co. October 1905, 38.

[2]) Pharm. Ztg. 45 (1900), 414.

[3]) Pharmaceutical Archives 4 (1901), 63.

In Jamaica ginger oil F. D. Dodge[1]) found a small amount of an aldehyde which is probably n-*decylic aldehyde.*

172. Oil of Gastrochilus pandurata.

According to Dr. A. J. Ultée of Salatiga, Java, the rhizome of *Gastrochilus pandurata,* Ridl.[2]) (family *Zingiberaceæ*), is known to the natives as *temu-kuntji* and used by them as a medicine and as a spice. Upon distillation it yields 0,1 to 0,37 p. c. of an almost colorless oil, the odor of which greatly resembles that of tarragon and basilicum oils. $d_{15°}$ 0,8746; $\alpha_D + 10° 24'$; $n_{D20°}$ 1,48957; A.V. 0; E.V. 17,3; incompletely soluble in 10 vols. of 80 p.c. alcohol, with 90 p.c. alcohol it forms a clear solution.

173. Malabar or Ceylon-Malabar Cardamom Oil.

Oleum Cardamomi. — Cardamomenöl. — Essence de Cardamome.

Origin and Production. Up to the beginning of this century, the official Malabar cardamoms from *Elettaria Cardamomum,* Maton (var. *α minor*) were but rarely used for the production of volatile oil.

Wheras formerly this variety was exclusively cultivated on the Malabar coast, it is now also produced in Ceylon and designated Ceylon-Malabar cardamom in commerce. The exports are made up partly of the entire fruit, partly of seeds, the latter being styled "Ceylon cardamom seeds". Upon distillation Malabar cardamoms yield 3,5 to 7 p.c. of oil. It should be noted that the Ceylon cardamom oil is at present distilled exclusively from the Ceylon-Malabar cardamoms[3]).

Cultivation[4]). The cardamom fruits are collected from the wild, the half wild, and cultivated plants. In the shady, wooded regions of Canara, Cochin and Travancore the cardamom plant

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[1]) Chem. Ztg. 34 (1912), 1217.

[2]) Report of Schimmel & Co. October 1910, 148.

[3]) *Ibidem* October 1901, 14 and October 1910, 32.

[4]) According to Chemist and Druggist 80 (1912), 367. Comp. also Flückiger, *Pharmakognosie,* III^rd ed. Berlin 1891, p. 898; G. Watt, The commercial products of India, London 1908, p. 514 and Oil, Paint and Drug Reporter 76 (1909), No. 12, p. 28 D; Report of Schimmel & Co. April 1910, 29.

grows at an altitude of 2500 to 5000 ft. It thrives best in a moist, rich, clay soil in protected localities. These conditions are met with in the betel and pepper plantations of Mysore and Canara, also in the cardamom gardens of Ceylon.

In the wooded districts of Coorg (Mysore), cardamom gardens are established in February by cutting down the trees. Between the individual gardens a 20 to 30 yd. strip of wood is left untouched. In all this, superstition plays an important role. Thus the deforestation must take place on certain days only, and then before 9 o'clock in the morning. The natives also believe that the presence of ebony and nutmeg trees, also of pepper plants, exercise a favorable influence on the development of the cardamom plants. From the fifth year the gardens are in full bearing and after seven additional years the plants begin to show signs of sickness. At this juncture some of the trees that have served as a sort of fence around the garden are felled. The falling trees destroy a large number of cardamom stems, thus inducing the rhizomes to send forth new shoots. The garden then remains productive for another eight years, after which time it has to be replanted.

In Ceylon the methods of cultivation are much more rational. Most of the cardamoms are cultivated in Matala, Medamahanwara and Hewahata. The place having been selected, the underbrush is removed. Holes 1,5 to 2 ft. in diameter and 12 to 15 inches deep are dug in rows 7 ft. apart, the holes in each row being likewise 7 ft. apart. The rhizomes must not be planted too deep, otherwise they rot. In recent years the cardamom plants are raised more and more from seeds, the Mysore variety being propagated mostly by seedlings. It is remarkable that but few of the seeds germinate. In Ceylon the cardamom plants bear flowers almost the entire year. The harvest begins in August and lasts until April. The fruits are carefully dried by exposure to the sun or, in rainy weather, by artificial means. With the aid of machinery they are deprived of stems and the remnants of the blossoms, then sorted, and in some cases even treated with sulphur dioxide vapors.

The accompanying table supplies information concerning the cultivation of cardamoms in Ceylon and their export during the past ten years.

Year	Acreage	Export in Engl. lbs.	Year	Acreage	Export in Engl. lbs.
1901	8621	559 704	1907	8451	789 495
1902	9746	615 922	1908	8350	715 418
1903	9500	909 418	1909	7738	824 008
1904	9300	995 680	1910	7426	639 007
1905	8870	874 625	1911	7300	564 819
1906	8744	732 136			

Calcutta is one of the large commercial centres for this drug. The annual consumption in India and Burma is estimated at 1 000 000 lbs.

Properties. Oil of cardamom is a spicy liquid, the odor being that of cardamoms: d_{15° 0,923 to 0,944; $\alpha_D + 24$ to $+ 41^\circ$; n_{D20° 1,462 to 1,467; A. V. up to 4,0; E. V. 94 to 150; soluble in 2 to 5 vol. and more of 70 p. c. alcohol[1]).

Composition. In an old Malabar cardamom oil, Dumas and Péligot[2]) found prismatic crystals of terpinhydrate. No doubt, they owed their formation to terpineol, the presence of which in the oil was shown later. According to Schimmel & Co.[3]), the high saponification value is due to *terpinyl acetate.* The analysis of the silver salt of the acid obtained from the saponification liquid agrees with silver acetate. From the saponified oil, fractionation in vacuum (150 to 164° under 14 mm.) yielded crystallizable d-*α-terpineol:* m. p. 35 to 37°; $\alpha_D + 81^\circ 37'$ in the super-cooled state. For its identification the following derivatives of terpineol were prepared: dipentene dihydriodide (m. p. 78 to 79°); terpinyl phenylurethane (m. p. 112 to 113°), which is also optically active ($[\alpha]_D$ in 10 p. c. alcoholic solution $+ 33^\circ 58'$ at

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[1]) From the variety known as the Ceylon-Mysore cardamom, which is also cultivated in Ceylon, E. J. Parry (Pharmaceutical Journ. **63** [1899], 105) obtained upon distillation 2,6 p.c. of oil, the odor of which could scarcely be distinguished from that of Malabar oil. Its constants were: $d_{15.5^\circ}$ 0,9418; $\alpha_D + 46^\circ 39'$.

[2]) Annal. de Chim. et Phys. II. **57** (1834), 335.

[3]) Report of Schimmel & Co. October **1897**, 10. — Wallach, Liebig's Annalen **360** (1908), 90.

20°) and the terpineol nitrosochloride. From the last a nitrolpiperidide was obtained, the melting point of which was found at 151 to 152°, hence 8° lower than that of the inactive terpineol nitrolpiperidide.

In the lowest fraction *cineol* was found, which was identified by its iodol compound melting at 112 to 113°.

Malabar cardamom oil does not contain terpinene, but, according to Parry[1]), it contains *limonene*.

174. Oil of the long Ceylon Cardamom.

Origin and Production. Up to the close of last century, cardamom oil of commerce was not distilled from the official cardamoms obtained from *Elettaria Cardamomum,* Maton, but from the long Ceylon cardamoms, a variety of the above-named species which Flückiger[2]) has named *Elettaria Cardamomum* var. *β.* Formerly this was regarded as a separate species to which the name *Elettaria major,* Smith, had been given. These cardamoms grow wild in the woods of the southern and more central Provinces of Ceylon, but are also cultivated in the island.

For distillation the fruits are ground and yield from 4 to 6 p. c. of oil. An experimental distillation of the seeds and shells, separately, yielded 4 p.c. of oil for the former, and 0,2 p.c. for the latter.

Properties. The oil of the long cardamoms is light yellow in color, somewhat viscid, has a strong aromatic odor of cardamom and a pleasant, cooling taste. The specific gravity lies between 0,895 and 0,906; $\alpha_D + 12$ to $+15°$; S. V. 25 to 70. The oil forms a clear solution with 1 to 2 or more vol. of 80 p.c. alcohol; with 70 p. c. alcohol it gives turbid mixtures.

The seed oil referred to above had the following properties: $d_{15°}$ 0,908; $\alpha_D + 13° 14'$; that of the shells $d_{15°}$ 0,908; $\alpha_D + 9° 48'$.

Composition. An exceedingly careful investigation of the oil by E. Weber[3]) led to the discovery of the hitherto unknown terpene *terpinene,* also of an isomeric *terpineol.*

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[1]) Pharmaceutical Journ. **63** (1899), 105.

[2]) Pharmacographia, II. ed., p. 644.

[3]) Liebig's Annalen **238** (1887), 98.

According to Wallach[1]) the lowest boiling portions consist of a mixture of hydrocarbons from which a fraction 165 to 167° (d 0,846) could be obtained which, when treated with hydrogen chloride, yielded terpinene dihydrochloride melting at 52°. The terpene yielding this compound was *sabinene,* since upon oxidation it was converted into sabinic acid, melting at 56 to 57°.

When Weber passed hydrogen chloride into fraction 170 to 178°, there resulted terpinene dihydrochloride, $C_{10}H_{16}2HCl$, melting at 52°. The terpinene nitrosite, m. p. 155°, was obtained from fraction 178 to 182°.

By treating fraction 205 to 220° with hydrogen chloride, Weber obtained a hydrochloride melting at 52°, and by shaking it with concentrated hydriodic acid, a hydriodide melting at 76°. He, therefore, believed that he had found α-terpineol, the only one known at that time. In spite of repeated attempts he could not obtain dipentene tetrabromide nor the terpinyl phenylurethane. As was shown later by Wallach, cardamom oil does not contain the ordinary α-terpineol but its isomer, the *terpinenol-4* (see Vol. I, p. 382). This he identified not only by the derivatives mentioned above but by the dihydrobromide melting at 59°, also by the glycerol $C_{10}H_{17}(OH)_3$ (m. p. 128 to 129°) obtained by oxidation.

During the process of distillation Weber observed the splitting off of formic and acetic acids, which seem to indicate the presence of esters of terpinenol. That the amount of these esters is not inappreciable (8 to 24 p. c.) is indicated by the saponification values. (Comp. Properties.)

From the distillation residue a solid compound separated which, upon recrystallization from alcohol, yielded light laminæ with a silvery lustre, melting at 60 to 61°.

175. Siam Cardamom Oil.

Origin. From time to time the seeds of Siam cardamoms, from *Amomum Cardamomum,* L. make their appearance in the London market, where they are known as camphor seeds because

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[1]) Liebig's Annalen **350** (1906), 168. — Nachr. K. Ges. Wiss. Göttingen **1907**, Session of July 20.

of their camphor-like odor. Upon distillation Schimmel & Co.[1]) obtained 2,4 p.c. of oil.

Properties. At ordinary temperature this oil constitutes a semi-solid mass with an odor of camphor and borneol. In order to dissolve the separated crystals, the oil had to be heated to 42°; at which temperature the specific gravity was 0,905 and the angle of rotation $+38^\circ 4'$. S. V. 18,8; S. V. after acetylation 77,2, corresponding to 22,5 p.c. of borneol in the original oil; soluble in 1,2 vol. of 80 p.c. alcohol.

Composition. In order to separate the stearoptene, the oil was cooled down in ice and treated by centrifugal machine. From 800 g. of oil 100 g. of crystals were thus obtained. Dissolved in hot light petroleum and after the solution had been allowed to cool, there resulted 40 g. of nearly pure *borneol* which, after having been purified through its benzoyl ester, melted at 204°. In a 10 p.c. alcoholic solution it showed a specific angle of rotation $[\alpha]_{D20^\circ} + 42^\circ 55'$.

The light petroleum mother liquor left upon evaporation, a crummy mass which, after recrystallization from 80 p.c. alcohol, melted at 176 to 178° and had the properties of *camphor*. Its oxime melted at 118°. Its optical rotation was determined in alcoholic solution, $[\alpha]_D + 45^\circ 17'$ at 20°.

Hence the crystalline mass which separates from Siam cardamom oil[2]) consists of a mixture of d-*borneol* and d-*camphor*, the two compounds being present in approximately equal parts.

176. Oil from Amomum Mala.

Origin. The comminuted fruits (seeds and shells of *Amomum Mala*, K. Schum., a zingiberaceous plant which is widely distributed in the forests of German East Africa, have been distilled in the Biologic-Agricultural Institute in Amani[3]), yielding 0,76 p.c. of a brownish-yellow oil.

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[1]) Report of Schimmel & Co. October 1897, 10.

[2]) The camphor mentioned by Flückiger in Pharmacographia IInd ed., p. 647, was probably not obtained from Ceylon cardamoms but from Siam cardamoms.

[3]) Report of Schimmel & Co. April 1905, 84.

Properties and Composition. d_{15° 0,9016; $\alpha_D - 10^\circ 54'$; A.V. 3,5; E.V. 1,7; E.V. after acetylation 67,05; with 1 to 1,5 vol. and more of 80 p.c. alcohol it forms a turbid solution.

Under 7 mm. pressure the oil distilled between 51 and 100°. The investigation revealed the presence of much *cineol* (m. p. of the iodol compound 112°); also of *terpineol.*

177. Grains of Paradise Oil.

Origin. The seeds of *Amomum Melegueta,* Roscoe (family *Zingiberaceæ*), are indigenous to the coast of tropical West Africa. Formerly they were used extensively as a spice and were known in the apothecary shops as *Grana Paradisi, Semina Cardamomi majoris* and as *Piper Melegueta.* The plant occurs from the Congo to Sierra Leone, and a part of this coast is named, after the drug, the Pepper or Melegueta coast. On an experimental scale the paradise grains yielded 0,3 p.c.[1]) of oil; distilled on a commercial scale they gave 0,75 p.c.[2]).

Properties. The oil of the grains of paradise is a yellowish liquid with a spicy but hardly characteristic odor. d_{15° 0,894[3]); $\alpha_D - 3^\circ 58'$. The oil begins to boil at 236°, the larger portion passing over between 257 and 258°. Elementary analysis yielded results in agreement with the formula $C_{20}H_{32}O$.

178. Bengal Cardamom Oil.

Origin. Bengal cardamoms derived from *Amomum aromaticum,* Roxb.[4]), yield upon distillation 1,12 p.c. of volatile oil.

Properties. The oil[5]) of Bengal cardamoms is light yellow in color, possesses a decided odor of cineol, and has a specific gravity of 0,920 at 15°; $\alpha_D - 12^\circ 41'$. It is soluble in one or several vol. of 80 p.c. alcohol.

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[1]) Flückiger and Hanbury, Pharmacographia, IInd ed., p. 653.

[2]) Report of Schimmel & Co. October 1897, 10.

[3]) Flückiger *(loc. cit.)* records as sp. gr. 0,825. Presumably this is a printer's error.

[4]) According to E. M. Holmes, Bengal cardamoms are derived from *Amomum aromaticum,* Roxb., and not, as Flückiger states in his Pharmacographia, from *Amomum subulatum,* Roxb.

[5]) Report of Schimmel & Co. April 1897, 43.

The bulk of the oil distils over below 220°, a comparatively large residue remaining in the flask.

Composition. *Cineol* is the only known constituent of this oil. Its presence was established by the preparation of its hydrogen bromide addition product, isolation of the pure cineol (b. p. 175 to 176°; sp. gr. 0,924), and the oxidation of the latter to cineolic acid (m. p. 197°).

Inasmuch as Bengal cardamom oil is devoid of the characteristic cardamom odor, it cannot be substituted for Ceylon cardamom oil and is therefore without practical importance.

179. Oil of Aframomum angustifolium.

Aframomum angustifolium, K. Schum.¹), is a kind of cardamom indigenous to German East Africa but it also occurs in Madagascar and the Seychelles islands. From the seeds of this plant which were sent to Schimmel & Co.²) from Usambara they obtained 4,5 p.c. of a colorless oil of the following properties: $d_{15°}$ 0,9017; α_D — 16° 50′; $n_{D20°}$ 1,46911; A.V. 0,4; E.V. 4,2; soluble in 6 vol. and more of 80 p.c. alcohol.

As to odor, this oil cannot enter into competition with the Ceylon cardamom oil. Its large *cineol* content reminds one of oil of cajeput. The amount of oil available was too small to ascertain anything as to its composition.

180. Cameroon Cardamom Oil.

Under the name of Cameroon cardamoms, the fruits of several closely related species of *Aframomum* appear to have entered commerce. The statement made by Sadebeck³) (*Kulturgewächse der deutschen Kolonien,* Jena 1899, p. 171) that the Cameroon cardamoms are derived from *Amomum angustifolium,* Sonnerat, is not correct. Neither is the statement correct which was made by D. Hanbury in an article on the cardamoms of

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¹) According to K. Schumann's monograph on the *Zingiberaceæ* (in Engler's *Pflanzenreich,* fascicle 20), the synonyms of this plant are: *Amomum angustifolium,* Sonnerat, *A. madagascariense,* Lam., *A. nemorosum,* Boj., *A. sansibaricum,* Werth. This nomenclature does not agree entirely with that of the Index Kewensis. The latter, however, is no longer authoritative in this case.

²) Report of Schimmel & Co. April 1912, 136.

³) *Ibidem* April 1912, 136.

tropical Africa (Pharmaceutical Journal III. 2 [1872], 642) according to which *Amomum Daniellii,* Hook. f. and *A. angustifolium,* Sonnerat, are identical.

According to K. Schumann's monograph on the *Zingiberaceæ* (Engler's *Pflanzenreich,* fascicle 20) the former species *Amomum angustifolium,* Bak., has been separated into two species, *viz., Aframomum Daniellii,* K. Schum. (*Amomum Daniellii,* Hook. f.), and *Aframomum Hanburyi,* K. Schum.

The Cameroon cardamoms distilled by Schimmel & Co. were derived from the first species, whereas the cardamoms distilled by H. Hænsel and described by W. Busse (Arbeiten aus dem Kais. Gesundheitsamt **14** [1898] 139) were probably derived from *Aframomum Hanburyi.*

Cameroon cardamom oil of Schimmel & Co.[1]. Yield 2,33 p.c.; d_{15° 0,907; α_D — 20° 34′; soluble in 7 to 8 vols. of 80 p.c. alcohol. It contains *cineol* (iodol reaction).

Cameroon cardamom oil of H. Hænsel[2]. Yield 1,6 p.c.; d_{15° 0,9071; α_D — 23,5°; n_{D25° 1,4675.

181. Korarima Cardamom Oil.

Korarima cardamoms, formerly called *Cardamomum majus,* are of the size and shape of a little fig. They originate from the countries to the south of Abyssinia and but rarely enter European commerce. The mother plant of this variety of cardamoms is the *Amomum Korarima,* Pereira. Of this plant the seeds and fruits only are known. Whether a separate species is justified or whether the fruits are derived from species of *Aframomum* already described, is uncertain at present[3].

The oil from these fruits was first distilled by Schimmel & Co.[4] in 1877 who obtained a yield of 2,13 p.c.

H. Hænsel[5] obtained 1,72 p.c. of oil upon distillation. d_{15° 0,903; α_D — 6,82°; S.V. 50; S.V. after acetylation 107; soluble in 1 vol. of 80 p.c. and in 17 vol. of 70 p.c. alcohol.

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[1] Report of Schimmel & Co. October **1897**, 12.

[2] W. Busse, *loc. cit.*

[3] Comp. K. Schumann, *Zingiberaceæ* in Engler's *Pflanzenreich,* fascicle 20.

[4] Schimmel's Bericht Januar **1878**, 8.

[5] Pharm. Ztg. **50** (1905), 929; Chem. Zentralbl. **1905**, II. 1792.

182. Oil of Cardamom Root.

From cardamom root shipped from Indo-China, the botanical origin of which could not be ascertained, Schimmel & Co.[1]) obtained upon distillation 0,64 p.c. of a lemon-yellow oil with a peculiar spicy odor which in no way resembled that of the seed oil. Its constants were: d_{15° 0,9066; $\alpha_D -32^\circ 57'$; n_{D20° 1,48151; A.V. 3,7; E.V. 87,9; E.V. after acetylation 96,7. The oil was soluble in 0,5 vol. of 95 p.c. alcohol, but the solution became turbid upon the addition of more alcohol, the turbidity disappearing only after 4 vol. of solvent had been added. Upon fractional distillation under diminished pressure (5 mm.), the following fractions were obtained:

1.		to 35°	5,4 %;	$\alpha_D - 0^\circ 10'$
2.	35	„ 40°	8,7 %;	$\alpha_D - 0^\circ 32'$
3.	40	„ 100°	5,4 %;	$\alpha_D - 17^\circ 5'$
4.	100	„ 110°	10,6 %;	$\alpha_D - 31^\circ 10'$
5.	110	„ 115°	44,2 %;	$\alpha_D - 45^\circ$
6.	115	„ 145°	6,4 %;	$\alpha_D - 33^\circ 14'$
7.	Residue		19,3 %;	$\alpha_D - 39^\circ 15'$.

Fractions 1 and 2 contained *cineol,* which was identified by means of its resorcinol addition product. From fractions 4 and 5 a second fractionation yielded a fraction which boiled between 117 and 120° under 5 mm. pressure. When hydrogen chloride was passed into its dry ethereal solution at -18°, there resulted a hydrochloride which, after recrystallization from methyl alcohol, melted at 79 to 80°. This chlorhydrate is optically inactive. A chlorine determination yielded the following results:

0,4306 g. of substance yielded 0,5928 g. AgCl

Found	Computed for $C_{15}H_{24} \cdot 3\,HCl$
Cl 34,06 p.c.	33,9 p.c.

The supposition that this might prove to be a chlorhydrate of *bisabolene* was verified by further investigation. With the aid of sodium acetate and acetic acid, a sesquiterpene was obtained which after two fractionations revealed the following constants: b.p. 265 to 267° (757 mm.); d_{15} 0,8748; $\alpha_D \pm 0^\circ$;

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[1]) Report of Schimmel & Co. October 1911, 105.

n_{D20° 1,49063. With hydrogen chloride this again yielded the trichlorhydrate melting at 79 to 80°. Owing to the presence of *paraffin,* the residue left upon the distillation of cardamom root oil solidified at about 15°. Recrystallized from alcohol, this paraffin melted at 62 to 63°.

Hence cardamom root oil contains *cineol, bisabolene* and a *paraffin.* Of these the bisabolene is the principal constituent.

Family: ORCHIDACEÆ.

183. Oil of Orchis militaris.

By extraction with ether or alcohol, Crouzel[1]) obtained from *Orchis militaris,* L., a small amount of oil, yellowish in color and of a pleasant, strong odor. The oil could not be obtained by steam distillation.

184. Oil of Vanilla.

Origin and Production. *Vanillin* is the principal aromatic substance of the vanilla, good vanilla beans containing about 2 p.c. However, the value of vanilla cannot be judged alone by its vanillin content. The aromatic substances accompanying the vanillin are of great importance in judging the character of the vanilla aroma.

Composition. W. Busse[2]) suspected that the fruits of inferior vanilla species, the so-called vanillons, and also the fruits of *Vanilla planifolia,* Andr. (family *Orchidaceæ*), cultivated in Tahiti contained piperonal in addition to vanillin. This supposition, however, could not be proved.

In order to study the aromatic principles of Tahiti vanilla apart from vanillin, H. Walbaum[3]) prepared the ethereal extract of 9,2 kilos of these beans. After the vanillin had been removed with sodium hydroxide solution, steam distillation of the residue yielded 7 g. of a light-brown oil having a pleasant characteristic

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[1]) Apotheker Ztg. **16** (1901), 6.

[2]) Arbeiten a. d. Kaiserl. Ges. Amt **15** (1898 to 1899), 107.

[3]) *Über das Vorkommen von Anisalkohol und Anisaldehyd in der Tahiti-Vanille.* Wallach-Festschrift. Gœttingen 1909, p. 649; Report of Schimmel & Co. October **1909**, 142.

odor. The boiling point of the oil, which was heavier than water, was between 105 and 118° (6 mm.). 6 g. of the oil distilled approximately at the boiling point of *anisic alcohol, viz.* at 115 to 118° (6 mm.). Artificial anisic alcohol from anisic aldehyde boiled at 117 to 118° under 5 mm. pressure. Fraction 115 to 118° of this vanilla oil also contained *anisic aldehyde,* the semicarbazone of which melted at 204°. With phenyl*iso*cyanate this fraction yielded an urethane which melted at 93°, and was identical with the urethane obtained from the artificial anisic alcohol. When oxidized with permanganate solution, this fraction yielded anisic acid, m. p. 180°. Besides, the presence of free *anisic acid* was demonstrated in the alkaline liquid from the extract. Piperonal, however, could not be detected. Whether anisic alcohol and anisic aldehyde are components of the aroma of the more valuable Bourbon vanilla has not yet been ascertained.

Family: PIPERACEÆ.

185. Oil of Black Pepper.

Oleum Piperis. — Pfefferöl. — Essence de Poivre.

Origin. The unripe, picked and dried berries of *Piper nigrum,* L. (family *Piperaceæ*), a climbing shrub, which was originally indigenous to southern India, constitute the black pepper of commerce, whereas white pepper consists of the fully matured berries deprived of their outer shell. Pepper is cultivated in southern India, in numerous islands of the Indian archipelago, in the Philippines and the West Indies.

Preparation. Black pepper contains 1 to 2,3 p. c. of volatile oil, which is obtained by steam distillation of the comminuted fruits. Noteworthy in this connection is the formation of ammonia which is also observed during the distillation of several other oils, *e. g.* ginger, pimento, and cubeb oils.

White pepper, also the shells removed in the preparation of white pepper, contain volatile oil¹). Whether this corresponds in its properties with that of the black pepper is not known.

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¹) Lucā (Trommsdorff's Taschenbuch für Chemiker und Pharmaceuten 1822, 81) obtained 1,61 p. c. of oil from white pepper.

Properties. A colorless to yellowish-green liquid with a more or less decided phellandrene odor and a mild, by no means pungent taste, d_{15° 0,87 to 0,916. Polarized light is deviated either to the left or right; $\alpha_D - 10$ to $+3^\circ$; n_{D20° 1,489 to 1,499. In alcohol pepper oil is difficultly soluble, 10 to 15 vol. of 90 p. c. alcohol being required to form a clear solution. On account of the large phellandrene content, the phellandrene reaction with sodium nitrite and glacial acetic acid yields direct results without previous fractionation.

Composition. As shown by the earliest analyses[1]), pepper oil is well-nigh free from oxygen. This result was substantiated by the investigation of L. A. Eberhardt[2]), whose elementary analysis of the oil yielded 87,26 p. c. carbon and 10,81 p. c. of hydrogen. The last fractions of the oil distilling over between 170 to 310° were green in color. Fraction 169,5 to 171° had the composition of a terpene. The fraction boiling at about 176° yielded terpin hydrate when treated with alcohol and acid.

Later, Schimmel & Co. found *phellandrene* in pepper oil[3]). Judging from the lævorotation of the fraction ($\alpha_D - 10^\circ$) from which the nitrite had been prepared, it may be concluded that the phellandrene of pepper oil is *l*-phellandrene.

The preparation of the tetrabromide showed that fraction 176 to 180° examined by Eberhardt contained *dipentene*. It is questionable, however, whether dipentene is an original constituent of the oil, or whether it has resulted from phellandrene upon repeated fractionation[4]).

It also remains undecided to which terpene the terpin hydrate owes its origin. That dipentene may be converted into terpin hydrate is known. Whether phellandrene can be converted into terpin hydrate under suitable conditions has not yet been investigated.

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[1]) An analysis of the oil by Dumas (Liebig's Annalen **15** [1835], 159) agreed with the formula $C_{10}H_{16}$; compare also Soubeiran and Capitaine, Liebig's Annalen **34** (1840), 326.

[2]) Arch. der Pharm. **225** (1887), 515.

[3]) Report of Schimmel & Co. October **1890**, 49.

[4]) With regard thereto Wallach makes the following statement (Liebig's Annalen **287** [1895], 372): Phellandrene-containing oils should not be fractionated at all, or at least not repeatedly, under ordinary pressure, since the hydrocarbon suffers changes when submitted even to this treatment.

From pepper oil O. Schreiner and E. Kremers[1]) have isolated a sesquiterpene, the physical constants of which agreed with those of *caryophyllene*. The proof of their identity was supplied by producing the nitrosite melting at 43°.

In the highest boiling fractions H. Hænsel[2]) found a substance that melted at 138°.

186. Oil of Long Pepper.

Origin. The berries, arranged in dense spikes, of two species of *Piper* or *Chavica, viz., Piper officinarum,* DC. (*Chavica officinarum,* Miq.) and *Piper longum,* L. (*Chavica Roxburghii,* Miq.) are known as long pepper. The former species grows in the islands of the Indian archipelago; the same applies to the latter which is also found in the Philippines, in southern India, Bengal, Malabar and Ceylon. The fruits are collected before maturity and dried.

Production and Properties. Upon distillation, long pepper yields 1 p. c. of a viscid, greenish-yellow oil, specific gravity 0,861 at 15°. It distils over between 250 and 300°, has a mild taste like pepper oil and its odor reminds one of that of ginger[3]).

187. Oil of Piper ovatum.

The leaves of *Piper ovatum,* Vahl, contain a terpene[4]) in addition to other constituents.

188. Oil of Piper Clusii.

According to Herlant[5]), the fruits of *Piper Clusii,* C. DC., Ger. *Aschantipfeffer,* contain 11,5 p. c. of volatile oil.

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[1]) Pharmaceutical Archives **4** (1901), 61.

[2]) Pharm. Ztg. **50** (1905), 412.

[3]) Schimmel's Bericht April **1890**, 48. Comp. also J. Dulong, Journ. de Pharm. II. **11** (1825), 59. — Trommsdorff's Neues Journ. d. Pharm. **11**, I. (1825), 104.

[4]) W. R. Dunstan and H. Garnett, Chem. News **71** (1895), 33; Jahresb. d. Pharm. **1895**, 142.

[5]) Acad. Roy. de Méd. de Belgique, **1894**, 115; Pharmaceutical Journ. III. **25** (1895), 643; Jahresb. d. Pharm. **1895**, 142.

189. Oil of Cubebs.

Oleum Cubebarum. — Cubebenöl. — Essence de Cubèbe.

Origin. The berry-like fruits of *Piper Cubeba,* L. *(Cubeba officinalis,* Miq., family *Piperaceæ),* a climbing shrub, mostly enter commerce from Batavia and Singapore. This shrub is indigenous to the larger Sunda archipelago and is cultivated there as well as in Ceylon and other tropical islands.

As several investigations have shown[1]), commercial cubebs are frequently adulterated with similar fruits. Frequently also the fruits of closely related species are exported, and not infrequently, stems are admixed in considerable amounts. As a means of distinguishing false cubebs from the genuine ones, the sulphuric acid test is recommended. If to the crushed berry, contained in a porcelain dish, some concentrated sulphuric acid be added, the genuine berry shows a beautiful pink color, the false a yellowish-brown color. The difference is still better revealed by the amount of the ether extract obtained, genuine cubebs yielding 20 to 25 p.c., the false article but 15 p.c.

According to Holmes the following varieties yield genuine cubebs: *Piper Cubeba* var. *Rinoe katoentjar* and *P. C.* var. *Rinoe tjaroeloek.* To the spurious cubebs belong the poisonous var. *Rinoe badak,* which differs from the genuine by its mace-like odor, *Piper ribesioides,* Wall., *P. crassipes,* Korth., *P. Lowong,* Blume, *P. venosum,* C. DC. and *P. mollissimum,* Blume, *also Tetranthera citrata,* Nees, *Bridelia tomentosa* and some *Rhamnus*-species. The fruits of *Piper mollissimum* are known in Java by the name of *Keboe*-cubebs. The berries of *P. ribesioides* have a somewhat pungent, those of *P. crassipes* a cajeput-like odor.

Preparation. When distilled with water vapor, comminuted cubebs yield 10 to 18 p.c. of volatile oil. During the process of distillation ammonia is given off to a considerable extent, the cause of which phenomenon is as little known as it is in the case of ginger, pepper, pimento and other drugs.

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[1]) C. E. Sage, Chemist and Druggist 67 (1905), 797. — J. C. Umney and H. V. Potter, *ibidem* 80 (1912), 331, 443. — Perfum. and Essent. Oil Record 3 (1912), 64. — J. Small, Pharmaceutical Journ. 88 (1912), 639. — E. M. Holmes, Perfum. and Essent. Oil Record 3 (1912), 125.

Properties. Cubeb oil is viscid, light-green to bluish-green. It is colorless only when the last portions of the distillate, which are blue, are not added to the oil. It possesses a characteristic cubeb odor and a warm, camphoraceous, finally grating taste. The specific gravity lies between 0,915 and 0,930; α_D —25 to —43°; $n_{D20°}$ 1,4938 to 1,4958.

The solubility of the oil in 90 p.c. alcohol varies considerably. Some oils, presumably those distilled from old cubebs, are soluble in an equal volume of 90 p.c. alcohol. Others require 10 vol. of such alcohol, and in individual cases the solution does not even then become clear.

The bulk of the oil boils[1]) between 250 and 280°. A quantitative fractionation[2]) yielded the following results:

1. from 175 to 250° 9,2 p.c.; 2. from 250 to 260° 26,8 p.c.; 3. from 260 to 270° 47,6 p.c.; 4. from 270 to 280° 7,2 p.c.; above 280° 9,2 p.c.

The fractions obtained by Schimmel & Co. upon distillation from a simple flask (745 mm.) were as follows: 1. 205 to 225° 4 p.c.; 2. 225 to 250° 14 p.c.; 3. 250 to 260° 16 p.c.; 4. 260 to 265° 22 p.c.; 5. 265 to 275° 24 p.c.; 6. 275 to 280° 5 p.c.; 7. Residue 15 p.c.

Oils distilled from old cubebs, which contain the cubeb camphor described below, are somewhat denser than the normal oils, and are recognized by their behavior towards alkali metal. If a piece of bright potassium or sodium be placed in such an oil, it loses its metallic lustre and is covered with a crust, whereas oils distilled from fresh cubebs do not attack the metal[3]).

Composition. From this behavior towards potassium, it is evident that the last-mentioned oils are fairly free from oxygen, and consist of terpenes and sesquiterpenes only, whereas the reaction with the metal is to be attributed to the cubeb camphor.

By means of systematic fractionation a lævogyrate terpene (α_D —35,5°) boiling between 158 to 163° can be separated from

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[1]) In the process of distillation oils containing cubeb camphor are decomposed in part with the formation of water. E. Schær and G. Wyss, Arch. der Pharm. **206** (1875), 322.

[2]) J. C. Umney, Pharmaceutical Journ. III. **25** (1895), 951.

[3]) E. A. Schmidt, Arch. der Pharm. **191** (1870), 23.

the lowest portions of the oil[1]). Presumably this is *pinene* or *camphene*. Moreover *dipentene* (m. p. of dichlorhydrate 48 to 49°) has been found in the distillate below 200°.

As already mentioned, the bulk of the oil distils between 250 and 280° and consists of two lævogyrate sesquiterpenes[2]).

One of these, which boils between 262 and 263°, has a lesser angle of rotation, does not combine with hydrogen chloride, and has not been further investigated.

The second yields a crystalline dihydrochloride[3]) which melts at 118° and is identical with *cadinene*.

Cubeb camphor[4]) is a sesquiterpene hydrate, probably an alcohol of the composition[5]) $C_{15}H_{24}H_2O$. Optically it is lævogyrate, crystallizes in the rhombic system, and, according to several investigators, melts at 65°[6]), 67°[7]) and 70°[8]) respectively. It is rather unstable, for when kept over sulphuric acid it is resolved into sesquiterpene and water[6]). It boils at 148°[9]) with partial splitting off of water. Complete dehydration results upon prolonged heating from 200 to 250°. The sesquiterpene thus obtained has not been further investigated.

The circumstance that cubeb camphor is met with only in old cubebs leads to the supposition that it is formed during the storage by the absorption of water from a moist atmosphere.

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[1]) Oglialoro, Gazz. chim. ital. **5** (1875), 467; Berl. Berichte **8** (1875), 1357.

[2]) Wallach, Liebig's Annalen **238** (1887), 78 ff.

[3]) This was first obtained by Soubeiran and Capitaine (Liebig's Annalen **34** [1840], 323) and recognized as sesquiterpene dichlorhydrate; later it was examined and described by Schmidt, by Schær and Wyss, also by Wallach *(loc. cit.)*.

[4]) Cubeb camphor was first observed by Teschemacher towards the beginning of the nineteenth century. Later it was investigated by C. Müller, Liebig's Annalen **2** (1832), 90, Blanchet and Sell, *Ibidem* **6** (1833), 294, Winckler, *Ibidem* **8** (1833), 203, E. A. Schmidt, Arch. der Pharm. **191** (1870), 23; Berl. Berichte **10** (1877), 188 and E. Schær and G. Wyss, Arch. der Pharm. **206** (1875), 316.

[5]) Schmidt, Schær and Wyss, *loc. cit.*

[6]) Schmidt, *loc. cit.*

[7]) Schær and Wyss, *loc. cit.*

[8]) Winckler, *loc. cit.*

[9]) The boiling point is remarkably low for a sesquiterpene. Possibly it may be explained by decomposition that takes place during boiling.

190. Oil of False Cubebs.

From spurious cubebs[1]), characterized by a striking mace odor and derived from an unknown species of *Piper,* J. C. Umney and H. V. Potter[2]) obtained 4 p.c. of an oil which had a distinct odor of mace: d 0,894; $\alpha_D + 16°$; S. V. 0; E. V. after acetylation 56,1. By way of comparison, genuine cubebs were distilled. These yielded more than twice as much oil, sp. gr. 0,917; optical rotation —43°.

A further decided difference in the two oils was noticeable in their boiling temperatures. The oil from the spurious cubebs began to boil below 160°, one half passed over below 200°, and an additional 30 p.c. between 200 and 270°. The oil from the genuine cubebs contained only 5 p.c. of constituents boiling below 200°; about 85 p.c. passed over between 200 and 257°.

191. Oil of Piper Lowong.

The fruits of *Piper Lowong,* Bl. are also known as spurious cubebs. Upon distillation with water vapor K. Peinemann[3]) obtained 12,4 p.c. of an almost colorless oil, sp.gr. 0,865.

By means of distillation it was resolved into two main fractions, but some decomposition set in, whether it was distilled under ordinary pressure or in vacuum.

Fr. 1, consisting of 40 p.c. of the oil, boiled between 165 and 175°, was water-white; $d_{20°}$ 0,854; $\alpha_D + 22°$.

Fr. 2, consisting of 34 p.c. of the oil, boiled between 230 and 255°; d 0,9218; optically inactive; of a decidedly yellow color.

At 270° an oil of bluish-green color passed over.

From fraction 110 to 148° of a vacuum distillation (17 mm.) small amounts of crystals separated upon standing. Upon re-crystallization from chloroform they melted at 164°[4]). An elementary analysis yielded results that were in agreement with the rather improbable formula $C_{10}H_{16}2H_2O$.

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[1]) See footnote 1 on p. 298.

[2]) Perfum. and Essent. Oil Record **3** (1912), 64.

[3]) Arch. der Pharm. **234** (1896), 238.

[4]) Possibly this substance is identical with the stearoptene of the same melting point which has been found in juniper oil.

192. Oil of Piper Volkensii.

Piper Volkensii, C. DC. occurs abundantly in the moist woods of Usambara. According to R. Schmidt and K. Weilinger[1]) the leaves yield 0,3 p.c. of a volatile oil light-brown in color, of a strong but pleasant odor and possessing the following properties: b. p. 90 to 175° (12 mm.); $d_{20°}$ 0,934; α_D — 8° 24′; n_D 1,5017; ester content (geranyl acetate) 6 p.c.; content of free alcohols $C_{10}H_{18}O$ 14 p.c. By means of phthalic acid anhydride 4 p.c. of a primary alcohol (possibly *citronellol*) was removed from the oil. The principal fraction (70 p.c.) of the saponified oil boiled between 135 and 148° (15 mm.) and added bromine with the formation of a bromide $C_{11}H_{12}O_3Br_2$ that melted at 122°. Reduced with zinc dust and glacial acetic acid the substance $C_{11}H_{12}O_3$ was regenerated. Inasmuch as this product contained 14,1 p.c. methoxyl, the investigator supposed that it might be a *methoxy-safrol.* Besides the principal fraction was found to contain *limene,* a sesquiterpene which has been isolated by Burgess and Page from limette oil, and which is identical, with *bisabolene* (see Vol. I, p. 328). Like this, the sesquiterpene in question added 3 molecules of hydrogen chloride (m. p. of the chlorhydrate 79 to 80°) and 6 atoms of bromine (m. p. of bromide 154°).

193. Matico Oil.

Oleum foliorum Matico. — Maticoöl. — Essence de Matico.

Origin. *Piper angustifolium,* Ruiz et Pavon (*Artanthe elongata,* Miq.), the matico tree, which is indigenous to South America, is regarded as the mother plant of the matico leaves. Inasmuch as the name matico is applied to a number of plants, the leaves of which can scarcely be distinguished from those of the above-named plant, it is not surprising that confusion frequently occurs, and that at times the genuine leaves cannot be had at all. A superficial examination of the matico leaves as imported for a number of years reveals but little external difference from leaves as formerly put on the market, but there is a material difference in the amount and quality of the oil which they yield. The cause of this lies in the fact that at

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[1]) Berl. Berichte **39** (1906), 656.

present no uniform matico leaves, *i.e.* originating from one and the same plant, can be obtained. At the suggestion of Prof. H. Thoms[1]), of Dahlem-Berlin, this vegetable drug has been carefully examined by Professor Gilg, of Dahlem-Berlin, and by Professor Casimir de Candolle, of Geneva. They have ascertained that the commercial drug includes the leaves from the following plants:

Piper angustifolium, Ruiz et Pavon.
Piper camphoricum, C.DC.
Piper lineatum, Ruiz et Pavon.
Piper angustifolium var. *Ossanum,* C.DC.
Piper acutifolium, Ruiz et Pavon var. *subverbascifolium.*
Piper mollicomum, Kunth.
Piper asperifolium, Ruiz et Pavon.

The yield of oil obtained upon distillation from these leaves varied between 0,3 and 6 p.c.

Properties of the Commercial Oils. The oil distilled in former years had a specific gravity of 0,93 to 0,99 and was slightly dextrogyrate. It was a viscid, more or less dark-colored liquid, the odor of which reminded one of both cubebs and mint.

The oil distilled in recent years is light-brown, and varies in its properties, as might be expected from the variation of the leaves from which it is distilled. d_{15° 0,940 to 1,135; $\alpha_D - 27^\circ 28'$ to $+ 5^\circ 34'$; n_{D20° 1,496 to 1,529; A. V. up to 4; E. V. 2,5 to 5,1; E. V. after acetylation 26 to 47. The solubility likewise varies greatly. Frequently the oil is soluble in 3 vols. of 80 p.c. alcohol, but occasionally 25 and more vols. are required. In some instances solution can be effected with 0,3 vol. of 90 p.c. alcohol, in other instances 6 vols. are required and even then the solution may be turbid.

For the properties of the oils distilled from material identified botanically, see p. 306.

Composition of the Commercial Oils. *Matico camphor,* the only known constituent of the older[2]) matico oil, was discovered

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[1]) Arch. der Pharm. 247 (1909), 591 (with 7 illustrations).

[2]) Whether the "old" matico oil from which the matico camphor used to separate, was distilled from the genuine matico leaves from *Piper angustifolium,* Ruiz et Pavon, must remain undecided.

by Flückiger[1]). He obtained it by distilling off that portion of the oil passing over below 200°, when the camphor separated from the residue in hexagonal prisms 2 cm. in length and 5 mm. in thickness. Frequently this camphor crystallized from the oil when cooled.

Matico camphor, when pure, is colorless and tasteless. It is soluble in alcohol, ether, chloroform, benzene, and light petroleum. The melting point of the crystals, which belong to trapazoedric tetartoedric division of the hexagonal system[2]), melt at 94°. Optically active[3]), the $[\alpha]_D$ of the molten camphor, computed for 15° is —29,17°. $[\alpha]_D$ for the chloroform solution at 15° is —28,73°. The specific angle of rotation of the crystals themselves is about eight times as great and, computed for a plate 100 mm. in thickness, is —240°.

Basing his supposition on an elementary analysis, K. Kügler[4]) thought that matico camphor might be identical with ethyl camphor $C_{10}H_{15}(C_2H_5)O$. This, however, is not the case, for, as H. Thoms[5]) has shown, matico camphor is a sesquiterpene alcohol which, when boiled with 25 p.c. sulphuric acid, yields a blue sesquiterpene $C_{15}H_{24}$.

Matico oil distilled in recent years contains no matico camphor. From an oil ($d_{15°}$ 1,077; α_D —0° 25′) distilled by Schimmel & Co.[6]) there separated a substance which, after repeated crystallization from light petroleum, melted at 62° and proved to be *asarone* (m. p. of dibromide 85 to 86°; m. p. of asarylic acid 144°). When oxidized with permanganate, the oil yielded an acid melting at 174° (veratric acid?), seeming to indicate the presence of methyleugenol. It is more probable, however, that the acid in question was a mixture of the apiolic acids to be described below.

While examining the "heavy portion" of matico oil, E. Fromm and K. van Emster[7]) supposed they had isolated as principal

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[1]) Berl. Berichte **16** (1883), 2841.

[2]) Hintze, Tschermak's Mineralogische Mitteilungen **1874**, 227.

[3]) H. Traube, Zeitschrift f. Krystallographie **22** (1893), 47.

[4]) Berl. Berichte **16** (1883), 2841.

[5]) Arbeiten a. d. Pharmaz. Institut Berlin **2** (1905), 125.

[6]) Report of Schimmel & Co. October **1898**, 33.

[7]) Berl. Berichte **35** (1902), 4347.

constituent an unsaturated "matico ether", to which they assigned the formula of a methylbutenyl dimethoxy methylenedihydroxy benzene. Upon oxidation this matico ether yielded an aldehyde, and furthermore an acid.

Later Thoms[1]) took up the investigation of the heavy matico oil and found, besides the matico ether, a hydrocarbon which congealed at — 18°, also another phenol ether. As shown by Thoms, the so called matico ether consists of two apiols, *viz.,* of smaller amounts of *parsley apiol,* and of *dill apiol* (see vol. I. pp. 490 and 491) as principal constituent. Accordingly two isomeric apiolic acids, melting at 175 and 151° respectively, resulted upon oxidation. The parsley apiol was identified by reduction of the isomerized phenol ether with sodium and alcohol, methylation of the resulting phenol, and nitration of the ether. The nitro compound was identical with the 1-propyl-2,3,5-trimethoxy-4-nitrobenzene.

An oil distilled in 1907 by Schimmel & Co. from Peru matico leaves (d_{20° 0,948; α_D — 16° 40′) was likewise examined by H. Thoms[2]). It was free from ketones, contained 0,1 p.c. of phenols and 0,7 p.c. of acids, principally *palmitic acid.* Possibly the oil contained *limonene* and *dill apiol,* but their presence could not be positively established. Fraction 136 to 140° (14 mm.) contained a *sesquiterpene* closely related to cadinene and caryophyllene; judging from its molecular refraction, it belongs to the group of dicyclic sesquiterpenes. Its properties are: b. p. 138 to 139° (17 mm.); d 0,914; n_{D21° 1,512537; n_{C21° 1,50808 (red H-line); mol. refr. 66,52.

Still another oil, distilled by Thoms with a yield of 0,4 p.c. from leaves obtained from a Hamburg firm, revealed very different properties: d 0,9185; α_D — 4° 55′. The oil contained 0,8 p.c. of phenols, 4 p.c. of acids (principally *palmitic acid*), a small amount of aldehydes, likewise *dill apiol.* An examination of the leaves showed that those distilled by Schimmel & Co. differed throughout from those obtained from Hamburg by Thoms. Neither were the leaves of the same parcels uniform.

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[1]) Arch. der Pharm. 242 (1904), 328. — The oil used for this investigation was distilled by Schimmel & Co. from leaves which, according to Prof. Gilg, were genuine matico leaves from *Piper angustifolium,* Ruiz et Pavon.

[2]) *Ibidem* 247 (1909), 591.

Properties and Composition of Matico Oils of known botanical Origin.

194. Oil of Piper angustifolium.

From matico leaves which were pronounced by Gilg and C. de Candolle as undoubtedly genuine, and from *Piper angustifolium,* Ruiz et Pavon, Schimmel & Co. distilled an oil which was examined by Thoms[1]. After standing for several days, a considerable amount of crystals separated, which were identified as *asarone* melting at 60 to 61°. From the first fractions about 10 p. c. of *terpenes* were obtained, however they were not characterized further. From fraction 70 to 71° (13 mm.) *cineol* was removed by means of concentrated solution of arsenic acid. The higher boiling fractions revealed an increasing methoxyl content, and yielded appreciable amounts of asarone, whereas neither of the two apiols mentioned above could be detected.

195. Oil of Piper angustifolium var. Ossanum.

According to H. Thoms[2], the oil of *Piper angustifolium* var. *Ossanum,* C. DC. (yield 0,87 p.c.), contains only traces of phenol ether. When distilled in vacuum, a camphor mixture separated, which melted at 195°, and which presumably consisted of camphor and borneol.

196. Oil from Piper camphoriferum[2].

The species *Piper camphoriferum,* C. DC., heretofore unknown, was described by C. de Candolle in 1909. Its oil was distilled by H. Thoms with a yield of 1,11 p.c. and had the following properties: d_{20° 0,9500; $\alpha_D + 19^\circ 21'$. Under a pressure of 25 mm. about one third of the oil distilled over below 115°. In these fractions the presence of d-*camphor* (m. p. of oxime

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[1] Paper read at the 76. Vers. D. Naturf. u. Ärzte in Breslau; Pharm. Ztg. **49** (1904), 811. — Arbeiten aus dem pharmazeutischen Institut der Universität Berlin **2** (1905), 121.

[2] H. Thoms, *Über Maticoblätter und Maticoöle.* Apotheker Ztg. **24** (1909), 411. — Arch. der Pharm. **247** (1909), 591.

118 to 119°) and of *borneol* (m. p. of phenylurethane 138°) was established. Moreover the oil contained terpenes, acids and phenols, also a *sesquiterpene alcohol* (analysis; $\alpha_D + 5°$; n_D 1,50208).

197. Oil of Piper lineatum.

From the leaves of *Piper lineatum,* Ruiz et Pavon, H. Thoms[1]) obtained 0,44 p.c. of a volatile oil (9,5 g.). Under 15 mm. pressure it boiled chiefly between 140 and 160°, and appeared to consist mainly of sesquiterpenes. The principal fraction had the following constants: d 0,958; $\alpha_D + 8° 45'$. Neither camphor nor phenol ethers could be identified.

198. Oil of Piper acutifolium Ruiz et Pavon var. subverbascifolium.

A few years ago there appeared in the Hamburg market a new variety of leaves labelled as being derived from *Piper Mandoni,* DC. According to H. Thoms[1]), it consisted largely of the leaves of *Piper acutifolium,* Ruiz et Pavon var. *subverbascifolium,* mixed with a few leaves of *Piper mollicomum,* Kunth. and *Piper asperifolium,* Ruiz et Pavon. From these leaves 0,8 p. c. of oil were distilled which had the following constants: $d_{20°}$ 1,10; $\alpha_D + 0° 24'$; $[\alpha]_D + 0° 21,8'$; methoxyl content 21,8 to 22,1 p.c.; acid content + phenols 1,5 p.c. After distillation in vacuum the oil, deprived of its acids and phenols, yielded the following fractions:

				Methoxyl content
I.	b. p. 70 to 148°	15 mm.	5 g.	0 %
II.	b. p. 148 to 153°	15 mm.	11 g.	15,6 %
III.	b. p. 153 to 155°	15 mm.	35 g.	22,5 %
IV.	b. p. 155 to 158°	15 mm.	43 g.	26,3 %
Residue	. . . .		2 g.	

Fraction I was shown to contain *pinene,* characterized by its nitrosochloride. Fraction II, after repeated distillation over sodium, boiled at 147 to 149° (12 mm.), and consisted largely of *sesquiterpenes.* Distilled over sodium, fraction III was shown to contain *dill*iso*apiol* (m. p. 44 to 45°). Fraction IV contained *dillapiol,* characterized by its tribromide melting at 110°.

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[1]) Footnote 2, p. 306.

The same leaves were also distilled by Schimmel & Co. and the oil with a sample of leaves placed at the disposal of Prof. Thoms[1]. The leaves were the same with the exception that their base was rounded on both sides and heart-shaped in outline. Prof. C. de Candolle is of the opinion that these are the lower leaves of plants of *Piper acutifolium*, Ruiz et Pavon, var. *subverbascifolium*, that have not yet reached the flowering stage[2].

The following constants were ascertained: d_{20° 0,939; $\alpha_D + 0^\circ 24'$; $[\alpha]_D + 0^\circ 25{,}5'$. The oil contained 1 p.c. of acid and phenols and a large percentage of sesquiterpenes. The methoxyl content was 4,2 p.c.

The oil was resolved into the following fractions:

I.	b. p. 50 to 150°	80 mm.	50 g.
II.	b. p. 130 to 155°	22 mm.	100 g.
III.	b. p. 155 to 165°	22 mm.	30 g.
IV.	b. p. 165 to 175°	22 mm.	7 g.
Residue			4 g.

Fraction I contained *pinene*, characterized by its nitrosochloride. *Dillapiol*, of which only traces were present, was identified by means of its bromide.

According to an elementary analysis, fraction 117 to 119° (11 mm.; n_D 1,4714) consisted of an *alcohol* $C_{10}H_{16}O$ which causes the decided odor of this matico oil. An additional constituent, making up about 55 p.c. of the oil, is a *sesquiterpene* of the following properties: d_{20° 0,916; $\alpha_D - 10^\circ 50'$; n_D 1,50542.

199. Oil of Artanthe geniculata.

The leaves of *Artanthe geniculata*, Miq. (*Piper geniculatum*, Sw.), a shrub known in Brazil as "false jaborandi", yields a small amount of light-green volatile oil with a spicy, somewhat mint-like odor, and a pungent, burning taste[3].

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[1] Report of Schimmel & Co. April **1909**, 70; October **1909**, 78.

[2] H. Thoms, Apotheker Ztg. **24** (1909), 412. — Arch. der Pharm. **247** 1909), 608.

[3] T. Peckolt, Pharm. Rundsch. (New York) **12** (1894), 286.

200. Oil of Betel Leaves.

Oleum foliorum Betle. — Betelöl. — Essence de Bétel.

Origin. The custom of betel chewing, which is common throughout India, the entire Malay archipelago, also in Southern China, consists in chewing a betel leaf *(Sirih)* from *Piper Betle,* L. (*Chavica Betle,* Miq.) together with lime, some gambier (from *Uncaria Gambir,* Roxb.), and a piece of areca or pinang nut (from *Areca Catechu,* L.)[1]. The betel leaves owe their spicy, burning taste to a volatile oil which has been distilled repeatedly, but which has found no practical application thus far[2].

Properties. Betel oil is a light yellow to dark brown liquid of an aromatic, somewhat creosote-like odor that also reminds one of tea, and has a sharp, burning taste. The specific gravity varies between 0,958 and 1,057, the oils from fresh leaves being less dense and lighter in color than those obtained from dry material.

The optical rotation has been determined for only six oils, four of which were lævogyrate (α_D up to $-1°55'$) and two dextrogyrate (α_D up to $+2°53'$).

The alcoholic solution of betel oil yields a green to blue-green color with ferric chloride.

Origin, yield, physical properties and composition of the betel oils examined thus far are specified in the following table (p. 310).

Composition. Of the two phenols which have so far been found in betel oil, *viz., betelphenol* and *chavicol,* the first only is contained in all oils and may therefore be regarded as the characteristic constituent of the oil. Chavicol, which has been found only in the Java oil, does not occur in Manila or Siam betel oil.

Betelphenol[3]) (Chavibetol) $C_{10}H_{12}O_2$ (comp. vol. I, p. 480) is isomeric with eugenol and contains the same side-chains, but in different position.

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[1] The details of the practice of betel chewing, also the several ingredients of the "betel box", which well-nigh every Malay family possesses, have been described by A. Tschirch in his *„Indische Heil- und Nutzpflanzen"* (Berlin 1892) p. 138.

[2] As to the cultivation of the betel plant see H. Gilbert, Journ. d'Agriculture tropicale 11 (1911), 227; Report of Schimmel & Co. October 1911, 22.

[3] Bertram and Gildemeister, *loc. cit.*

	Origin, material distilled and yield	Sp. gr.	α_D	Constituents
I.	*Siam*[1]). Leaves dried on hot plates. Yield 0,6 %.	1,024 at 15°	—	Betelphenol, cadinene.
II.	*Siam*[1]). Leaves dried by exposure to sun. Yield 0,9 %.	1,020 at 15°	—	
III.	*Manila*[2]). Fresh leaves. Yield 0,127 %.	1,044 at 15°	—	Betelphenol.
IV.	*Java*[3]). Fresh leaves.	0,959 at 27°	— 1° 45′	Chavicol, betelphenol, sesquiterpene.
V.	*Java*[4]). (Probably fresh leaves)	0,958 at 15°	+ 2° 53′	Not examined.
VI.	*Bombay*[5]). Fresh leaves.	0,9404 at 28°	Slightly lævo-gyrate	
VII.	*Manila*	1,0566 at 15°	— 1° 10′	55 % phenols; sol. in 3 vol. 70 p.c. alc.
VIII.	*Manila*	1,0551 at 15°, n_{D20° 1,52146	+ 0° 40′	52 % phenols; sol. in 1,7 vol. 70 p.c. alcohol.
IX.	*Java*[6])	1,0325 at 15°	— 1° 55′	Betelphenol, allylpyrocatechol, cineol, eugenolmethylether, caryophyllene.

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[1] J. Bertram and E. Gildemeister, Journ. f. prakt. Chem. II. **39** (1889), 349. — Schimmel's Bericht April **1888**, 8; April **1889**, 6; Report of Schimmel & Co. October **1889**, 6; April **1890**, 6; October **1891**, 8.

[2] Report of Schimmel & Co. April **1891**, 14 and October **1891**, 8.

[3] J. F. Eykman, Berl. Berichte **22** (1889), 2736.

[4] Report of Schimmel & Co., October **1893**, 49.

[5] D. S. Kemp, Pharmaceutical Journ. III. **20** (1890), 749.

[6] Report of Schimmel & Co. October **1907**, 16.

It is a strongly refractive liquid of peculiar, not unpleasant, persistent betel odor, which differs materially from that of the closely related eugenol. When pure, betelphenol boils without appreciable decomposition at 254 to 255° (131 to 132° under 12 to 13 mm., 107 to 109° under 4 mm. pressure); $d_{15°}$ 1,067 to 1,069; $n_{D20°}$ 1,54134. In alcoholic, but not in aqueous, solution it yields an intensely blue-green color with ferric chloride.

For the identification of betelphenol the preparation of its benzoyl compound, crystallizing in laminæ and melting at 49 to 50°, is resorted to. Acetylbetelphenol boils at 275 to 277°, melts at — 5°, and upon oxidation with permanganate is oxidized to acet*iso*vanillic acid, which melts at 207°.

Chavicol[1]), also a phenol, the presence of which in the Java betel oil has been definitely established by Eykman, is *p*-hydroxyallyl benzene (comp. Vol. I, p. 475). It boils at 237°; sp. gr. 1,041 at 13°. Its aqueous solution is colored intensely blue by ferric chloride, the alcoholic solution becomes but faintly blue.

An oil, distilled in Java by de Vrij and examined in the laboratory of Schimmel & Co.[2]), was found to contain a second phenol which is probably identical with chavicol. Its benzoyl compound crystallized in long needles, and melted at 72 to 73°.

Another oil, distilled in Manila from fresh leaves and examined in the laboratory of Schimmel & Co.[3]), contained no phenol other than betelphenol. The phenol separated from the sodium hydroxide solution, boiled uniformly between 128 and 129° (11 mm.) and yielded exclusively the benzoyl derivative of betelphenol crystallizing in laminæ and melting at 50°.

An additional constituent is *cadinene* $C_{15}H_{24}$. By means of its dihydrochloride melting at 118°, it was identified in the Siam betel oil[4]) only.

Java oils, distilled from fresh leaves, contain an appreciable amount of lower boiling constituents, the composition of which has not yet been ascertained. From fraction 173 to 190°

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[1]) Eykman, *loc. cit.*

[2]) Report of Schimmel & Co. April 1890, 7.

[3]) *Ibidem* October 1891, 8.

[4]) Bertram and Gildemeister, *loc. cit.*

Eykman[1] failed to isolate a pure terpene of constant boiling point and to identify it with one of the known terpenes. Presumably several terpenes are present, but no pinene. Fraction 173 to 175° (d_{16° 0,848; $\alpha_D - 5^\circ 20'$) yielded neither a solid bromide nor a crystalline chlorhydrate. Fraction 190 to 220° contains a substance with mint-like odor (menthone or menthol?).

An oil distilled from dried Siam leaves was totally devoid of these lower fractions, only a few drops passing over below 200°. On the one hand, the absence of terpenes in this oil may be regarded as being explained satisfactorily by the character of the material from which it was distilled. On the other hand, the cause of the absence of chavicol in Siam and Manila oils, and its occurrence in Java oils may possibly be accounted for by the varying conditions of climate and soil of the countries of origin.

A new phenol which had not been found so far in any oil, was observed by Schimmel & Co.[2] in the Java betel oil marked IX on p. 310. During fractionation of the phenols, separated by means of their sodium compounds, a substance distilled over between 137 to 139° (4 mm.), which congealed when cooled and consisted of allylpyrocatechol (elementary analysis; m.p. 48 to 49°). For its properties and derivatives see Vol. I, p. 480.

The same oil also contained a lævogyrate *terpene,* which boiled between 155 and 162°, but which was not further characterized, *cineol* (m.p. of iodol compound 112°), *eugenolmethylether* (m.p. of veratric acid 179°), and *caryophyllene* (m.p. of nitrosate 158°). A fraction with the properties of cadinene was not observed in this oil.

201. Oil of Kissi Pepper.

According to A. Barillé[3], the seeds of *Piper Famechoni,* Heck., indigenous to French Guiana, yield, upon extraction with ether, 4,47 p.c. of a volatile oil of an agreeable odor. The bulk of it boils between 255 and 260°.

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[1] *Loc. cit.*

[2] Report of Schimmel & Co. October **1907**, 16.

[3] Compt. rend. **134** (1902), 1512. — Journ. de Pharm. et Chim. VI. **16** (1902), 106.

202. Oil of Potomorphe umbellata.

The fresh leaves of *Potomorphe umbellata,* Miq. *(Piper umbellatum,* L., family *Piperaceæ)* contain 0,05 p.c. of an oil[1]) the odor and taste of which remind one of pepper.

203. Oil of Ottonia Anisum.

12 kilos of the wild jaborandi, *Ottonia Anisum,* Spreng. *(O. Jaborandi,* Vell.; *Serronia Jaborandi,* Guill., family *Piperaceæ)* yielded 10,54 g. (= 0,088 p.c.) of a viscid, volatile oil with a sp.gr. of 1,0356. It possesses a peculiar, somewhat pepper-like odor and a strongly burning, benumbing taste[2]).

Family: SALICACEÆ.

204. Oil of Poplar Buds.

Origin. The leaf-buds of the black poplar, *Populus nigra,* L. (family *Salicaceæ*) were formerly kept in apothecary shops under the name of *Oculi Populi,* and were used in the preparation of an ointment. Upon distillation they yielded about 0,5 p.c. of volatile oil.

Properties. Oil of Poplar buds is pale-yellow to light-brown in color, and has an agreeable odor somewhat suggestive of chamomile. It is insoluble in 70 to 90 p.c. alcohol, but occasionally yields a clear solution with $^1/_2$ vol. and more of 95 p.c. alcohol. At times 3,5 to 10 vol. of 95 p.c. alcohol are required, and even then flocculent precipitation of paraffin takes place. d 0,890 to 0,905; $\alpha_D + 1° 54'$[3]) to $+6°$; A.V. 2 to 11; E.V. 8 to 14; E.V. after acetylation 18 to 53[4]).

Composition. Poplar-bud oil distils between 255 and 265°[3]). According to J. Piccard[5]) it consists principally of a hydrocarbon $(C_5H_8)x$, boiling between 260 and 261°. Basing his conclusion

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[1]) T. Peckolt, Pharm. Rundsch. (New York) 12 (1894), 241.

[2]) T. Peckolt, *ibidem* 287.

[3]) Schimmel's Bericht April 1887, 86.

[4]) Report of Schimmel & Co. October 1908, 103; October 1912, 95.

[5]) Berl. Berichte 6 (1873), 890 and 7 (1874), 1486.

on a determination of the vapor density according to Dumas, he regards the compound as a diterpene $C_{20}H_{32}$.

According to the more recent investigations by F. Fichter and E. Katz[1]), it has been ascertained that the bulk of the oil consists of a fraction 263 to 269°, the vapor density of which, determined according to Victor Meyer with the Lunge gas-volumeter, gave results that agreed with a sesquiterpene $C_{15}H_{24}$. It was characterized by means of its nitrosochloride, nitrolpiperidine, and nitrolbenzylamine bases, nitrosate, &c., all of which were humulene derivatives.

E. Deussen[2]) has recently demonstrated that humulene is identical with *α-caryophyllene,* hence this is to be regarded as a constituent of poplar bud oil. Inasmuch as the corresponding fractions of hop oil yield results that are more nearly quantitative than those obtained with poplar bud oil, it is assumed that the latter contains still another sesquiterpene. Moreover, the dextrorotation of the poplar bud sesquiterpene may possibly be attributed to a contamination of the α-caryophyllene with an optically dextrogyrate hydrocarbon.

In addition, poplar bud oil contains about 0,5 p. c. of *paraffin* melting between 53 and 68°, which is presumably of the formula $C_{24}H_{50}$.

The substance that imparts its agreeable odor to the oil passes over with the lower fractions when distilled.

Family: MYRICACEÆ.

205. Oil of Dutch Myrtle Leaves.

Upon the distillation of the fresh leaves of *Myrica Gale,* L. (Ger. *Gagelblätter,* family *Myricaceæ*), Rabenhorst[3]) obtained 0,65 p. c. of a brownish-yellow oil, the specific gravity of which was 0,876. It congealed partly at 17,5° and completely to a crystalline mass at 12,5°. G. Laloue[4]) distilled, with water,

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[1]) Berl. Berichte **32** (1899), 3183.

[2]) Journ. f. prakt. Chem. II. **83** (1911), 483.

[3]) Repert. Pharm. **60** (1837), 214. — Gmelin, *Organ. Chemie,* IV. ed. vol. 7, p. 335.

[4]) Berichte von Roure-Bertrand Fils April **1910**, 61. — Bull. Sciences pharm. **17** (1910), 253.

branches which had been obtained from the neighborhood of Nantes, France. Computed with reference to fresh material he obtained 0,0369 p.c. of oil that had separated from the water. By shaking out the cohobation water, he obtained an additional 0,0083 p.c., making a total of 0,045 p.c. of oil. The oil which had separated of its own accord was greenish-yellow in color, possessed a myrtle-like odor and gave the following constants: $d_{25°}$ 0,8984; $\alpha_{D20°}$ — 5° 16′; A. V. 3,48; E. V. 15,5; E. V. after acetylation 50,23. It was soluble in one-half volume of 90 p.c. alcohol, but after the addition of 5 vol. the solution became turbid; insoluble in 80 p.c. alcohol. When cooled, the oil became turbid at + 5°, became completely opaque at — 5°, but remained limpid and changed neither appearance nor consistence at — 17°.

The oil has been investigated pharmacologically by Chevalier¹). He showed that it is rather poisonous, hence the use of the leaves of *Myrica Gale* as emmenagogue and as abortive, to which use they are put in western France, is not without danger. In intraperitoneal injections the fatal dose for guinea-pigs was 1 cc. per kilo body weight. A dog died with symptoms of total paralysis after a dose of 12 cgr. pro kilo body weight.

An oil distilled by S. S. Pickles²) from a mixture of fresh leaves and twigs (yield 0,076 p.c.) was pale-yellow and gave the following constants: $d_{15°}$ 0,915; α_D — 5° 17′; A.V. 7,0; E.V. 24,7. Another oil obtained from partly dried material, consisting almost entirely of leaves (yield 0,203 p.c.), had the following properties: $d_{15°}$ 0,912; α_D — 11° 26′; A. V. 4,0; E. V. 19,2; E. V. after acetylation 56,4.

The leaf oil contained about 0,75 p.c. of a *paraffin* $C_{29}H_{60}$, which melted at 63 to 64°, and which separated in the cold upon the addition of methyl alcohol. By means of a solution of sodium carbonate, Pickles isolated about 2,5 p.c. of fatty acids, principally *palmitic acid* (m.p. 62°). Other constituents are *cineol* (m.p. of iodol compound 112 to 114°) and *dipentene* (m.p. of tetrabromide 124 to 125°). Of cineol and terpenes the oil contains about 50 p.c. In addition to esters of high molecular fatty acids, the oil presumably consisted of a mixture of

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¹) Bull. Sciences pharm. **17** (1910), 258.

²) Journ. chem. Soc. **99** (1911), 1764.

high boiling alcohols and sesquiterpenes, which Pickles did not examine farther for want of sufficient material.

206. Oil of Dutch Myrtle Flowers.

From the catkins of *Myrica Gale,* C. J. Enklaar[1]) distilled 0,4 to 0,6 p. c. of volatile oil (d_{15° 0,899; α_D — 5° 36′). The lowest boiling fraction (b. p. 162 to 163° under 760 mm.; d_{15° 0,862; α_D — 25° 34′) contained *pinene.* However, Enklaar could not decide whether it was α- or β-pinene. A nitrosochloride was not obtained. Upon oxidation with potassium permanganate, an acid melting at 102 to 103° was obtained, which was probably *i*-pinonic acid or impure *l*-nopinic acid. d-*α-phellandrene* also appears to be present in the oil (m. p. of the nitrite 112 to 113°). The presence of *cineol* was proven by means of its hydrobromide and its iodol compound (m. p. 114°). Among the high boiling constituents of the oil there was found a *sesquiterpene* (b. p. 150 to 152° under 17 mm., 263 to 265° under 760 mm. pressure; d_{15° 0,928; α_D — 4° 30′), possibly *caryophyllene.* Finally the high boiling portions of the oil contain a *solid,* difficultly volatile *substance,* which crystallizes from alcohol in long needles, and possesses the agreeable odor peculiar to the plant.

207. Bayberry Oil.

Myrica cerifera, L. (Ger. *Wachsmyrte*), is a North American shrub that grows to a height of 1 to 3 metres. Its leaves contain 0,021 p. c. of a volatile oil[2]) of a greenish color and a very agreeable, aromatic, spicy odor. Sp. gr. 0,886; α_D — 5° 5′.

A bayberry oil distilled by F. Rabak[3]) revealed the following constants: d 0,9168; $[\alpha]_D$ — 1,5°; n_{D25° 1,4945; A. V. 3,5; E. V. 21; E. V. after acetylation 58. The oil was soluble in one-half its volume of 90 p. c. alcohol, but the solution became turbid upon the addition of 2 or more volumes. It was insoluble in 80 p. c. alcohol. The yield (computed with reference to the fresh material?) was 0,015 p. c.

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[1]) Chem. Weekblad 9 (1912), No. 11.

[2]) Report of Schimmel & Co. October 1894, 70. — Comp. also Hambright, Americ. Journ. Pharm. 35 (1863), 193.

[3]) Midland Drugg. and pharm. Review 45 (1911), 484.

208. Sweet Fern Oil.

The leaves of the North American *Myrica asplenifolia,* Endl. (*Comptonia asplenifolia,* Ait.), yields upon distillation 0,08 p. c. of a volatile oil. It has a strong spicy, cinnamon-like odor. Sp. gr. 0,926. When cooled in a freezing mixture the oil congeals[1].

Family: *JUGLANDACEÆ.*

209. Oil of Walnut Leaves.

The aromatic odor of the fresh leaves of *Juglans regia,* L. (family *Juglandaceæ*), is due to a volatile oil which they contain. Upon distillation, fresh German leaves yield 0,012[2] to 0,029 p.c.[3] of a yellowish-green to brown oil, with a tea- and ambra-like odor, and which upon cooling separates paraffin or becomes solid. d_{30° 0,9037[2] to 0,9137[4]; α_D inactive[4]; A.V. 9,3[4] to 16,8; E.V. 18,4[2] to 27[4]. It is soluble in 90 p.c. alcohol with the separation of paraffin which, after repeated recrystallization from alcohol, melts at 61 to 62°.

Of somewhat different behavior, especially as to its optical rotation, was an oil distilled by Schimmel & Co.[4] in Barrême, southern France. The oil which separated spontaneously from the aqueous distillate was examined by itself, as was also the oil obtained by shaking out the aqueous distillate with ether, finally the total product was obtained by pouring the two oils together.

	Yield	d_{30°	α_D	n_{D25°	A.V.	E.V.	E.V. after acetyl.
83 % Principal oil .	0,0072 %	0,9174	−17°36′	1,49177	3,7	9,3	—
17 % Cohobated oil	0,0015 %	0,9231	−16°12′	1,49366	4,7	9,7	—
100 % Total oil . .	0,0087 %	0,9185	−17° 0′	1,49215	—	—	98,5

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[1] Report of Schimmel & Co. October 1890, 61.

[2] H. Hænsel, Chem. Zentralbl. 1907, II. 1620.

[3] Report of Schimmel & Co. October 1890, 61.

[4] *Ibidem* April 1912, 131.

Family: BETULACEÆ.

210. Oil of Sweet Birch.

Oleum Betulæ lentæ. — Birkenrindenöl (Wintergrünöl). — Essence de Betula.

Origin and Production. Sweet birch, black birch or cherry birch, *Betula lenta,* L. (family *Betulaceæ*), is a tree 15 to 20 m. in height that grows in good forest soil throughout southern Canada and the northern United States, westward as far as Minnesota and Kansas and southward as far as Georgia and Alabama.

The oil is mostly distilled in Tennessee, in the north western counties of Ashe, Watanga and Mitchell, also in the south eastern part of the state. As a rule there are about 10 to 20 trees on an acre. These the distiller occasionally buys for 10 cts. a piece.

The trees, which have a diameter of 12 to 24 inches, are cut down while the sap is in the trunk and are deprived of their bark. This is comminuted with the aid of a cutting machine. Frequently, so-called mountain tea or wintergreen is added, occasionally the twigs are also used for distillation.

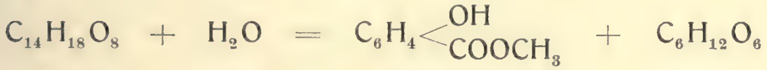
The still is of the most primitive type. It is made of planks and is about 2½ ft. wide, 3 ft. deep and 7 to 8 ft. long. The bottom consists of galvanized iron, is nailed to the wooden box and made watertight. The still is placed on a stone foundation which serves as fire-box. The bark rests on a false bottom of laths, which is about 4 in. above the iron bottom. Iron pipes about one inch in diameter connect the still with the condenser, which is fed by the water of a creek. The receiver consists of a tin can which stands in a larger container. The water which flows over and is saturated with oil is returned to the still by a separate pipe.

The principal season for distillation is from May to the latter part of September.

As soon as the distiller has obtained about 2 to 10 lbs. of oil, he sells it to the nearest general merchant. Occasionally he goes somewhat farther in order to obtain a better price. These merchants send the oil either direct to New York or sell it to herbalists.

The oil enters the market at Wilkesborro (North Carolina), Lenoir, Elk Park and Marion, Virginia, also at Abingdon, Virginia and Johnson City, Tennessee[1].

W. Procter[2] had already observed that the volatile oil does not occur as such in the bark, but results by the interaction of two substances in the presence of water, similar to the formation of bitter almond oil, of mustard oil and other ferment oils. According to later investigations, these two substances were found to be the enzyme betulase[3] and the glucoside gaultherin[4] which crystallizes with 1 mol. of water. The latter is hydrolyzed to sugar and methyl salicylate.



$$C_{14}H_{18}O_8 + H_2O = C_6H_4{<}\begin{matrix}OH\\ COOCH_3\end{matrix} + C_6H_{12}O_6$$

Gaultherin Water Methyl salicylate Glucose.

These changes must be taken into consideration in the production of the oil. According to Kennedy[5] a twelve hour's maceration should precede the distillation in order to obtain a satisfactory yield. Every ton of 2240 lbs. of birch bark should yield about 5 lbs. of oil = 0,23 p.c., whereas a like amount of wintergreen leaves yields about 18 lbs. of oil = 0,83 p.c. A more rationally conducted distillation, however, may yield as much as 0,6 p.c. of oil.

In order to ascertain the most favorable conditions for the production of the oil, E. F. Ziegelmann[6] made a series of experiments. The best results were obtained when working with small amounts, 0,62 p.c. being obtained after a twelve hour maceration period at room-temperature. Longer standing did not influence the yield. If the maceration was conducted at 40 to 50°, the yield was somewhat smaller. When distilled without previous maceration, the yield was much smaller. When working with larger amounts, birch bark yielded 0,306 p.c. Upon

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[1] Report of Schimmel & Co. October **1900**, 64.

[2] Americ. Journ. Pharm. **15** (1843), 241.

[3] A. Schneegans, Journ. d. Pharm. v. Elsaß-Lothr. **23** (1896), No. 17; Chem. Zentralbl. **1897**, I. 326.

[4] A. Schneegans and J. E. Gerock, Arch. der Pharm. **232** (1894), 437.

[5] Americ. Journ. Pharm. **54** (1882), 49.

[6] Pharm. Review **23** (1905), 83.

cohobation of the aqueous distillate an additional amount of 0,076 p.c. of oil was obtained.

Properties. Inasmuch as sweet birch oil and wintergreen oil have practically the same properties, the two oils were not always kept apart formerly, moreover birch bark and wintergreen leaves were frequently distilled together. Since 1906, the Pure Food and Drugs Act demands that they be kept distinct in the United States, the designation of sweet birch oil as wintergreen oil being regarded as a violation of the law.

Sweet birch oil is a colorless or yellowish liquid which is at times colored red by traces of iron. As to odor and taste it can scarcely be distinguished from methyl salicylate; its odor differs, however, materially from that of *Gaultheria procumbens*. The sp. gr. fluctuates between 1,180 and 1,188[1]. Whereas gaultheria oil is slightly lævogyrate, sweet birch oil is optically inactive. With 5 to 8 vol. of 70 p.c. alcohol, it yields a clear solution at ordinary temperature. In moderately concentrated solution of potassium hydroxide, it dissolves readily with the formation of the readily soluble so-called potassium ester salt. From this solution it can be separated unchanged upon the addition of acids. The so-called sodium ester salt, however, is difficultly soluble. When heated with an excess of alkali, both ester salts are saponified.

Water shaken with sweet birch oil yields a deep violet color with ferric chloride. When distilled over a direct flame, sweet birch oil passes over between 218 and 221°.

Composition. As already pointed out, no distinction was formerly made in commerce between sweet birch oil and gaultheria oil, indeed this holds true to a large extent to-day. Hence it is doubtful whether the salicylic acid of A. Cahours[2] was discovered in a sweet birch oil or in a gaultheria oil. However, it may be definitely assumed that Procter made a distinction

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[1] In connection with oils prepared by himself, Ziegelmann observed d_{15° 1,1578 to 1,1786 (d_{25° 1,1502 to 1,171), which low densities are probably due to some extraordinary circumstance in the preparation. Oils with such low specific gravities never occur when they are distilled on a large scale.

[2] Ann. de Chim. et Phys. III. **10** (1844), 327. — Liebig's Annalen **48** (1843), 60 and **52** (1844), 327.

between the two oils. It is also certain that Cahours worked with an adulterated oil, for he found 10 p.c. of a terpene boiling at 160° (presumably turpentine oil), which he designated gaultherilene. From recent investigations, however, made with unquestionably genuine oils, it is evident that neither of the oils contains terpenes.

According to F. B. Power and C. Kleber[1]), sweet birch oil consists of *methyl salicylate*[2]) to the extent of 99,8 p.c.[3]). If the oil, diluted with ether, is shaken repeatedly with 7½ p.c. potassium hydroxide solution, the methyl salicylate passes into aqueous solution as potassium methyl salicylate, and can thus readily be separated from the other components of the oil, which remain in the ethereal solution.

The semi-solid ethereal residue can be separated, by steam distillation, into two parts. The non-volatile part congeals upon cooling. It is readily soluble in ether, difficultly in alcohol, crystallizes in laminæ, is not acted upon by sulphuric or nitric acids, and consists of a paraffin. Judging from its elementary analysis and its melting point, which lies at 65,5°, it should be regarded as *triacontane*, $C_{30}H_{62}$. The part which is volatile with water vapor is soluble in 80 p.c. alcohol, and boils at 230 to 235° (under 25 mm. pressure at about 135°). Its composition is expressed by the formula $C_{14}H_{24}O_2$. It is an ester which upon saponification is resolved into its components, an alcohol $C_8H_{16}O$ and an acid $C_6H_{10}O_2$.

Examination. Inasmuch as the oils of sweet birch and gaultheria are the heaviest of all known oils, the presence of foreign oils or petroleum invariably produces a lowering of the specific gravity. Most adulterants also reduce the solubility of the oil in 70 p.c. alcohol. A convenient means of detecting adulteration is afforded by the property of methyl salicylate to form with

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[1]) Pharm. Rundsch. (New York) **13** (1895), 228.

[2]) The assertion made by H. Trimble and H. J. M. Schröter (Americ. Journ. Pharm. **61** [1889], 398 and **67** [1895], 561), that benzoic acid, ethyl alcohol and a sesquiterpene $C_{15}H_{24}$ are contained in gaultheria oil and in sweet birch oil has been proved to be wrong, as shown by Power (Pharm. Rundsch. [New York] **7** [1889], 283), also by Power and Kleber (*Ibidem* **13** [1895], 228).

[3]) Ziegelmann *(loc. cit.)* found but 90,2 to 97,83 % ester in oils distilled by himself. These low results are presumably due to incomplete saponification.

potassium hydroxide, a water-soluble salt ($C_6H_4[OK]COOCH_3$). The test is carried out in the following manner: To 1 cc. of either sweet birch oil or wintergreen oil to be tested, 10 cc. of a 5 p.c. potassium hydroxide solution are added and the mixture is shaken. If the oil is pure, a clear, colorless or but slightly yellow-colored liquid results. If foreign oils or petroleum, chloroform, &c. be present, the mixture becomes turbid, and after standing for some time, oily drops will separate either at the surface or at the bottom. In this manner the presence of 5 p.c. foreign, non-phenolic constituents can be detected. Inasmuch as the odor of methyl salicylate disappears completely upon saponification, the particular kind of adulterant can mostly be recognized by the odor of the saponified oil.

The methyl salicylate content can be determined either by separating and weighing the salicylic acid, or volumetrically.

For the quantitative determination by weight¹) 1,5 to 2 g. of oil are saponified in a flask of 50 cc. capacity with a slight excess of concentrated sodium hydroxide solution. The liquid is then transferred to a separating funnel, an excess of hydrochloric acid is added and the salicylic acid set free is shaken out with ether. In order to remove traces of sodium chloride from the ethereal solution, this is shaken out with water. The ether is evaporated from a tared dish on a water-bath. The remaining salicylic acid is weighed after it has been brought to constant weight in a desiccator over sulphuric acid.

This method of determination presupposes a pure oil, since foreign admixtures, such as sassafras oil, would also enter the ethereal solution and, upon evaporation of the ether, would be but partly volatilized and partly weighed with the salicylic acid.

The amount of salicylic acid can also be determined according to the method of J. Messinger and G. Vortmann²). It is based on the fact, that, in the presence of much alkali, iodine converts salicylic acid into diiodosalicylic acid. Using an iodine solution of known strength, the excess of iodine can be titrated

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¹) B. H. Ewing, Proceed. Americ. Pharm. Assoc. **40** (1892), 196.

²) Berl. Berichte **22** (1889), 2321 and **23** (1890), 2755. As to the usefulness of the method comp. W. Fresenius and L. Grünhut, Zeitschr. f. anal. Chem. **38** (1899), 292; also J. Messinger, Journ. f. prakt. Chem. II. **61** (1900), 237.

with volumetric thiosulphate solution. The reaction is expressed by the following equations:—

$$C_6H_4(OH)COOK + 3KOH + 6I = C_6H_2I_2(OI)COOK + 3KI + 3H_2O.$$

The application of this method to wintergreen oil is recommended by E. Kremers and M. James[1]).

A weighed amount of oil is saponified with a normal potassium hydroxide solution, care being taken that for every molecule of methyl salicylate at least 7 mol. of potassium hydroxide are used. The liquid is then diluted with water to exactly 250 or 500 cc. Of this solution 5 or 10 cc. are transferred to a flask and heated to about 60°. Sufficient $^1/_{10}$ normal iodine solution is then added until the decidedly yellow color remains permanent. Upon shaking, a deep red precipitate is produced. After cooling, the solution is acidulated with dilute sulphuric acid and diluted with water to 250 or 500 cc. In an aliquot part of the filtrate, about 100 cc., the excess of iodine is titrated with $^1/_{10}$ normal sodium thiosulphate solution.

$$\frac{1\text{ mol. methyl salicylate}}{6\text{ atoms iodine}} = \frac{151{,}64}{759{,}2} = 0{,}19974314$$

By multiplying the amount of iodine consumed with the factor 0,19974314, the corresponding amount of methyl salicylate can be computed and from this its percentage in the oil.

The simplest way to ascertain the methyl salicylate content of the oil is to determine its ester value, from which the amount of ester can be computed (Comp. Vol. I, p. 574)[2]). In this connection it should be noted that the oil should be boiled with a large excess of alkali (30 cc. alcoholic half-normal potassium hydroxide to about 1,5 g. oil) for 2 hours, otherwise results that are too low are likely to be obtained.

A good oil contains at least 98 p.c. of methyl salicylate.

211. Oil of Birch Buds.

Origin and Production. The resinous leaf buds of the white birch, *Betula alba,* L., contain a relatively large amount of an

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[1]) *Loc. cit.*

[2]) Compare also E. Kremers and Martha M. James, Pharm. Review 16 (1898), 130.

agreeably smelling, balsamic oil, which was first prepared by H. Hænsel[1]). Upon distillation, the buds yield 4 to 6,5 p.c. of oil.

Properties[2]). Oil of birch buds is a yellow, somewhat viscid liquid, which, even at room temperature, is often permeated with crystals of paraffin. Upon cooling the oil at first separates *paraffin* crystals, finally it congeals to a solid mass. d_{15° 0,962 to 0,979; α_D — 2 to — 14°; A.V. 1 to 4; E.V. 35 to 75; E.V. after acetylation 140 to 180. Soluble in 1 to 2 vol. of 80 p.c. and in 0,25 vol. of 90 p.c. alcohol. At times the solution is clear, frequently, however, paraffin separates. The latter separation always takes place upon the addition of more solvent.

Composition. According to H. von Soden and F. Elze[3]) the oil contains a sesquiterpene alcohol which they have designated *betulol*. For the isolation of the betulol its acid phthalic ester was prepared. It results readily when the oil, in benzene solution, is heated with phthalic anhydride. The pure betulol obtained by saponification of the phthalic acid compound with alcoholic potassium hydroxide had the following constants:

B.p. 138 to 140° under 4 mm., 284 to 288° under 743 mm. pressure with partial decomposition; d_{15° 0,975; α_D — 35°; soluble in 3 parts of 70 p.c. alcohol. Its composition is presumably $C_{15}H_{24}O$.

When boiled with acetic anhydride, betulol is acetylated quantitatively. The acetate boils at 142 to 144° (4 mm.); d_{15° 0,986. The content of free betulol of the oil investigated was about 47 p.c.

Another oil contained 73,2 p.c. of total betulol, of which 29,6 p.c. was esterified and 47,1 p.c. free. The esterified betulol is partly bound to acetic acid, partly to formic acid[4]).

212. Oil of Birch Leaves.

Upon the distillation of birch leaves from *Betula alba*, L., H. Hænsel[5]) obtained 0,04 to 0,049 p.c. of an oil which was

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[1]) Chem. Zentralbl. **1902**, II. 1208.

[2]) Comp. Report of Schimmel & Co. October **1905**, 13; October **1909**, 28.

[3]) Berl. Berichte **38** (1905), 1636.

[4]) H. Hænsel, Chem. Zentralbl. **1909**, II. 1556.

[5]) Apotheker Ztg. **19** (1904), 854. — Chem. Zentralbl. **1908**, I. 1837.

liquid at higher, but solid at lower temperatures. d_{35° 0,9074 and d_{80° 0,8683; A. V. 99 and 30; S. V. 146,7 and 111; optically inactive. It contains a *paraffin* which crystallizes from hot alcohol in laminæ, and melts at 49,5 to 50°.

213. Oil of White Birch Bark.

Like the buds and leaves, so the bark of the white birch, *Betula alba,* L., contains a volatile oil which has been obtained with a yield of 0,052 p.c.[1]). Its odor resembles that of the bud oil, it is brown in color and, when cooled, becomes turbid because of the separation of crystals. d_{22°8953, and d_{20°0,9003; α_D—12,08°; A.V. 13,3 and 9,1; E.V. 11,5 and 11,4; E.V. after acetylation 56,9 and 36,5. It contains *palmitic acid* and a *sesquiterpene* which is probably monocyclic and possesses the following properties: b.p. 255 to 256° (744 mm.); d_{20° 0,8844; α_D — 0,5°. In ethereal solution it combines with 1 mol. of hydrogen chloride. When boiled with anhydrous sodium acetate, the liquid chlorhydrate (d_{20° 0,9753) yields a hydrocarbon which boils at 258 to 260° (747 mm.) and has a specific gravity of 0,8898 at 20°.

214. Oil of Hazel Nut Leaves.

The leaves of *Corylus Avellana,* L., a shrub belonging to the family *Betulaceæ,* contain a volatile oil with a spicy odor, which has been distilled with a yield of 0,0425 p.c., computed with reference to the dry leaves[2]). d_{25° 0,8844; A.V. 60,4; E.V. 24,6; E.V. after acetylation 158. It begins to congeal at +30° and contains 18 p.c. of *palmitic acid* and a *paraffin* melting at 49 to 50°.

Family: ULMACEÆ.

215. Oil of Celtis reticulosa.

The wood of *Celtis reticulosa,* Miq. (family *Ulmaceæ*), is classed with the odoriferous woods of Java[3]), since it is utilized as an ingredient of fumigating mixtures and face powders.

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[1]) H. Hænsel, Chem. Zentralbl. **1907**, II. 1620, and **1908**, II. 1436.

[2]) H. Hænsel, Apotheker Ztg. **24** (1909), 283.

[3]) W. R. Dunstan, Pharmaceutical Journ. III. **19** (1889), 1010; Berl. Berichte **22** (1889), 441. Abstracts.

However, the odor of the hard, yellow or brown to black modulated wood, which contains *skatol,* is by no means agreeable, hence the native designation *kaju tai,* or stink wood. The presence of skatol was demonstrated by Dunstan and by Greshoff[1]. The fecal odor, however, diminishes greatly when the wood is dried. In a dry, old wood W. G. Boorsma[2] could find no skatol. The light petroleum and ether extracts, though they possessed an offensive odor, gave no reactions for skatol and indol. However, the alcoholic extract yielded a nitrogenous substance which is possibly related to skatol.

According to C. A. Herter[3] the wood of the trunk also contains *indol.* The skatol, which is not found in the wood of the twigs, bark and roots, amounted to 0,01 p.c.

Family: MORACEÆ.

216. Oil of Hops.

Oleum Humuli Lupuli. — Hopfenöl. — Essence de Houblon.

Origin and Production. Oil of hops is obtained by distillation of hops, *i. e.* the female inflorescences, also from the lupulin, the glands of *Humulus Lupulus,* L. (family *Moraceæ*). From hops the yield amounts to from 0,5 p. c. to more than p.c.; from lupulin up to 3 p. c. The latter, however, possesses a less agreeable odor, and hence is of inferior quality. The aqueous distillate, more particularly that of the lupulin, is strongly acid and contains valeric acid (Personne), and probably also butyric acid (Ossipoff).

Hops which have been bleached with sulphur should not be used for distillation, otherwise the oil will have an unpleasant odor and contain sulphur.

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[1] Mededeelingen uit 's Lands Plantentuin **25** (1898), 175.

[2] Bulletin du Département de l'Agriculture aux Indes Néerlandaises **1907**, No. 7, 32. Pharmacologie III. Boorsma mentions *Celtis reticulata,* Miq., as the mother plant, whereas the Index Kewensis enumerates *Celtis reticulosa,* Miq. = *C. cinnamomea,* Lindl. = *C. reticulata,* Torr.

[3] Journ. biol. Chem. **5** (1909), 489; Apotheker Ztg. **24** (1909), 885.

Properties. Oil of hops is a light-yellow to reddish-brown, thin liquid which becomes viscid upon prolonged standing. It has an aromatic odor and a non-bitter taste. d_{15° 0,855[1]) to 0,893; α_D almost inactive or but slightly lævogyrate or dextrogyrate; n_{D20° 1,4852 to 1,4914; A.V. 0,5 to 10; E.V. 15 to 40; E.V. after acetylation (one determination) 74,0. In alcohol the oil is difficultly soluble. Older oils at times yield no clear solution with even 95 p.c. alcohol, due possibly to the polymerization product of the myrcene contained in the oil.

Composition. Although oil of hops has early been subjected to investigations[2]), nevertheless these did not result in the isolation and identification of a single constituent. However, the presence of several hydrocarbons and oxygenated substances has been established by more recent investigations.

In the lowest boiling fractions, A. C. Chapman[3]) found *dipentene* as well as a less dense myrcene-like, olefinic hyrocarbon. When hydrated according to Bertram and Walbaum, it yielded an ester of a lavender-like odor.

Later F. W. Semmler and W. Mayer[4]) demonstrated that the hydrocarbon in question is *myrcene,* by converting it into dihydromyrcene and into tetrabromodihydromyrcene, the latter melting at 87 to 88°, furthermore by its conversion into myrcenol.

In the middle fraction Chapman[3]) found linalool and a volatile acid $C_9H_{18}O_2$, probably iso*nonylic acid,* as ester. The presence of a geranyl ester was suspected.

Almost two thirds of the oil of hops consist of a sesquiterpene that boils between 263 and 266° and has a specific gravity of 0,900 at 15°. Upon fractionation it is obtained either slightly lævogyrate or dextrogyrate; when perfectly pure it presumably is optically inactive. Chapman[5]) obtained derivatives

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[1]) A. C. Chapman (Journ. chem. Soc. **83** [1903], 505. — Pharm. Review **21** [1903], 155) observed $d_{15^\circ}^{15^\circ}$ 0,8403 in connection with one oil.

[2]) Payen & Chevallier, Journ. de Pharm **8** (1822), 214 and 533. — R. Wagner, Journ. f. prakt. Chem. **58** (1853), 351. — J. Personne, Compt. rend. **38** (1854), 309. — G. Kühnemann, Berl. Berichte **10** (1877), 2231; Chem. Zentralbl. **1878**, 573. — J. Ossipoff, Journ. f. prakt. Chem. II. **28** (1883), 447; **34** (1886), 238.

[3]) Journ. chem. Soc. **83** (1903), 505.

[4]) Berl. Berichte **44** (1911), 2009.

[5]) Journ. chem. Soc. **67** (1895), 54 and 780.

of this sesquiterpene, similar to those of caryophyllene, but not identical therewith. Hence he regarded it as a new hydrocarbon and named it *humulene*.

By means of the nitrosochloride and nitrosate, E. Deussen[1]) succeeded in demonstrating that humulene consists in the main of i-*α-caryophyllene,* with which is admixed some *β-caryophyllene*[2]).

Upon oxidation of oil of hops with chromic acid mixture, Chapman[3]) obtained succinic acid and asymmetric dimethyl succinic acid in addition to volatile acids (acetic acid and homologues).

Adulteration. As adulterants of oil of hops the oils of copaiba balsam and gurjun balsam are mentioned. Both can be detected without difficulty. In one instance the addition of gurjun balsam was observed by Schimmel & Co.[4]). The oil in question had a specific gravity of 0,9189 (15°) and an optical rotation of —40°40′; besides, its solubility was not as good as commonly met with in hop oils. The differences observed upon fractionation are also noteworthy: a pure oil yielded fractions which were but slightly optically active; the adulterated oil yielded fractions with a rotation up to —86°50′.

From the behavior recorded above, also from the greenish though slight fluorescence, the conclusion could be drawn with certainty that the oil had been adulterated with very appreciable amounts of gurjun balsam.

217. Oil of Hemp.

The several statements concerning the composition and properties of hemp oil vary considerably. In this connection it should be remembered that the investigations were conducted partly with common hemp, *Cannabis sativa,* L. (family *Moraceæ*), partly with Indian hemp. The latter cannot be distinguished botanically from the former and differs only in that it produces the peculiar physiological effect known as hashish intoxication.

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[1]) Journ. f. prakt. Chem. II. 83 (1911), 483.

[2]) E. Deußen, Liebig's Annalen 388 (1912), 149.

[3]) Journ. chem. Soc. 83 (1903), 505.

[4]) Report of Schimmel & Co. April 1905, 49.

L. Valente¹) examined an oil of hemp obtained from Italian *Cannabis sativa.* It consisted principally of a *sesquiterpene* $C_{15}H_{24}$ which boiled at 256 to 258°, had a specific gravity of 0,9299 at 0° and an optical rotation of $[\alpha]_D - 10{,}81°$. With hydrogen chloride it yielded a solid chlorhydrate. The same sesquiterpene is contained in the male plants of *Cannabis gigantea.*

According to Personne²) the oil of *Cannabis indica* is an oily liquid lighter than water congealing to a butyraceous mass at 12 to 15°. It consists of two hydrocarbons, *viz.,* the liquid *cannabene* $C_{18}H_{20}$ which boils between 235 and 240°, and *"cannabene hydrate",* $C_{12}H_{24}$, which crystallizes from alcohol in scales with a fatty lustre.

Upon distillation of the female, flowering Indian hemp, G. Vignolo³) obtained a mobile liquid which boiled between 248 and 268° and possessed an aromatic odor. When cooled to — 18° it did not congeal. When distilled over sodium there remained in the residue a stearoptene, which has not yet been farther examined, whereas a sesquiterpene (b. p. 256°; $d_{15{,}3°}$ 0,897) passed over. The formula $C_{15}H_{24}$ was established by elementary analysis and vapor density. A crystalline chlorhydrate could not be obtained.

Upon distillation of the non-flowering herb of *Cannabis indica,* Schimmel & Co.⁴) obtained 0,1 p. c. of a limpid oil with a narcotic but not disagreeable odor. At 0° it congealed to a butyraceous mass. The specific gravity was 0,932.

Whether the sesquiterpene contained in the oil is identical or not with any of the known ones cannot be gathered from the scant information contained in the literature. The cannabene hydrate of Personne is possibly nothing more or less than one of the paraffins so frequently found in volatile oils.

According to S. Fraenkel⁵) and M. Czerkis⁶) the active constituent of hashich is *cannibinol,* a phenol-like substance of

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¹) Gazz. chim. ital. **10** (1880), 540 and **11** (1881), 191; Berl. Berichte **13** (1880), 2431 and **14** (1881), 1717.

²) Journ. de Pharm. et Chim. III. **31** (1857), 48.

³) Gazz. chim. ital. **25** (1895), I. 110.

⁴) Report of Schimmel & Co. October **1895**, 63.

⁵) Arch. f. experiment. Patholog. u. Pharmakolog. **49** (1903), 266; Chem. Zentralbl. **1903**, II. 199.

⁶) Liebig's Annalen **351** (1907), 467. — Apotheker Ztg. **24** (1909), 742.

the formula $C_{21}H_{29}O \cdot OH$. From the petroleum ether extract it was isolated by distillation in a vacuum (b. p. 230° under 0,1 mm. pressure). It is not known whether the cannabinol is volatile with water vapor and hence might be contained in the volatile oil.

Family: URTICACEÆ.

218. Pilea Oil.

Origin. The oil distilled in the island of Réunion from an unknown species of *Pilea* (family *Urticaceæ*) was first described by Schimmel & Co.[1]).

Properties. Two samples of the oil, which is water-white to greenish and very limpid, have been examined. The oil has a terpene-like and not unpleasant odor. d_{15° 0,8533 and 0,8520; $\alpha_D + 33^\circ 53'$ and $+ 58^\circ 20'$; n_{D20° 1,46862 and 1,46902; E. V. 5,1 and 7,7; E. V. after acetylation 24,2 and 34,4; soluble in about 5 vol. of 90 p. c. alcohol, the solution being slightly turbid. When distilled under 748 mm. air pressure the following fractions were obtained: 1) 158 to 159° 6 p. c.; 2) 159 to 160° 35 p. c.; 3) 160 to 161° 10 p. c.; 4) 161 to 161,5° 10 p. c.; 5) 161,5 to 163° 10 p. c.; 6) 163 to 165° 10 p. c.; 7) 165 to 168° 7 p. c.; 8) 168 to 174° 2 p.c.; 9) 174 to 194° 8 p.c. Residue (yellow, decomposed) 2 p. c.

Composition. The oil contains *α-pinene* and *sabinene.* Fraction 157 to 158° (d_{15° 0,8545; $\alpha_D + 14^\circ 35'$; n_{D20° 1,46684) was used in the preparation of the nitrosochloride, which, when reacted upon with benzylamine, yielded pinene nitrolbenzylamine melting at 122°[2]).

In fraction 167 to 168° Semmler[3]) found sabinene (d_{20° 0,8402; $\alpha_D + 61^\circ 20'$; n_D 1,46954), which was identified by oxidation with potassium permanganate to sabinene glycol (b. p. 150 to 154° under 9 mm. pressure; d_{20° 1,0332; n_D 1,48519; mol. refr. found 47,17, computed for $C_{10}H_{18}O_2$ 46,97).

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[1]) Report of Schimmel & Co. October **1906**, 83 and April **1907**, 105.

[2]) Report of Schimmel & Co. *loc. cit.*

[3]) Berl. Berichte **40** (1907), 2963.

Family: SANTALACEÆ.

219. Oil of Sandal Wood.

Oleum ligni Santali. — Sandelholzöl, Ostindisches Sandelholzöl. — Essence de Santal.

Origin. *Santalum album* (family *Santalaceæ*), a tree 6 to 10 m. high, is indigenous to the mountains of India. It grows wild or is cultivated in south eastern Asia in dry open spaces, more rarely in forests[1]. Inasmuch as it belongs to the root parasites, this has to be taken into consideration in the establishment of a plantation[2]. The parasitic mode of life begins a few months after germination. At first genuine haustoria of the sandal roots are sent out into the roots of grasses, herbs and smaller shrubs, later into those of trees[3]. Hence the rational method of procedure is to plant the young sandal plant with some other young plant in a basket made from the sheaths of bamboo leaves. Later they are cultivated in mixed gardens. The harvest is most profitable when the trees are 27 to 30 years old. The trees are felled and the larger roots dug up. The wood is deprived of the bark, split and sorted. In the sorting, the color has to be considered, for it is commonly said that the darker the wood the larger its oil content. Moreover, the wood of trees raised in rocky, hilly and dry soil is said to be firmer and richer in oil than the wood of trees raised in a more fertile soil[4].

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[1] E. M. Holmes, Pharmaceutical Journ. III. **16** (1886), 819. — A. Petersen, *ibidem* 757. — W. Kirkby, *ibidem* 857. — J. C. Sawer, Odorographia. Vol. I, p. 315.

[2] A. Zimmermann, Mitteilungen aus dem Biologisch-Landwirtschaftlichen Institut Amani. May 21. 1904, No. 25. Reprint from the "Usambara Post".

[3] A list of the plants which act as hosts for the sandal wood tree may be found in D. Brandis, Indian Forester, Jan. 1903. Abstracted in Rev. cultures coloniales **14** (1904), 47. — M. Rama Rao (Indian Forest Records **2** [1911], No. 4. Abstracted in Bull. Imp. Inst. **10** [1912], 325), enumerates not less than 144 species on the roots of which haustoria of the sandal wood tree had been found. In addition he has prepared a list of 252 plants ecologically related to the sandal wood tree.

[4] Comp. Puran Singh, Forest Bulletin No. 6. Calcutta 1911; Report of Schimmel & Co. October **1912**, 101.

The territory in India from which most of the wood is obtained constitutes a strip about 240 miles long and 16 miles wide. From the Nilgiri mountains it extends northward and to the northwest through Mysore (Maisur). In this region the sandal wood tree grows from the sea level to altitudes of more than 1000 m. The total area of sandal wood plantations extends over about 5450 square miles[1]. Seven eighths of this area are in Mysore (Maisur), the remaining portion is distributed principally over Coorg (Kurg) and a few districts of the presidencies of Bombay and Madras. In the districts Kolar and Chitaldrug, sandal wood is scarce and of inferior quality. This is also true of parts of Tumkur and Bangalore. It is totally absent in the highlands bordering the province to the east and south. In India proper the sandal wood tree is the property of the state. The government stores the wood of the trunks and the roots in special warehouses and from time to time sells it by auction[2].

The fully grown and the dead trees[3] are dug out and taken to the warehouses, known as *Kotis*. Here they are deprived of their bark and splint wood and sorted into roots, trunk wood and branch wood. According to the new classification, introduced in 1898, there are 18 grades offered for sale[4], from the best trunk wood to the chips and sawdust.

1. First Class Billets *(Vilayat Budh)*	Thoroughly sound billets weighing not less than 20 lbs. and of which not more than 112 make a ton.
2. Second Class Billets *(China Budh)*	Slightly inferior billets weighing not less than 10 lbs. each and of which not more than 224 are required to make a ton.

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[1] J. L. Pigot, Conservator of Forests in Mysore: Mysore Sandal wood. Pamphlet prepared for the exhibit by the British Colonial Government in Paris, 1900; Report of Schimmel & Co. April **1900**, 40.

[2] Comp. also: R. G. Pearson, Commercial guide to the forest economic products of India. Calcutta 1912, p. 89, 90 and 122.

[3] A hitherto unknown disease, the "spike disease" caused a large number of trees to die at the beginning of the present century. For detailed information see: Selections from reports and notes on spike disease in Sandal. Cola Lodge 1906; Report of Schimmel & Co. October **1902**, 77; April **1903**, 70; October **1905**, 64; April **1906**, 60; April **1907**, 91.

[4] Report of Schimmel & Co. October **1898**, 39.

Fig. 31.

Sandalwood koti in Bangalore.

3. Third Class Billets *(Panjam)*	Billets with small knots, cracks and hollows, weighing not less than 5 lbs. each and of which not more than 448 are required to make a ton.
4. *Ghotla* (short billets)	Short sound pieces, without reference to weight and number.
5. *Ghat badala*	Billets with knots, cracks and small hollows at both ends that do not weigh less than 10 lbs. each and of which not more than 240 are required to the ton.
6. *Bagaradad*	Solid pieces without special reference to weight and number. NB. Pieces belonging to classes 5 and 6 are not planed, neither are the ends rounded off.
7. Roots (first class)	Pieces of not less than 15 lbs. of which not more than 150 are required to the ton.
8. Roots (second class)	Pieces of not less than 5 lbs. of which not more than 448 are required to the ton.
9. Roots (third class)	Small and lateral roots weighing less than 5 lbs. each.
10. *Jugpokal* (first class) or *Badala*	Hollow pieces of not less than 7 lbs. of which not more than 320 are required to the ton.
11. *Jugpokal* (second class)	Hollow pieces of not less than 3 lbs.
12. *Ain Bagar*	Solid cracked and hollow pieces, of not less than 1 lb.
13. *Cheria* (large *Chilta*)	Pieces and chips of heart wood of not less than 0,5 lb.
14. *Ain Chilta*	Pieces and small chips of heart wood.
15. *Hatri Chilta*	Chips of heart wood and shavings obtained by planing billets with the *Hatri* or *Randha*, Indian tools.
16. *Milwa Chilta*	Mixed pieces and shavings of both heart wood and sap wood.
17. *Basola Bukni*	Small mixed heart wood and sap wood chips.
18. Sawdust	Obtained by sawing sandal wood.

At present there are ten kotis located at the following places:

Hunsur,
Seringapatam,
Bangalore,
Hassan,
Chikmagalur,
Tirthahalli,
Shimoga,
Sagar,
Tarikere,
Fraserpet.

The first nine are in Mysore, the last one in Coorg. The warehouses in Seringapatam, Bangalore, Shimoga and Tarikere are situated on the railroad and in direct communication with Bombay, Madras, Marmagoa, &c. The others are but a short distance from the railroad and connected with the coast by means of good roads.

In November and December the supplies of wood are taken alternately to the various kotis for public auction. In accordance with private arrangements, unsold wood can be purchased after the auction, but mostly at higher prices. Practically all the wood sold finds its way by rail to Bombay or to the following sea ports along the west coast of India: Goa, Hanovar, Kundapur, Mangalore, &c. From these places it is shipped to Europe, China and other places in India.

Sandal wood is also obtained in eastern Java, in the Sandal wood islands (Soemba or Tjendana) and Timor. This variety enters commerce via Macassar (in Celebes), hence is known as Macassar sandal wood. Though generally speaking it is a little less rich in oil, the quality of the oil is scarcely inferior to the East Indian article. More recently sandal wood has also been exported from New Caledonia, however, this is not derived from *Santalum album,* L., but from *S. austro-caledonicum,* Vieillard (see p. 349).

The best grades of sandal wood are used in India, more particularly in Kanara, for artistic carving, especially of idols, cupboards, tables, canes, chests, &c. In religious rites, especially as incense, the wood plays an important role. Most of the wood, however, is used for distillation.

Production. Formerly the distillation of sandal wood played a more important role in India than it does at present. Up to 1860 it was carried on in Mysore. At present the distillation is still conducted along the west coast of India, in South Kanara, more particularly in the Udipi district. But even here the old industry is constantly dwindling.

According to Mr. Werner Reinhardt of the firm of Gebr. Volkart, who has himself visited the distilleries[1]), the industry in southern India is located principally north east of Karkul as far as the river Ghat. The distilling apparatus consists of a spherical earthenware vessel provided with a circular opening. It is $2^1/_2$ ft. high and about $6^1/_2$ ft. in circumference. There is no head. When charged, the still is closed with an earthenware cover, into the center of which is fastened a bent copper tube about $5^1/_2$ ft. in length. The tube ends in a copper receiver placed in a porous earthenware vessel which is filled with water. For the purpose of distillation the wood is cut up into chips and a charge of 50 lbs. placed into the still. Water is then added and the distillation of a single charge is continued uninterruptedly day and night for an entire month. The condensed water of the receiver is returned to the still about 15 times. The yield of oil is recorded as follows:

for roots . . .	about	4,34 %
„ Jugpokals .	„	3,47 %
„ Ain Chiltas	„	2,60 %.

The oil enters commerce in part via Udipi, in part via Mangalore. Of the two, the latter place is more important. According to local statements, the exports for 1909 from this port are said to have reached the value of Rs. 150000 (?). No doubt, this figure also includes Mysore oil which found its way to Mangalore. Practically all the oil is taken to Bombay by steamer, thence it is re-exported to the Persian gulf and to China.

It is evident that with such a primitive method of distillation no really good sandal wood oils can be obtained. Owing to the prolonged distillation, decomposition products are inevitable. These interfere with the quality of the oil, exerting an unfavorable influence on both color and odor. The anomaly of the Indian oils is also shown by their constants. (See below.)

Sandal wood oil is also distilled in the northern parts of India, namely in Kanouj (Kanauj)[2]), a city in Oudh (Audh) between

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[1]) Report of Schimmel & Co. October 1910, 114.

[2]) Comp. Watt, Commercial products of India, London 1908, p. 977.

Fig. 32.

Sandal wood tree (*Santalum album,* L.)

Cawnpur and Allahabad. In Lucknow and Jaunpur, where the distillation was formerly carried on, it has been discontinued. Kanouj is the center of the ancient perfume industry of India where the several attars, *i. e.* floral perfumes, were prepared with sandal wood oil as base.

Because of the more perfect comminution, and also because of improved stills, larger yields are obtained in Europe than by the primitive methods employed in India. As much as 6 p. c. and more of oil are obtained, the light color and agreeable odor of which are in striking contrast with the Indian distillates as they are contaminated with empyreumatic products.

Composition. More than 90 p. c. of the sandal wood oil consists of santalol, a mixture of two isomeric alcohols to which the oil owes its medicinal virtues. The other constituents play a minor role. They are of interest, however, because they are genetically related to the principal components.

1. Iso*valeric aldehyde,* together with other aldehydes that boil between 50 and 130°, is found in the first portions that distil over. The presence of *iso*valeric aldehyde was established by means of its thiosemicarbazone[1]), melting at 49 to 53°, which had been obtained from the aldehyde isolated from fraction 90 to 95° by means of its bisulphite addition product.

2. *Santene,* C_9H_{14}. This hydrocarbon is remarkable as the next lower homologue of the terpenes. (Comp. vol. I, p. 289). It was discovered in the oil by F. Müller[2]). A very pure santene, obtained through fractionation by Schimmel & Co.[1]), had the following properties: b. p. 140 to 141° (770 mm.), d_{15° 0,869, $\alpha_D - 0^\circ 16'$, n_{D20° 1,46436.

3. *Hydrocarbon* $C_{11}H_{18}$ (Nortricycloeksantalane?). This hydrocarbon, found by Schimmel & Co.[3]) in the first fractions of the oil after having been distilled over sodium, had the following properties: d_{15° 0,9133; d_{20° 0,9092; $\alpha_D - 23^\circ 55'$; n_{D20° 1,47860; mol. refr. found 46,74, computed for $C_{11}H_{18}$ 46,40, for $C_{11}H_{18}/\overline{1}$ 48,11. The elementary analysis yielded results agreeing with the formula

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[1]) Report of Schimmel & Co. October **1910**, 118.

[2]) Arch. der Pharm. **238** (1900), 366.

[3]) Report of Schimmel & Co. October **1910**, 121.

for a homoterpene $C_{11}H_{18}$. This hydrocarbon, of which sufficient quantities of solid derivatives have not yet been obtained, is permanent toward permanganate at ordinary temperatures and apparently identical with Semmler's nortricycloeksantalane. In connection with his work on the constitution of the santalols of the eksantal series, this investigator[1]) had obtained a hydrocarbon, named nortricycloeksantalene, by splitting off carbon dioxide from tricycloeksantalic acid, to which he assigned the formula $C_{10}H_{16}$ because of the method of formation. The more recent investigations of Semmler[2]), however, have revealed that tricycloeksantalic acid contains twelve carbon atoms, hence the nortricycloeksantalane must be $C_{11}H_{18}$ with which formula Semmler's analyses agree.

4. *Santenone,* $C_9H_{14}O$. In the lowest fraction of sandal wood oil F. Müller[3]) had found a ketone, the semicarbazone of which melted at 224°. According to Schimmel & Co.[4]) this ketone is identical with the π-norcamphor obtained by Semmler[5]) from teresantalic acid and with the santenone obtained by Aschan[6]) from santene. The ketone obtained from sandal wood oil by fractional distillation has an odor reminding one of camphor and cineol. It has the following properties: m. p. 48 to 52°; b. p. 193 to 195°; $[\alpha]_D - 4°40'$ in 18,9 p. c. alcoholic solution. It forms a liquid oxime which boils at 110 to 113° (6 mm.).

5. *Santenone* alcohol (π-nor*iso*borneol). The fractions freed from santenone contain an alcohol which can be isolated by the aid of phthalic acid anhydride[7]). There results a liquid acid phthalate, the sparingly soluble silver salt of which melts at 230°.

The solid alcohol regenerated from the acid phthalate has the odor of borneol and camphor and boils between 196 and 198°. M. p. about 58 to 62°. Its phenyl urethane is liquid. Upon oxidation with chromic acid santenone results.

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[1]) Berl. Berichte **40** (1907), 1124.

[2]) *Ibidem* **43** (1910), 1722.

[3]) Arch. der Pharm. **238** (1900), 372.

[4]) Report of Schimmel & Co. October **1910**, 118.

[5]) Berl. Berichte **40** (1907), 4465; **41** (1908), 125.

[6]) *Ibidem* **40** (1907), 4918.

[7]) Report of Schimmel & Co. October **1910**, 120.

6. *Teresantalol,* $C_{10}H_{16}O$. Upon heating the santalone-containing fraction (b. p. 210 to 220°) with phthalic acid anhydride, Schimmel & Co.[1]) obtained an acid phthalic ester which, upon saponification, yielded an alcohol. Recrystallized from petroleum ether, it showed a great capacity to crystallize, forming well shaped prisms several centimetres in length. Thus purified it melted at 111 to 112°. It sublimed in long thin needles which melted at 112 to 114°. Elementary analysis agreed with the formula $C_{10}H_{16}O$. Comparison with the teresantalol obtained by Semmler by reduction of teresantalic acid established the identity of the two substances.

7. *Nortricycloeksantalal,* $C_{11}H_{16}O$. When the fraction that boils higher than santenone is treated with bisulphite, there results a slimy mass[2]) that is readily soluble in water and from which the aldehyde can be regenerated by means of soda. It has a spicy odor and the following constants: b.p. 86 to 87 (6 mm.), 222 to 224° (760 mm.); d_{20° 0,9938; α_D — 38° 48′; n_{D20° 1,48393; mol. refr. found 47,20, computed for $C_{11}H_{16}O$ 46,409, for $C_{11}H_{16}O/_1$ 48,142.

This aldehyde is identical with the *nortricycloeksantalal* obtained by Semmler and Zaar[3]) as an "Abbau" product of tricycloeksantalal. Its semicarbazone melts at 223 to 224°, the liquid oxime boils at 135 to 137° (7 mm.). Upon oxidation with ammoniacal silver nitrate solution, the nortricycloeksantalal is oxidized to nortricycloeksantalic acid (m. p. 91 to 93°; $[\alpha]_D$ — 33° 17′ in 13,8 p. c. alcoholic solution). Upon treating the enolacetate of the aldehyde with permanganate, there results teresantalic acid (m. p. 154 to 156°).

By shaking the normal sandal wood oil with bisulphite solution the aldehyde can also be obtained and in small amounts it may be identified by its semicarbazone.

8. *Santalone,* $C_{11}H_{16}O$. The second ketone occurring in the lower boiling portions of sandalwood oil is santalone. According to F. Müller[4]), it boils at 214 to 215°, 88 to 89° under 15 mm. pressure (?); d_{15° 0,9906; α_D — 62°. Schimmel & Co.[5])

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[1]) Report of Schimmel & Co. October **1910**, 125; April **1911**, 105.

[2]) *Ibidem* October **1910**, 122.

[3]) Berl. Bericht **43** (1910), 1890.

[4]) Arch. der Pharm. **238** (1900), 373.

[5]) Report of Schimmel & Co. October **1910**, 124.

found the following constants: b. p. 213 to 216°; $d_{15°}$ 0,9909; α_D — 41° 32′; $n_{D20°}$ 1,50021.

Santalone semicarbazone melts at 174 to 176°, santalone oxime at 74,5 to 75,5°. From the latter santalone cannot be regenerated by treatment with dilute sulphuric acid.

9. *Ketone,* $C_{11}H_{16}O$. The santalone fraction contains a second, presumably isomeric ketone, the difficultly soluble semicarbazone of which melts at 208 to 209°, the oxime at 97 to 99°.

10. *Santalene,* $C_{15}H_{24}$. The occurrence of sesquiterpenes in sandal wood oil was first pointed out by H. von Soden and F. Müller[1]. M. Guerbet[2] then showed that two sesquiterpenes were present which he designated as α- and β-santalene. Properties and derivatives of both are recorded in vol. I, p. 336. There should be added, however, the physical constants of both which have since been determined more accurately by Schimmel & Co.[3].

α-Santalene: b.p. 252° (753 mm.) and 118° (7 mm.); $d_{15°}$ 0,9132; α_D — 3° 34′; $n_{D15°}$ 1,49205; mol.-refr. 64,87, computed for $C_{15}H_{24}/^{=}_{1}$ 64,45.

β-Santalene: b.p. 125 to 126° (7 mm.); $d_{20°}$ 0,8940; α_D — 41°3′; $n_{D20°}$ 1,49460; mol.-refr. 66,53, computed for $C_{15}H_{24}/^{=}_{2}$ 66,16.

In their attempt to hydrate santalene by means of glacial acetic acid-sulphuric acid, von Soden and Müller[1] obtained small amounts of a sesquiterpene alcohol with a strong cedar wood odor (b.p. 160 to 165° under 7 mm.; $d_{15°}$ 0,978; α_D inactive).

For the hydration Schimmel & Co. used a fraction, the molecular refraction of which showed that it consisted mostly of the tricyclic santalene, and from it obtained 5 to 10 p.c. of an alcohol with the odor of cedar wood: b.p. 154 to 157° (5 to 6 mm.); $d_{15°}$ 0,9787; $d_{20°}$ 0,9753; $n_{D20°}$ 1,51725; mol. refr. found 68,81, computed for $C_{15}H_{26}O/^{=}_{1}$ 68,07.

With concentrated formic acid the alcohol readily gave off water even at body temperature. It could not be oxidized with chromic acid. Hence it probably is a tertiary alcohol.

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[1] Pharm. Ztg. **44** (1899), 258. — Arch. der Pharm. **238** (1900), 363.

[2] Compt. rend. **130** (1900), 417.

[3] Report of Schimmel & Co. October **1910**, 126.

The hydrocarbon which, in the hydration experiment, was not converted into an alcohol possessed properties different from those of the hydrocarbon employed.

Santalene employed	Recovered hydrocarbon
$d_{20°}$ 0,9034; $\alpha_D - 9° 13'$	$d_{20°}$ 0,8973; $\alpha_D - 1° 15'$.

11. *Santalol,* $C_{15}H_{24}O$. To the extent of over 90 p.c., oil of sandal wood consists of santalol, which is not only quantitively but also medicinally its most important constituent, since the therapeutic action of the oil depends upon it. Santalol is not a chemical unit, as one might have inferred from the investigations of P. Chapoteaut[1]). As first pointed out by Schimmel & Co.[2]), it can be resolved into two isomers by fractional distillation, namely into α- and *β-santalol.* Moreover, the formula assigned to santalol by Chapoteaut and later by Guerbet[3]), *viz.,* $C_{15}H_{26}O$ is not correct[4]). Acetylation and analyses[5]) of the alcohols purified through the phthalic acid derivatives, as described below, revealed the formula $C_{15}H_{24}O$.

For the properties and derivatives of the santalols see vol. I, p. 400. These data should be supplemented by the constants since determined by Schimmel & Co.[6]) for the santalols regenerated from the acid phthalates and carefully fractionated.

α-Santalol: b. p. 148° (4,5 mm.); $d_{15°}$ 0,9788; $\alpha_D + 1° 13'$; $n_{D20°}$ 1,49915, mol.-refr. found 66,23, computed for $C_{15}H_{24}O/\overline{1}$ 65,93.

β-Santalol: b. p. 158 to 158,5° (5 mm.); $d_{15°}$ 0,9728; $\alpha_D - 41° 47'$; $n_{D20°}$ 1,50910, mol.-refr. found 67,77, computed for $C_{15}H_{24}O/\overline{2}$ 67,64.

On the strength of his extensive researches, Semmler[7]) assigns to the α-santalol the accompanying constitutional formula which also explains its relation to α-santalene.

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[1]) Bull. Soc. chim. II. **37** (1882), 303; Chem. Zentralbl. **1882**, 396.

[2]) Report of Schimmel & Co. April **1899**, 38.

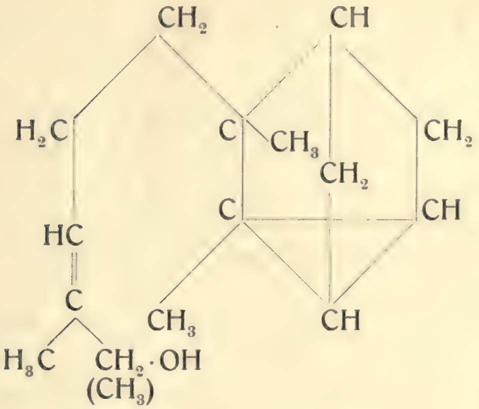
[3]) Compt. rend. **130** (1900), 417 and 1324. — Bull. Soc. chim. **23** (1900), 540 and 542.

[4]) Report of Schimmel & Co. April **1900**, 42.

[5]) von Soden, Arch. der Pharm. **238** (1900), 353.

[6]) Report of Schimmel & Co. October **1910**, 127.

[7]) Berl. Berichte **40** (1907), 1120, 1124; **41** (1908), 1488; **42** (1909), 584; **43** (1910), 1893.



α-Santalol and α-Santalene.

In order to obtain pure santalol, the following process is used[1]: —

100 g. of East Indian sandal wood oil are heated with an equal weight of phthalic acid anhydride and benzene for an hour on a water bath to 80°. The acid phthalate thus formed is combined with alkali by shaking the mixture with soda solution and dissolved in much water. In order to remove the nonalcoholic constituents, the aqueous solution is shaken out three times with ether. The acid esters are removed from the aqueous solution by the addition of more than the computed amount of diluted sulphuric acid. They are then separated and saponified with alcoholic potassium hydroxide. The liberated santalol is freed from excessive alkali and alcohol by washing with water.

12. *Santalal,* $C_{15}H_{22}O$. According to Chapoteaut and Guerbet[2]) the aldehyde corresponding to santalol likewise occurs in sandal wood oil. It has an odor strongly reminding one of pepper and, according to Guerbet, boils at 180° (40 mm.). Its semicarbazone, which crystallizes in small needles, melts at 212°.

Inasmuch as more recent investigations have not verified the occurrence of an aldehyde of the above mentioned properties, the statements made by Guerbet should be taken with caution.

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1) Report of Schimmel & Co. April 1899, 38.

2) *Loc. cit.*

It is possible that the semicarbazone obtained by Guerbet was an impure derivative of nortricycloeksantalal of which the pure compound melts at 223 to 224°.

A. C. Chapman and H. E. Burgess[1]) designate as santalal fraction 301 to 306° of sandal wood oil, which they have oxidized with potassium permanganate to santalenic acid $C_{13}H_{20}O_2$[2]). In a second contribution Chapman[3]) designates this fraction santalol without further comment. Probably he had his doubts as to the aldehyde nature of the substance in question. As santalal Semmler and Bode[2]) designate the aldehyde $C_{15}H_{22}O$ corresponding to santalol and which they obtain by oxidizing the alcohol with chromic acid in acetic acid solution. Regenerated from its semicarbazone (m. p. abt. 230°), it has the following properties: b.p. 152 to 155° (10 mm.); d_{20° 0,995; $\alpha_D + 13$ to $+ 14°$; n_D 1,51066; mol. refr. found 65,6, computed for $C_{15}H_{22}O/^{=}$ 64,63.

13. *Teresantalic acid,* $C_{10}H_{14}O_2$. The acid constituents of sandal wood are contained therein partly in the free state, partly as ester. According to F. Müller[4]), teresantalic acid, which crystallizes in well formed prisms, boils at about 150° (11 mm.), melts at 157° and shows $[\alpha]_D - 70° 24'$ in a 25 p.c. alcoholic solution[5]). It occurs principally in the free state (about 0,5 p.c.) in the oil and can be removed by shaking the oil with dilute sodium hydroxide solution. According to the investigations of F. W. Semmler and K. Bartelt[5]) teresantalic acid is tricyclic.

14. *Santalic acid,* $C_{15}H_{22}O_2$ is the second acid which, according to Guerbet[6]) occurs in sandal wood oil. It is described as a viscid colorless liquid with slightly acid properties, boiling at 210 to 212° (20 mm.).

Upon saponification of the nitrile obtained from α-santalal, Semmler and Bode[7]) obtained an acid $C_{15}H_{22}O_2$ which they call

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[1]) Proceed. chem. Soc. No. 168 (1896), 140.

[2]) Before oxidation with permanganate Semmler and Bode (Berl. Berichte **40** [1907], 1124, comp. also *ibidem* **43** [1910], 1722) obtained dihydroxydihydrosantalol, $C_{15}H_{26}O_3$ and tricycloeksantalic acid $C_{12}H_{16}O_2$ (m.p. 71 to 72°).

[3]) Journ. chem. Soc. **79** (1901, 134.

[4]) Arch. der Pharm. **238** (1900), 374.

[5]) Berl. Berichte **40** (1907), 3101.

[6]) *Loc. cit.*

[7]) Berl. Berichte **40** (1907), 1129.

santalic acid and which boils at 192 to 195° (9 mm). It has not been ascertained whether it is identical with the one described above.

According to F. Müller the saponification liquids of sandal wood oil contain another or even several other acids which have not yet been investigated.

According to von Soden and Müller[1]) sandal wood oil contains, in addition to the constituents already enumerated, strong and unpleasantly smelling *phenols,* also *lactones* with a fruity odor. The presence of *borneol,* both free and as ester, is also looked upon as probable. Possibly the borneol-like odor of the santenone alcohol (π-nor*iso*borneol) may have given rise to this supposition.

Properties. East Indian sandal wood oil is a rather viscid, pale yellowish to yellow liquid. It possesses a peculiar, faint, but very persistent odor and a not unpleasant, resinous, harsh taste. d_{15° 0,974 to 0,985; α_D — 16 to — 20° 45′, in exceptional cases lower rotation has been observed; n_{D20° 1,504 to 1,508; A. V. 0,5 to 8,0[2]); E. V. 3 to 17; E. V. after acetylation not less than 196, corresponding to a santalol content of at least 90 p. c. The value of the oil increases with its santalol content, which rises as high as 94 p. c. and more in good oils.

For the solution of sandal wood oil 3 to 5 vol. of 70 p. c., 5 to 6 vol. of 69 p. c. and 6 to 7 vol. of 68 p. c. alcohol are requisite. In all cases the solution should remain clear upon the addition of more alcohol. However, turbidity is not necessarily a sign of adulteration, but may be caused by products of decomposition and resinification, due to improper methods of distillation. The solubility of sandal wood oil suffers also through age and by exposure to light and air. Such oils yield turbid solutions under the above conditions.

Inasmuch as some pharmacopœias demand a solubility of 1:5 in a dilute alcohol the strength of which may vary from

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[1]) Pharm. Ztg. 44 (1899), 259.

[2]) Upon water distillation (Comp. von Rechenberg, *Theorie der Gewinnung und Trennung der ätherischen Öle.* Miltitz near Leipzig 1910, p. 286) the acid value of the oil increases. Upon rectification and removal of the first fraction which contains the teresantalic acid, it decreases.

68 to 70 p.c., it should be pointed out that this requirement will be fulfilled only if the strength of the alcohol corresponds to the higher limit.

As already pointed out, the oils distilled in India are characterized by a dark color, an empyreumatic odor due to decomposition products, and an abnormally high specific gravity[1]), properties due to the irrational and crude methods of distillation.

An oil distilled in India and examined by Schimmel & Co.[1]) had the following properties: d_{15° 0,9898; α_D −8°; A. V. 3,7; E. V. 7,1; E. V. after acetylation 205,3 = 95,4 p. c. total alcohol ($C_{15}H_{24}O$); insoluble in 70 p. c. alcohol, soluble in 1 vol. and more of 80 p. c. alcohol. As indicative of the presence of decomposition products, its high specific gravity[2]) should first be pointed out. In good oils this never exceeds 0,985. There was also an exceedingly unpleasant, fish oil odor that could not be removed by rectification. A further disadvantage is to be found in its insufficient solubility. In spite of its high santalol content the oil was of inferior quality.

The following oils were distilled from wood not obtained from India proper, Macassar or Timor. Although most of the properties are fairly normal, deviations were observed especially in the optical rotation. It could not be ascertained with certainty whether these woods were derived from *Santalum album* or from a closely related species.

OIL FROM WOOD OF THE NEW HEBRIDES.

d_{15° 0,9675; α_D — 1° 2′; n_{D20° 1,50893; A. V. 1,8; E. V. 3,6; E. V. after acetylation 199,8 = 92,4 p. c. santalol. Soluble in 3,5 vol. and more of 70 p. c. alcohol.

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[1]) Report of Schimmel & Co. October **1910**, 115.

[2]) The high specific gravity in connection with Indian oils has been previously observed. (Chemist and Druggist May 26th, 1894). The cause thereof is to be sought in the prolonged contact of the oil with the hot water. Conroy has demonstrated that by heating sandalwood oil with water of 50° for ten days its specific gravity increased from 0,975 to 0,989. (Chemist and Druggist August 19th, 1893).

OIL FROM TAHITI WOOD[1]).

d_{15° 0,9748; $\alpha_D - 8^\circ 29'$; n_{D20° 1,50848; A. V. 2,0; E. V. 5,1; E. V. after acetylation 203,6 = 94,4 p. c. santalol. Soluble in 4 to 4,5 vol. and more of 70 p. c. alcohol.

OIL OF SANDALWOOD FROM THURSDAY ISLAND.

d_{15° 0,9635 to 0,9687; $\alpha_D - 27^\circ 10'$ to $-37^\circ 30'$; n_{D20° 1,504 to 1,507; A. V. to 2,0; E. V. after acetylation 196,7 to 202,6 = 90,6 to 93,8 p.c. santalol. Soluble in 4 to 5 vol. and more of 70 p.c. alcohol.

Concerning the properties of New Caledonia sandalwood oil see p. 349.

Examination. Owing to the slight variations in its physical constants to which oil of sandalwood is subject, additions of all kinds can be readily ascertained with certainty by means of its specific gravity, its optical rotation and its solubility in 70 p. c. alcohol. The principal adulterant, *viz.,* cedarwood oil[2]) can be detected by the increase of the optical rotation and by the diminution of the specific gravity and solubility. Practically the same changes are brought about by the oils of copaiba balsam and gurjun balsam. Copaiba balsam oil, however, usually causes a slight lowering of the optical rotation. West Indian sandalwood oil, which is occasionally used as adulterant, rotates to the right and is very difficultly soluble in dilute alcohol.

How frequently sandalwood oil is adulterated may be seen in a communication by Schimmel & Co.[3]) according to which not one of 6 samples obtained in the London market contained the required percentage of santalol. The oil sold in capsules[4]) is even more frequently adulterated with substances such as castor oil[5]). In one instance terpineol[6]) was found in an oil; in an other, guaiac wood oil and an ester of benzoic acid[7]).

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[1]) Presumably derived from *Santalum Freycinetianum,* Gaud.

[2]) Comp. Report Schimmel & Co. April **1912**, 112.

[3]) *Ibidem* October **1910**, 116.

[4]) R. Peter, Pharm. Ztg. **48** (1903), 573. — P. Runge, *ibidem* **49** (1904), 671. — G. Wendt, *ibidem* **50** (1905), 898. — E. J. Parry, Chemist and Druggist **68** (1906), 951.

[5]) Report of Schimmel & Co. April **1905**, 73.

[6]) E. J. Parry, Chemist and Druggist **68** (1906), 211.

[7]) Report of Schimmel & Co. October **1911**, 81.

It is reported that the oil distilled in India is occasionally adulterated with castor oil or with the fatty oil from the seeds of the sandalwood tree which is used as a lamp oil. Admixtures of sesame oil, liquid paraffin and linseed oils are said not to be uncommon in India.

The best method to determine the purity of sandalwood oil or to ascertain the amount of adulterant present, is to determine its santalol percentage. Good oils contain mostly from 94 to 98 p. c., but never below 90 p. c. of santalol.

Parry[1]) was the first to suggest the test for santalol by heating the oil with glacial acetic acid in a closed container to 150°, thus converting the alcohol into its acetate and to saponify the ester by means of alcoholic potassium hydroxide. According to Schimmel & Co.[2]), however, it is more expedient to determine alcohols in volatile oils by means of acetic acid anhydride.

The process is carried out in the following manner:[3])

In an acetylation flask 10 cc. of sandalwood oil are mixed with an equal volume of acetic acid anhydride, 2 g. of fused sodium acetate and a few fragments of porous tile are added and the mixture is heated to gentle boiling for an hour. Upon cooling some water is added to the contents of the flask, the mixture heated for $^1/_4$ hour on a water bath with occasional shaking in order to decompose the excess of acetic acid anhydride. The mixture is again allowed to cool, the oily layer separated from the aqueous layer by means of a separating funnel, and the oil washed with water or, better still, with sodium chloride solution until the wash water remains neutral. Of the acetylized oil, dried with anhydrous sodium sulphate, 1,5 to 2 g. are saponified with 20 cc. of half normal alcoholic potassium hydroxide solution after any free acid that may have remained in the oil has been carefully neutralized. The amount of potassium hydroxide consumed is ascertained by titration with half-normal sulphuric acid.

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[1]) Pharmaceutical Journ. 55 (1895), 118.

[2]) Report of Schimmel & Co. October 1895, 43.

[3]) See also vol. I, p. 570.

The santalol content $C_{15}H_{24}O$[1]) is then ascertained by means of the following formula[2]): —

$$P = \frac{a \cdot 11}{s - a \cdot 0{,}021}.$$

P = the santalol content of the original oil.
a = the number of cc. of half-normal potassium hydroxide solution.
s = the amount in grams of acetylated oil used for saponification.

Frequently the determination of the physical constants suffices to distinguish a pure oil from an adulterated one. In all cases, however, adulterations can be definitely ascertained by means of the santalol test which has been introduced by the more recent pharmacopœias. Hence it is unnecessary to resort to the wholly unscientific and misleading color reactions that are still recommended occasionally[3]).

220. New Caledonian Sandal wood Oil.

Origin. Upon distillation, the wood of *Santalum austrocaledonicum,* Vieillard, which is indigenous to New Caledonia, yields an oil very similar to that obtained from *Santalum album* and the principal constituent of which is likewise santalol. In 1906 as much as 194206 kg. of this wood were exported from New Caledonia and in 1907 as much as 141602 kg.[4]).

Properties. It is a very viscid oil of intensely yellow color. d_{15° 0,9647 to 0,978; $\alpha_D + 6^\circ 29'$ to $-21^\circ 42'$[5]); n_{D20° 1,5062; A.V. 0,9 to 6,4; E.V. 3,2 to 5,4; E.V. after acetylation 196,5 to 206,7 = 90,5 to 96,2 p.c. of santalol; soluble in 2[5]) to 4,5 vol. and more of 70 p.c. alcohol.

221. Fiji Sandal wood Oil.

The wood of *Santalum Yasi,* Seem.[6]) obtained from the Fiji islands was exhibited at the Colonial Exhibition in South

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[1]) Frequently manufacturers guarantee the santalol content computed with the wrong formula $C_{15}H_{26}O$, thereby feigning one more per cent.

[2]) See also the tables at the end of vol. I, pp. 618 to 641.

[3]) Report of Schimmel & Co. April **1904**, 82.

[4]) Zeitschr. f. angew. Chem. **21** (1908), 1571.

[5]) H. Hænsel, Chem. Zentralbl. **1909**, II. 1557.

[6]) E. M. Holmes, Pharmaceutical Journ. III. **16** (1886), 820. — A. Petersen, *ibidem* p. 757.

Kensington in 1886. Upon distillation it yielded 6 ½ p.c. of a volatile oil, the odor of which was faint and not delicate, hence it could not be used in perfumery[1]. Specific gravity 0,9768; $\alpha_D - 25,5°$[2].

222. West Australian Sandal wood Oil.

The wood of *Fusanus spicatus,* R. Br. (*Santalum cygnorum,* Miq.) is shipped from Fremantle, Western Australia, and is sold in the Singapore market as Swan river sandal wood. In India and China it is used as a substitute for Indian sandal wood from *Santalum album.* According to E. J. Parry[3], at least three other closely related species come into consideration, *viz., Santalum lanceolatum, S. acuminatum* and *S. persicarium.* The wood contains 2 p.c. of oil of an unpleasant resinous odor: $d_{15°}$ 0,953[4] to 0,965[3]; $\alpha_D + 5° 20'$.

Hence West Australian sandal wood oil differs considerably in properties, and presumably also in its composition from East Indian sandal wood oil and can never be used as a substitute for the latter.

As early as 1875 the oil was distilled by Schimmel & Co. in Leipzig. Later the distillation was taken up in Fremantle[5].

As saponification numbers Parry[3] found 1,1 to 1,6. After acetylation he obtained saponification numbers corresponding to a santalol content of 75 p.c. Whether the alcohol of the West Australian sandalwood oil is identical with santalol or not must, however, first be ascertained.

223. South Australian Sandal wood Oil.

Fusanus acuminatus, R. Br. (*Santalum Preissianum,* Miq.; *S. acuminatum,* A. DC.; *S. cognatum,* Miq.; *S. lanceolatum,* Schlecht.), known as "Quandong" in Australia, bears edible fruits which are known as native peaches[6]. The wood of the

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[1] Schimmel's Bericht April 1888, 39.

[2] Mc. Ewan, Pharmaceutical Journ. III. 18 (1888), 661.

[3] Notes on Santal Wood Oil. Bristol 1898, p. 9.

[4] Schimmel's Bericht October 1888, 36; Report of Schimmel & Co. April 1891, 55.

[5] Report of Schimmel & Co. October 1898, 40.

[6] F. von Müller, Select Extra-Tropical Plants. IX. ed. Melbourne 1895, p. 491.

tree is dark brown in color, exceedingly dense and tough as to texture, and very hard and heavy. It contains 5 p.c. of a viscid, cherry-red oil, the sp. gr. of which is 1,022 at 15°. Its odor is agreeably balsamic reminding one of roses. Upon standing, the oil separates crystals which, upon re-crystallization, are obtained as colorless prisms melting at 104 to 105°[1]).

Composition. The crystalline constituent of the oil has been examined by A. Berkenheim[2]). He found its melting point to be 101 to 103° and proposed $C_{15}H_{24}O_2$ as its formula. The substance is an alcohol, the acetic ester of which crystallizes in hexagonal plats that melt at 68,5 to 69,5°. With phosphorus trichloride a derivative $C_{15}H_{23}OCl$ is obtained that melts at 119 to 120,5. Phosphorus pentachloride does not act on the alcohol. The methyl ether obtained with the aid of the sodium compound is liquid. By means of potassium permanganate the alcohol is oxidized to the acid $C_7H_{14}O_2$ which also is liquid.

224. Osyris Oil.

Upon distillation with water vapor of so-called East African sandal wood, which, as was ascertained by a botanical investigation, probably originated from a species of *Osyris*, presumably *tenuifolia*, Engl.[3]), Schimmel & Co.[4]) obtained 4,86 p.c. of a light brown oil. Its odor reminded one somewhat of that of vetiver oil and at the same time of that of gurjun balsam, but was quite distinct from that of sandal wood oil. d_{15° 0,9477; α_D — 42° 50′; n_{D20° 1,52191; E.V. 11,1; E.V. after acetylation 72,8 which corresponds to 30,5 p.c. of a sesquiterpene alcohol $C_{15}H_{26}O$ if such be present. The oil is rather difficultly soluble, since it requires 7 to 8 vol. of 90 p.c. alcohol to dissolve 1 vol. of the oil.

Two oils from African sandal wood, about the botanical origin of which nothing is reported, are described by H. Hænsel[5]).

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[1]) Report of Schimmel & Co. April **1891**, 62 and October **1891**, 44.

[2]) Journ. russ. phys. chem. Ges. **24** (1892), 688; Chem. Zentralbl. **1893**, I. 986.

[3]) Comp. also A. Engler and G. Volkens, *Über das wohlriechende ostafrikanische Sandelholz* (*Osyris tenuifolia*, Engl.). Notizblatt des Königl. botan. Gartens und Museums zu Berlin. No. 9. Published Aug. 7, 1897.

[4]) Report of Schimmel & Co. October **1908**, 109.

[5]) Chem. Zentralbl. **1906**, II. 1496 and **1909**, I. 1477.

Judging by the similarity of properties, a like botanical origin with that of the osyris oil does not seem improbable: d_{20° 0,9589 and 0,9630; α_D — 40,6 and — 60,96°; A.V. 1,7; S.V. 17,9 and 8,1; S.V. after acetylation 88,3 and 68,6. These oils contain a *sesquiterpene* (b.p. 263,5 to 265° under 447 mm. pressure; d_{20° 0,9243; α_D — 32,91°) and a *sesquiterpene alcohol* (b.p. 186 to 188° under 25 mm. pressure).

225. African Sandal wood Oil.

The botanical origin of the oil is not known. The sandal wood from which the oil was distilled was dark brown in color, decidedly hard and tough and had been brought to Europe from Tamatave, Madagascar, via Zanzibar. Upon distillation it yielded 3 p.c. of a ruby red oil of the consistency of East Indian sandal wood oil. The specific gravity was 0,969. Its odor resembled that of West Indian sandal wood oil[1]).

Possibly the wood is identical with that of the wood of *Osyris tenuifolia,* Engl. (see above) or with the wood which occurs in northern Madagascar and is there known as *Hasoranto.* It is said to possess properties similar to that of sandal wood[2]).

Family: ARISTOLOCHIACEÆ.

226. Oil of Asarum europæum.

Oleum Asari europæi. — Haselwurzöl. — Essence d'Asaret.

Origin and Properties. The root of *Asarum europæum,* L. (family *Aristolochiaceæ*), which grows in the shady hardwood forests of Europe, Siberia and the Caucasus, yields upon distillation about 1 p.c. of a viscid, heavy oil that sinks in water. It is brown in color, of a strong aromatic odor and a pepper-like, burning taste. Frequently the oil congeals shortly after distillation, often, however, crystals of asarone separate only after long standing. The specific gravity of the oil lies between 1,018 and 1,068. On account of its dark color, the angle of rotation has not yet been determined.

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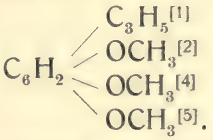
[1]) Report of Schimmel & Co. April 1891, 62.

[2]) J. C. Sawer, Odorographia. London 1892. Vol. 1, p. 325.

Composition. The separation of a solid body from this oil was first observed by Görz[1]) in 1814. J. L. Lassaigne and H. Feneulle[2]) seem to have regarded as camphor the stearoptene obtained by the distillation of the root with water. Additional communications concerning this substance were made by Gräger[3]) and by Blanchet and Sell[4]) who made the first elementary analysis of asarum camphor. C. Schmidt[5]) ascertained the crystallographic properties of the substance and gave to it the name *asarone* which is still in use.

B. Rizza and A. Butlerow[6]) recognized the presence of three methoxyl groups in asarone and proposed the formula $C_{12}H_{16}O_3$ which later proved to be correct. T. Poleck and F. Staats[7]), however, first favored the formula $C_8H_{10}O_2$, later $C_{13}H_{17}O_3$ and finally $C_{13}H_{18}O_3$.

The relative position in the molecule of the three methoxyl groups was ascertained by W. Will[8]) who showed that asarone is a hydroxyhydroquinone derivative. The synthesis of asarone, as accomplished later by L. Gattermann and F. Eggers[9]), revealed the following formula 

$$C_6H_2\begin{cases}C_3H_5^{[1]}\\OCH_3^{[2]}\\OCH_3^{[4]}\\OCH_3^{[5]}.\end{cases}$$

Concerning the internal arrangement of the C_3H_5 group J. F. Eykman[10]) made observations and derived from the index of refraction as well as the capacity for dispersion the conviction that asarone is a propenyl and not an allyl compound.

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[1]) Pfaff, *System der Materia Medica* III. (1814), 230.

[2]) Journ. de Pharm. **6** (1820), 561 ff. — Trommsdorff's Neues Journ. der Pharm. **5**, II (1821), 71.

[3]) J. N. Gräger, *Dissertatio de Asaro Europæo.* Götting. 1830.

[4]) Liebig's Annalen **6** (1833), 296.

[5]) *Ibidem* **53** (1845), 156.

[6]) Berl. Berichte **17** (1884), 1159. — Journ. russ. phys. chem. Ges. **19** (1887), I. 1; Berl. Berichte **20** (1887), 222, Abstracts.

[7]) Berl. Berichte **17** (1884), 1415. — Chem. Ztg. **9** (1885), 1465; Jahresb. f. Pharm. **1885**, 331. — Tagebl. der 59. Versammlung deutscher Naturforscher **1886**, 127; Jahresb. f. Pharm. **1886**, 233.

[8]) Berl. Berichte **21** (1888), 614.

[9]) *Ibidem* **32** (1899), 289.

[10]) *Ibidem* **22** (1889), 3172.

The properties and derivatives of asarone are described in vol. I, p. 487.

Upon distillation of the constituents of the asarum oil that accompany the asarone, A. S. F. Petersen[1]) obtained a lævogyrate fraction boiling between 162 and 165° containing l-*pinene*. Upon direct bromination it yielded a liquid monobromide and, after heating to 250°, dipentene tetrabromide melting at 122°.

The higher boiling constituents of the oil distilled principally in the neighborhood of 250° and had the composition $C_{11}H_{14}O_2$. With sodium nitrite and glacial acetic acid a nitrite melting at 118° was obtained. When heated with hydrogen iodide, methyl iodide was split off. When oxidized with potassium permanganate, veratric acid was formed. On the strength of these results, Petersen regarded the substance boiling at about 250° as *methyleugenol*.

Mittmann[2]), however, is of opinion that not methyleugenol but *methyl*iso*eugenol* is present. He bases his conclusion on a comparison with synthetic methyleugenol produced from bay oil eugenol and with the natural methyleugenol found in this oil. Inasmuch, however, as the phenol of the oil of bay, from which Mittmann prepared his methyl ether, was a mixture of eugenol and chavicol, as was shown later, his methyl ether could not have been a pure body. Hence the conclusions based thereon are valueless. For the present, it must, therefore, remain undecided as to whether asarum oil contains eugenol methyl ether or *iso*eugenol methyl ether.

The highest boiling fraction of the oil is colored green by a substance not further investigated.

227. Oil of Canada Snakeroot.

Oleum Asari canadensis. — Canadisches Schlangenwurzelöl. — Essence de Serpentaire du Canada.

Origin and Production. *Asarum canadense,* L. is known in the United States by the popular names of Canada snakeroot, wild ginger and Canadian asarabacca. The rhizome contains a fragrant volatile oil which is largely used in perfumery in North

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[1]) Arch. der Pharm. **226** (1888), 89. — Berl. Berichte **21** (1888), 1057.

[2]) Arch. der Pharm. **227** (1889), 543.

America. Upon distillation the dry rhizome yield 3 to 4,5 p. c. of oil, the rootlets, which are less rich in oil, 1 to 3 p. c.

Properties. The oil possesses a yellow or yellowish-brown color, and a strong, pleasant, aromatic odor and taste. The properties of the oil from the rootlets differ but little from those of the oil distilled from the rhizome[1]). The constants of two oils distilled from comminuted rhizome with rootlets were as follows: —

1. d_{15° 0,9508; α_D — 22° 0′; n_{D20° 1,48537; A. V. 3,7; E. V. 115,9; E. V. after acetylation 140,1; soluble in 2,7 vol. and more of 70 p. c. alcohol.

2. d_{15° 0,9519; α_D — 10° 30′; n_{D20° 1,48987; A. V. 4,7; E. V. 74,7; E. V. after acetylation 125,0; soluble in 2,5 vol. and more of 70 p. c. alcohol.

Oils obtained from the rhizomes without the rootlets had the following properties: —

1. d_{15° 0,9516; α_D — 2° 50′; n_{D20° 1,48508; A.V. 3,7; E.V. 117,6; E. V. after acetylation 137,2; soluble in 2,3 vol. and more of 70 p. c. alcohol.

2. d_{15° 0,9520; α_D — 10° 42′; n_{D20° 1,48863; A.V. 3,1; E.V. 86,1; E. V. after acetylation 125,8; soluble in 2,3 vol. and more of 70 p. c. alcohol.

An oil distilled from the *rootlets* had the following properties: d_{15° 0,9659; α_D — 39° 40′; n_{D20° 1,50280; A.V. 2,2; E.V. 39,2; E. V. after acetylation 110,2; not soluble in 10 vol. of 70 p.c. alcohol, soluble in 0,9 vol. and more of 80 p. c. alcohol.

Two normal distillates (commercial oils) showed d_{15° 0,9593 and 0,952; α_D — 1° 42′ and — 3° 24′.

A distillate from dry rhizome and herb began to congeal at 20° and had the following properties: d_{20° 1,0446; d_{25° 1,0406; it was soluble in 0,5 vol. of 80 p. c. and in 2 vol. of 70 p. c. alcohol; upon the addition of 8 vol. of alcohol of the same strength the latter solution deposited crystals.

Composition. After the oil had been examined as early as 1880 by F. B. Power[2]) it was subjected to a renewed examination in

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[1]) Report of Schimmel & Co. April 1908, 98 and April 1909, 85.

[2]) On the constituents of the rhizome of Asarum canadense, L., Dissertation, Straßburg 1880. — Proceed. Americ. Pharm. Ass. 28 (1880), 464. — Pharm. Rundsch. (New York) 6 (1888), 101.

1902 by the same investigator in collaboration with F. B. Lees[1]). The following constituents are now known: 1. A *phenol* $C_9H_{12}O_2$[2]). 2. *α-Pinene* (m. p. of nitrol piperidide 118 to 119°), apparently a mixture of both optically active modifications. 3. d-*Linalool* (oxidation to citral; m. p. of naphthocinchoninic acid 195 to 198°). In the first investigation this alcohol was named asarol. 4. l-*Borneol* (oxidation to camphor; m. p. of oxime 115 to 116°). 5. l-*α-Terpineol* (m. p. of dipentene dihydriodide 80°; oxidation to ketolactone $C_{10}H_{16}O_3$, m. p. 62°). 6. *Geraniol* (m. p. of diphenylurethane 81 to 82°). 7. *Methyleugenol* (oxidation to veratric acid; m. p. of bromeugenol methyl ether dibromide 78 to 79°). 8. A blue oil of doubtful composition, consisting of oxygenated compounds alcoholic in character. 9. A *lactone* $C_{14}H_{20}O_2$. 10. *Palmitic acid*. 11. *Acetic acid* and 12. a mixture of higher and lower *fatty acids*.

The eugenol methyl ether content, determined for the original oil according to Zeisel's method, amounted to 36,9 p. c.; the ester content, computed as $C_2H_3O_2 \cdot C_{10}H_{17}$, to 27,5 p. c. The total alcohol content $C_{10}H_{18}O$ was found to be 34,9 p. c. which shows that about 13,3 p. c. of the alcohol were present not as ester but free. As there were likewise about 2 p. c. of pinene, the high boiling portion, including the blue oil, amounts to about 20 p. c.

228. Oil of Asarum arifolium.

Origin and Production[3]). The leaves and more particularly the roots of the American *Asarum arifolium*, Michx. contain a volatile oil of which from 7 to 7,5 % are obtained upon distillation with water vapor.

Properties[3]). A colorless oil with a bitter taste and an aromatic odor recalling that of sassafras. d 1,0585 to 1,0609; $\alpha_D - 2° 55'$ to $- 3° 7'$; $n_{D20°}$ 1,531065 to 1,531875.

Composition. According to E. R. Miller[3]), the principal constituent of the oil is *safrol* (m. p. of *α*-homopiperonylic acid 127 to 128°; of piperonylic acid 227 to 228°). In addition the presence of the following substances was ascertained: l-*α-pinene*

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[1]) Journ. chem. Soc. 81 (1902), 59.

[2]) According to a communication from Dr. C. Kleber in Clifton, N. J., the oil contains *eugenol*, which was identified by means of its benzoate.

[3]) Arch. der Pharm. 240 (1902), 371.

(m. p. of nitrolpiperidide 118 to 119°); *eugenol* (m. p. of benzoyl eugenol 69 to 70°); a small amount of a second *phenol* that produced a green color reaction with ferric chloride; *methyl eugenol* (m. p. of tribromide 78 to 79°), *methyl*iso*eugenol* (m. p. of dibromide 99 to 101°) and *asarone* (m. p. 62 to 63°).

229. Oil of Asarum Blumei.

According to Y. Asahina[1]), the Chinese drug *To-ko* consists of the entire plant (herb, rhizome and rootlets) of *Asarum Blumei,* Duch. It contains 1,4 p. c. of a volatile oil of a yellow color and an odor similar to that of sassafras; d_{15° 1,0788; $[\alpha]_D + 5° 3'$; A. V. and S. V. 0. As to its constituents, the presence of *eugenol, safrol* and of a *terpene-like* body was proved. According to Asahina the drug known in commerce by the names of *Sai-sin* or *Si-sin* and which is said to be obtained from *Asarum Sieboldi,* is likewise obtained from *A. Blumei,* and is therefore identical with *To-ko.*

230. Oil of Virginia Snakeroot.

Origin and Production. The roots of *Aristolochia Serpentaria,* L. as well as those of *A. reticulata,* Nutt. are official in the U. S. Pharmacopœia as *Serpentaria.* Not only are the roots of the two plants similar, both as to external appearance and as to action, but the two oils resemble each other as well.

Upon distillation, the root of *Aristolochia Serpentaria,* L. yields 1 to 2 p.c. of a light brown oil, the odor of which resembles that of valerian, and reminds one, besides, of ginger. d_{15° 0,961 to 0,990; $\alpha_D + 21$ to $+ 26°$; n_{D20° 1,4972 to 1,4980; A. V. 2 to 3; E. V. 65 to 80; E. V. after acetylation 105 to 115. Soluble in 15 to 20 vol. of 80 p. c. and in 0,5 vol. and more of 90 p. c. alcohol.

According to M. Spica[2]), *borneol* has been found as principal constituent.

Upon the distillation of small amounts of *Aristolochia reticulata,* Nutt. J. C. Peacock[3]) obtained but 0,61 to 0,94 p. c. of

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[1]) Journ. of the pharm. Soc. of Japan **1907**, 361; Report of Schimmel & Co. October **1907**, 15.

[2]) Gazz. chim. ital. **17** (1887), 313; Jahresb. f. Pharm. **1887**, 45.

[3]) Americ. Journ. Pharm. **63** (1891), 257.

oil of a golden-yellow color and a camphor- and valerian-like odor; $d_{15,5^\circ}$ 0,974 to 0,978; $\alpha_D - 4^\circ$.

The oil contains a terpene boiling at 157°, probably *pinene,* also *borneol* which occurs as the ester of an acid not yet identified (possibly tiglic acid?).

231. Oil of Aristolochia Clematitis.

The oil from the roots of *Aristolochia Clematitis,* L. was prepared by Winckler[1]) and Frickhinger[2]). The former obtained 0,4 p.c. from the dry roots. Walz[3]) distilled the entire plant and obtained a golden-yellow, viscid oil with an acid reaction and a sp. gr. of 0,903.

232. Oil of Micania Guaco.

The South American drug *Micania Guaco*[4]) is obtained either from *Aristolochia Sellowiana,* Duch. or *A. macroura,* Gom. According to O. Tunmann, it is to be designated *Rhizoma Aristolochiæ Paraguay* for the present.

It contains 1 p.c. of a light yellow oil of a pleasant, minty odor and a burning, cooling taste. d_{15° 0,853; $\alpha_D - 9^\circ 35'$; A. V. 4,06; S. V. 16,25. Upon distillation the bulk of the oil distilled over at 240° (760 mm.) or 160 to 170° (65 mm.). It contains a crystalline *acid,* a crystalline *phenol,* an *ester* and a *terpene-like* substance.

Family: POLYGONACEÆ.

233. Rhaponticum Oil.

The comminuted root of *Rheum Rhaponticum,* L. (family *Polygonaceæ*) yields upon distillation 0,0041 p.c. of an intensely yellow, concrete oil that melts at 25,5°. It contains *chrysophanic acid:* m. p. 158°[5]).

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[1]) Jahrb. f. prakt. Pharm. 19 (1849), 71.

[2]) Repertorium f. d. Pharm. III. 7 (1851), 1.

[3]) Jahrb. f. prakt. Pharm. 26 (1853), 65.

[4]) Handelsbericht von Gehe & Co. 1910, 150.

[5]) H. Hænsel, Apotheker Ztg. 17 (1902), 498.

234. Oil of Polygonum Persicaria.

During the investigation of the constituents of *Polygonum Persicaria,* L. (Ger. *Knœterich*), the herb of which is much used in Russia as a popular remedy, P. Horst[1]) obtained 0,053 p.c. of volatile oil. It consisted in large part of a mixture of volatile, fatty acids, of which *acetic acid* and *butyric acid* were isolated in the form of their silver salts. The balance of the oil contained a crystalline camphor-like substance named *persicariol,* and a liquid body.

Family: CHENOPODIACEÆ.

235. American Wormseed Oil.

Oleum Chenopodii anthelmintici. — Amerikanisches Wurmsamenöl. — Essence de semen-contra d'Amérique; Essence d'Ansérine vermifuge.

Origin. In the neighborhood of Baltimore the oil is distilled from the entire wild or cultivated[2]) plant of *Chenopodium ambrosioides,* L. var. *anthelminticum,* Gray (American wormseed), family *Chenopodiaceæ*[3]).

Production. Westminster in Maryland is the centre of this industry. On account of the unstable nature of the ascaridol, the principal constituent of the oil, its distillation is coupled with difficulties. Several years ago the quality of the commercial oil suffered a marked depreciation: the oils became less dense, the solubility in 70 p.c. alcohol decreased, whereas at the same time the ascaridol content diminished. An investigation undertaken by Schimmel & Co.[4]) revealed the causes of these changes. It was ascertained that when ascaridol is heated with water for long periods, decomposition sets in with the formation of substances that are specifically lighter and at the same time more

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[1]) Chem. Ztg. 25 (1901), 1055.

[2]) Statements concerning the cultivation of this plant may be found under: Cultivation and Collection of Medicinal Plants, The Chemists' and Druggists' Diary 1908, 234.

[3]) Americ. Journ. Pharm. 22 (1850), 304 and 26 (1854), 503.

[4]) Report of Schimmel & Co. April 1908, 110.

difficultly soluble in 70 p.c. alcohol. The constants of a normal oil before and after boiling with water were as follows:—

normal oil:	after boiling for two hours with water:
d_{15° 0,9878	0,9632
α_D $-4^\circ 28'$	$-5^\circ 44$
soluble in 3 vol. of 70 p.c. alcohol.	not soluble in 70 p.c. alcohol.

Taking these changes into consideration, the mode of distillation was changed repeatedly. It was found that a normal oil could be obtained by reducing the length of distillation as much as possible and by using stills of moderate size; that, in order to secure a better separation of oil and water, it is necessary to allow the condenser to run warm, even hot. The aqueous distillate thus obtained contains little oil and is best thrown away. If it is used for the next distillation, the ascaridol contained therein is partly decomposed by heat and hence contributes to the deterioration of the subsequent oil, the density of which it diminishes. Moreover, it is advantageous to use large receivers in order to give the oil as much time as possible to separate from the water.

As becomes evident from the above statement, the yield will vary materially according to the kind of still used and the method of distillation. Under favorable conditions, the seeds yield 0,6 to 1 p.c. of oil, the leaves up to 0,35 p.c.

Properties. The odor of the colorless or yellowish oil is camphor-like, very penetrating and disagreeable. The taste is bitter and burning. The sp. gr. of good, commercial oils lies between 0,965 and 0,990 and above; $\alpha_D - 4$ to $-8^\circ 50'$. Soluble in 3 to 10 vol. of 70 p.c. alcohol¹).

Inferior oils have d_{15° 0,93²) to 0,965 and do not yield a clear solution with 70 p.c. alcohol. At times, however, adulteration with turpentine oil is the cause of the poor solubility and the low specific gravity. Its detection can be brought about by fractional distillation, since turpentine oil will pass over below

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¹) The oils mentioned by Schimmel & Co. in their Report April 1894, 56 (seed oil, d_{15° 0,900; $\alpha_D - 18^\circ 55'$; leaf oil, d_{15° 0,879; $\alpha_D - 32^\circ 55'$; both insoluble in 70 p.c. alcohol) appear to have been distilled under the unfavorable circumstances enumerated above, hence cannot be regarded as normal distillates.

²) E. Kremers, Pharm. Review 25 (1907), 155.

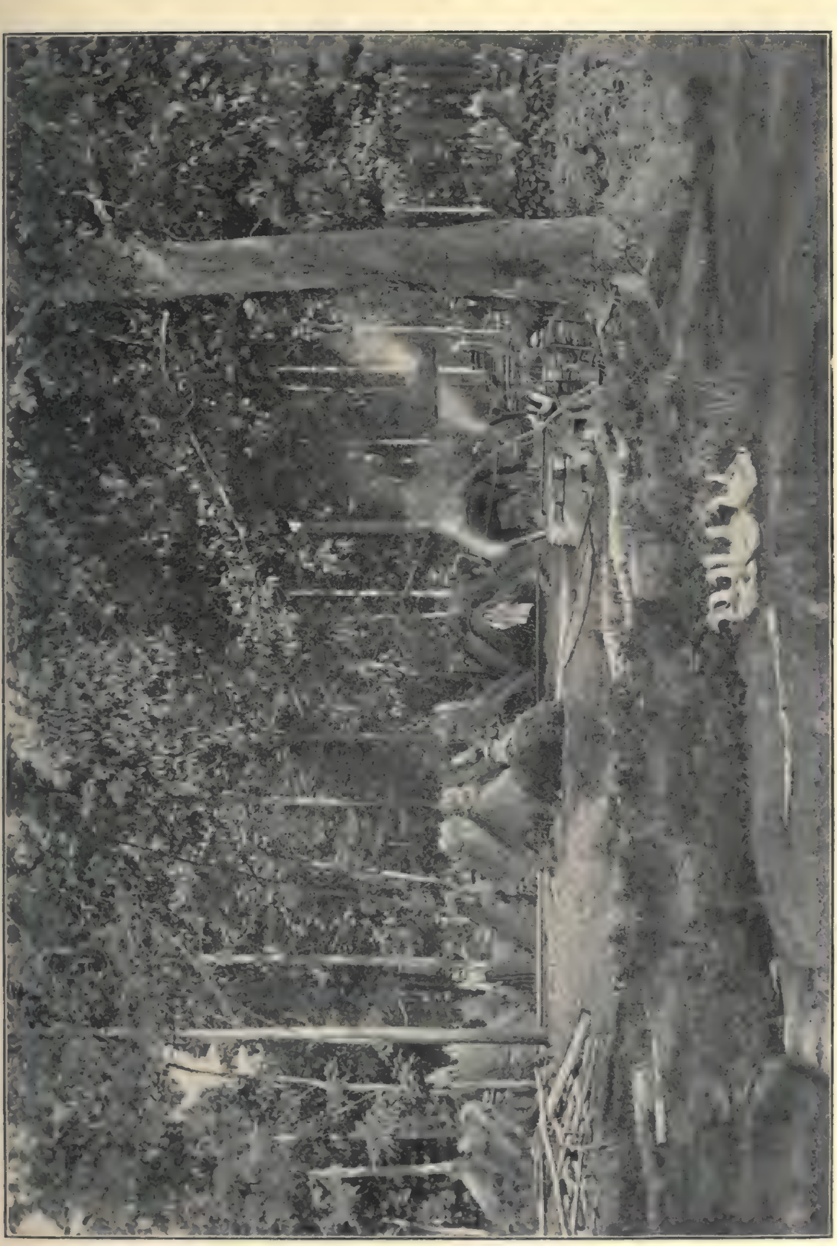

Fig. 33.
Distillation of American Wormseed oil in Maryland.

170°, whereas pure oils yield no fractions below 170°. If the oil be heated with acetic acid anhydride and sodium acetate, the product yields a comparatively high ester value (about 280). This, however, cannot be regarded as an analytical constant, since radical changes are produced during the acetylation of the oil[1]).

Composition. An investigation made in 1854[2]) contributed but little to our knowledge of the composition of the oil. It was not until 1908 when an investigation, undertaken by Schimmel & Co.[3]), revealed the presence of several known substances in the oil and also the composition of the principal constituent thereof, the ascaridol $C_{10}H_{16}O_2$.

The lowest fractions which begin to boil at 172° consist of p-*cymene* (*p*-hydroxy*iso*propyl benzoic acid; m.p. of *p*-propenylbenzoic acid 159 to 160°), with which are admixed small amounts of a terpene, presumably *sylvestrene* (sylvestrene reaction). In the middle fraction traces of d-*camphor* were found (m.p. of semicarbazone 236°; of oxime 118°).

The principal constituent of the oil, the *ascaridol*[4]) $C_{10}H_{16}O_2$, has a disagreeable, benumbing odor and a disagreeable taste; $d_{15°}$ 1,0079; $\alpha_D - 4° 14'$; $n_{D20°}$ 1,4731; b.p. 83° (4 to 5 mm.). Under ordinary pressure this substance cannot be distilled, since it decomposes, even before the boiling point has been reached, with explosive[5]) violence which is frequently accompanied by a flame.

In his attempt to ascertain the constitution of ascaridol, E. K. Nelson[6]) used a product that had the following constants: b.p. 96 to 97° (8 mm.); $d_{20°}$ 0,9985; $\alpha_D + 0,7°$; $n_{D20°}$ 1,4719.

As ascertained by Nelson, ascaridol, when acted upon by a saturated solution of ferrous sulphate at ordinary temperature, is decomposed with the evolution of considerable heat and the formation of a combustible gas. As one of the reaction products, *iso*propyl alcohol was isolated from the viscid mass by distillation with steam. It was recognized as such by its oxi-

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[1]) E. Kremers, Pharm. Review 25 (1907), 155.

[2]) Garrigues, Americ. Journ. Pharm. 26 (1854), 405.

[3]) Report of Schimmel & Co. April 1908, 109.

[4]) So called because of its action against Ascaridæ.

[5]) Already observed by E. Kremers *(loc. cit.)*.

[6]) Journ. Americ. chem. Soc. 33 (1911), 1404.

dation to acetone with chromic acid (m. p. of dibenzylidene acetone 111 to 112°). At temperatures below 35° the reaction runs smoothly and without decomposition. Under these conditions ascaridol adds the elements of a molecule of water and is converted into a glycol $C_{10}H_{18}O_3$ which, when benzoylated according to Schotten-Baumann, yielded a solid benzoate melting at 136 to 137°. Regenerated from this ester by saponification, this glycol is obtained as a colorless and odorless, sticky oil that boils at 271 to 272° and which upon prolonged standing in vacuum separates crystals that melt at 62,5 to 64°. The glycol has the following constants: $d_{20°}$ 1,0981; $\alpha_D \pm 0$; $n_{D20°}$ 1,4796; mol. refr. 48,63 (computed 48,65). That the substance $C_{10}H_{18}O_3$ contains a second OH group is proved by the formation of a dibenzoate which results when the glycol is heated with benzoic acid anhydride to 150° for two hours. From alcohol the ester crystallizes in needles that melt at 116,5 to 117,5°.

Fused with caustic alkali or boiled with sodium, the glycol is partly converted into a compound which is colored greenish-violet when exposed to the air. When acidulated and after ferric chloride has been added, steam drives over a substance which can be shaken out of its ethereal solution by caustic alkali with a violet color. When acidulated, there were obtained small amounts of orange-yellow crystals that melted at 164 to 166° and apparently were α-hydroxythymoquinone. With concentrated sulphuric acid these gave a purple-red color. Its aniline derivative crystallizes in dark-violet needles.

When the glycol is oxidized with permanganate solution, there results a mixture of volatile acids (acetic acid, butyric acid?) in addition to a dibasic acid $C_{10}H_{16}O_5$ that is difficultly soluble in water, melts at 116,5 to 117° and which has been named *ascaridolic acid.* Its silver salt is well-nigh insoluble in water. As shown by its behavior toward acetic acid anhydride, hydroxylamine or semicarbazide, its molecule contains neither a hydroxyl nor a ketone group. Its behavior during titration excludes the possibility of its being an anhydride or lactone. When heated beyond its melting point, methyl heptenone¹) appears to be formed.

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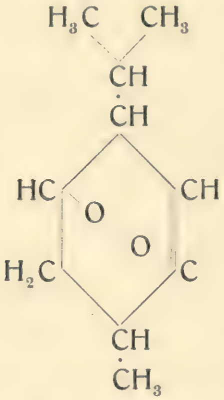
¹) The formation of methyl heptenone when the acid $C_{10}H_{16}O_5$ is distilled was unquestionably established by Schimmel & Co.

When oxidized the glycol yields another solid acid which melts at 186 to 187° and is dibasic. Nelson assigns to it the provisional formula $C_{10}H_{16}O_6$.

Basing his conclusions on the foregoing results, Nelson assumes that ascaridol is a *peroxide* of the following formula:



Wallach[1]), however, who examined ascaridol at about the same time, but who persued another course, arrived at somewhat different conclusions.

Suspended in water and in the presence of colloidal palladium, ascaridol adds with unprecedented rapidity 4 atoms of hydrogen. Hence, lest the heat generated during the reduction becomes too great, the addition of hydrogen must be regulated. Two products result that are easily separated: an oil readily volatile with water vapor, and a solid substance that is difficultly volatile. This is best extracted from the residue with chloroform after the bulk of the readily volatile substance has been distilled over. The solid reduction product is a new terpin, 1,4 *terpin (terpinene terpin).* It consists of large prisms that melt at 116 to 117°. This terpin can exist in two stereoisomeric forms, one of which melts at 137° and was described by Wallach[2]) several years ago. The product melting at 116 to 117° evidently represents the second form. When 1,4 terpin is heated with oxalic acid, there results as principal product 1,4-cineol[3]) (b. p. 172°; $d_{18°}$ 0,9010;

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[1]) Liebig's Annalen **392** (1912), 59.

[2]) Berl. Berichte **40** (1907), 577.

[3]) Liebig's Annalen **356** (1907), 197.

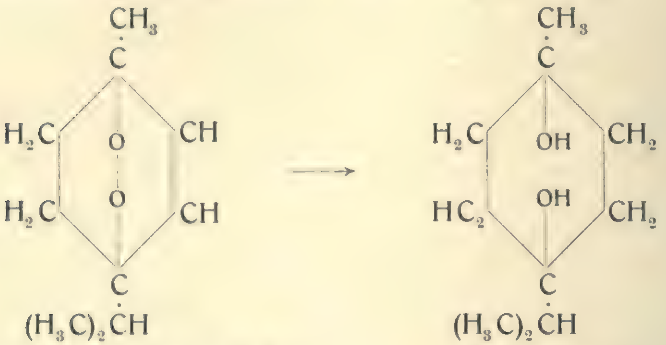
$n_{D18°}$ 1,4479) which when mixed with hydrogen bromide in acetic acid yields terpinene dihydrobromide melting at 58 to 59°. Upon prolonged heating with potassium permanganate there did not result an acid corresponding to cineolic acid, but a sparingly soluble acid melting at 157° and containing less oxygen. When 1,4 terpin is acted upon with oxalic acid there results, in addition to much 1,4 cineol, a small amount of an unsaturated alcohol. This alcohol could not be obtained in a pure state. However, it was possible to identify its oxidation product. For this purpose the reaction product of the terpin was distilled off with water vapor and oxidized at 0° with 1 p.c. potassium permanganate solution. The 1,4 cineol present was distilled off with water vapor. The residue contained a glycerol which, when heated with dilute sulphuric acid, yielded cymene and a ketone, Δ^1-menthenone-3. Upon further oxidation, the two terpinenols yielded α-α'-dihydroxy-α-methyl-α'-*iso*propyladipic acid, which can readily be identified by conversion into its dilactone. As a matter of fact, it was possible to obtain a dilactone $C_{10}H_{14}O_4$ melting at 72° by the corresponding treatment of the oxidation mixture. Thus was proved the presence of a terpinenol in the product obtained by the reaction of oxalic acid on terpin and the terpin itself characterized as a derivative of terpinene.

The oil, together with the terpin that resulted upon the reduction of ascaridol, contained saturated and unsaturated constituents. The product was, therefore, further reduced in the presence of palladium and the last traces of unsaturated compound were removed by potassium permanganate. An alcohol $C_{10}H_{19}OH$ (b.p. 207 to 208°; $d_{19°}$ 0,9080; n_D 1,4656) results, which when heated with zinc chloride yields a hydrocarbon (b. p. 173,5 to 175,5°; $d_{19°}$ 0,821; $n_{D19°}$ 1,4558; mol. refr. found 45,67, computed for $C_{10}H_{18}$ = 45,63). These figures agree well with those for menthene. Presumably, however, the product is a mixture.

The results communicated above justify the assumption that ascaridol adds 4 atoms of hydrogen with the formation of 1,4 terpin (II). Provided that no re-arrangement of the atoms has taken place during the reduction to 1,4 terpin, formula I may be assumed for ascaridol.

Wallach suspects that the acid $C_{10}H_{16}O_6$, melting at 186 to 187°, obtained by Nelson from ascaridol has the formula $C_{10}H_{18}O_6$

and that it is identical with α',α'-dihydroxy-α-methyl-α'-*iso*propyladipic acid. Wallach regards the formulas proposed by Nelson for ascaridol and ascaridolglycol as of little probability.



(I) Ascaridol according to Wallach. (II) 1,4-Terpin.

In order to ascertain the approximate amount of ascaridol present, Schimmel & Co.[1]) fractionated several oils that showed great variation in their physical constants. They obtained the following results: Normal American oil (d_{15° 0,9708) contained 62 to 65 p.c. of ascaridol and about 22 p.c. of cymene. A light oil (d_{15° 0,9426) contained but 45 to 50 p.c. of ascaridol and as much as about 38 p.c. of hydrocarbons. The high percentage of the latter accounts for its lack of solubility. An oil distilled by Schimmel & Co. contained 65 to 70 p.c. ascaridol and only about 20 p.c. hydrocarbons (cymene). In spite of the high percentage of the readily soluble principal constituent, this oil was sparingly soluble. An explanation for this anomaly was found in the large percentage of resinous residue that remained upon fractionation. In the case of this oil it amounted to 12,5 p.c., whereas in the oils just mentioned it amounted to only 4 p.c. and 6 p.c., respectively.

An observation, made during the oxidation of an ascaridol obtained by fractional distillation, seems to indicate the presence of *safrol* in American wormseed oil. The acids obtained upon treatment with permanganate (see above) yielded upon vacuum distillation a residue from which homopiperonylic acid (m. p. 127 to 128°) and piperonylic acid (m. p. 226 to 228°) could be obtained.

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[1]) Report of Schimmel & Co. April 1908, 118.

Physiological action. In North America the American wormseed oil is used very successfully as anthelmintic. According to H. Brüning[1]) ascaridæ become lifeless after a short time in water, sodium chloride solution, or Ringer's solution of 38° C. to which some ascaridol or wormseed oil has been added, whereas in the control experiments the animals continued to move about for a long period. Even in solution of 1:5000 a paralysing, narcotizing action results within two hours. However, when the animals are transferred to a non-poisonous solution, they regain their mobility after a short time. Basing his conclusions on extended experimental studies and on a series of successful treatments on patients afflicted with worms, Brüning regards American wormseed oil as an anthelmintic equal, if not superior, in its effect to santonin. Varying with the age, the dose for children is from 8 to 15 drops, mixed with sugar water three times during the forenoon. If a medicine dropper be used 0,5 to 1,0 g. of pure oil is taken. This is followed by a cathartic, such as castor oil, *Pulv. Curellæ,* or a similar preparation, at intervals of an hour.

According to W. Salant[2]) American wormseed oil produces temporary excitement, then general paralysis and coma. If a dose of 0,2 cc. per kg. body weight be administered into the stomach, death results after 24 to 48 hours. The active constituent of the oil, the ascaridol, is twice as active. It lowers the blood pressure.

236. Oil of Chenopodium ambrosioides, L.

The seeds of *Chenopodium ambrosioides,* L., which are closely related to *C. ambrosioides,* L., var. *anthelminticum,* are

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[1]) H. Brüning, *Zur Behandlung der Ascaridiasis.* Medizinische Klinik **1906**, No. 29. Additional literature: H. Brüning, Ztschr. f. exp. Patholog. u. Therap. **3** (1906), 564. — H. Brüning, Zentralbl. f. d. ges. Therapie **24** (1906), 659. — H. Brüning, Deutsche Medizinische Wochenschrift **1907**, No. 11. — F. Thelen, *Klinische Erfahrungen über das amerikanische Wurmsamenöl als Antiascaridiacum bei Kindern. Inaug. Dissert.,* Rostock 1907. — Münch. med. Wochenschr. **57** (1910), 1643. — H. Brüning, Arch. f. Schiffs- u. Tropenhygiene **14** (1910), 733. — W. Salant, Journ. of Pharmacology and experim. Therap. **2** (1911) 391; Abstract in Therap. Monatsh. **25** (1911), 498. — H. Brüning, Zeitschr. f. experiment. Pathologie u. Therapie **11** (1912), 154.

[2]) Journ. of Pharmacology and experimental Therapeutics **2** (1911), 391; Therap. Monatsh. **25** (1911), 498.

used by the people of Brazil as anthelmintic. According to Th. Peckolt[1]) they contain a volatile oil possessing a strong aromatic odor, and a bitter, burning taste. Sp. gr. 0,943.

The leaves of this plant, which were official formerly as *Hb. Chenopodii ambrosioides seu Botryos americanæ,* yielded upon distillation 0,25 p.c. of an oil of a disagreeable, camphor-like, narcotic odor that reminded one of trimethylamine. Sp. gr. 0,901[2]).

237. Oil of Camphorosma monspeliaca.

According to Cassan[3]) the herb of *Camphorosma monspeliaca,* L. (family *Chenopodiaceæ*), which was formerly officinal as *Herba Camphoratæ,* upon distillation with water vapor yields about 0,2 p.c. of a volatile oil. It is greenish-yellow, has an odor reminding one of bitter almonds and congeals at $+4°$; $d_{17°}$ 0,970; $n_{D15°}$ 1,3724.

Family: CARYOPHYLLACEÆ.

238. Oil of Herniaria glabra.

Upon distillation of the flowering herb of *Herniaria glabra,* L. (family *Caryophyllaceæ*), which was formerly officinal as *Herba Herniariæ,* H. Hænsel[4]) obtained 0,585 p.c. of a solid volatile oil a that melted at 36°.

Family: RANUNCULACEÆ.

239. Oil of Pæonia Moutan.

Origin and Production. The root bark of *Pæonia Moutan,* Sims (family *Ranunculaceæ*), a drug that is used extensively in Japan and China, contains on its inner surface as well as on fracture surfaces small white crystals of *pæonol* that can be isolated by distillation with water vapor or, better still, by extraction with ether. The crude oil is purified by first shaking

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[1]) Pharm. Rundsch. (New York) **13** (1895), 89.

[2]) Report of Schimmel & Co. April 1891, 61.

[3]) Thèse, Montpellier 1901.

[4]) Apotheker Ztg. **16** (1901), 281.

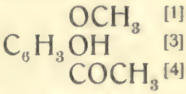
out its ethereal solution with soda solution which takes up the impurities only; then by removing the pæonol by means of aqueous sodium hydroxide and separating it by means of sulphuric acid.

According to W. Will[1]) the yield amounts to 3 to 4 p.c., whereas Schimmel & Co. could obtain but 0,4 p.c. of oil upon distillation of the root with water vapor.

Properties. The oil obtained by distillation consists, at ordinary temperature, of a yellowish, solid mass, saturated with a brown liquid. It melts at about 40°; d_{15° (super-cooled) 1,1502; α_D inactive; n_{D20° (super-cooled) 1,56460; A. V. 12,6; E. V. 24,5; E. V. after acetylation 220,7; not completely soluble in 10 vol. of 70 p.c. alcohol, soluble in 1 vol. and more of 80 p.c. alcohol.

Composition. *Pæonol* was first isolated by Martin and Jagi[2]). Basing their conclusions on an elementary analysis and an examination of its calcium compound, they regarded it as a fatty acid closely related to caprinic acid. According to W. N. Nagai[3]), pæonol possesses an aromatic odor, crystallizes in needles, melts at 50°, and has the composition $C_9H_{10}O_3$[4]). It is but sparingly soluble in cold water, readily so in hot water, alcohol, ether, benzene, chloroform and carbon disulphide. Ferric chloride colors the aqueous as well as the alcoholic solution a red-violet. Aqueous caustic alkalies dissolve pæonol forming well crystallizable salts therewith.

As ascertained by Nagai, the constitution of pæonol is expressed as *p*-methoxy-*o*-hydroxyphenylmethyl ketone:



$$C_6H_3\begin{matrix}OCH_3 & [1]\\ OH & [3]\\ COCH_3 & [4]\end{matrix}$$

When fused with potassium hydroxide or when boiled with hydrogen iodide, resacetophenone $C_6H_3\cdot OH^{[1]}\cdot OH^{[3]}\cdot COCH_3{}^{[4]}$, melting at 142°, results. Acetylpæonol, m. p. 46,5°, is oxidized by means of permanganate to *p*-methoxysalicylic acid $C_6H_3OCH_3{}^{[1]}\cdot OH^{[3]}\cdot COOH^{[4]}$. The oxime of pæonol crystallizes in fine

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[1]) Berl. Berichte **19** (1886), 1776.

[2]) Arch. der Pharm. **213** (1878), 335.

[3]) Berl. Berichte **24** (1891), 2847.

[4]) Tiemann, Berl. Berichte **24** (1891) 2854, found the melting point of pure pæonol at 48°. Other derivatives of pæonol are described: *Ibidem* **25** (1892), 1284 and **29** (1896), 1754.

needles, the phenyl hydrazone in needles that are faintly yellow in color and melt at 170°.

Tahara[1]) prepared pæonol synthetically by methylating resacetophenone.

240. Oil of Nigella sativa.

The oil of the seeds of *Nigella sativa,* L. (Ger. *Schwarzkümmel,* family *Ranunculaceæ*) (yield 1,4 p.c.) is yellow in color, does not fluoresce and has an unpleasant odor. d_{15° 0,875 to 0,877; $\alpha_D + 1^\circ 26'$ to $+ 2^\circ 20'$; n_{D20° 1,48364 to 1,48441; A. V. 0 to 0,5; E. V. 1 to 6; E. V. after acetylation 15 to 25; soluble in 4,5 and more vol. of 90 p.c. alcohol. It boils between 170 and 260°[2]).

241. Oil of Nigella damascena.

Origin, Production and Properties. The seeds of *Nigella damascena,* L., known occasionally as *Schwarzkümmel,* yield upon distillation 0,4 to 0,5 p. c. of an oil with a beautifully blue fluorescence, which has the agreeable odor and taste of juniper berries. d_{15° 0,895 to 0,915[3]); $\alpha_D + 1^\circ 4'$ to $- 7,8^\circ$[3]); n_{20° 1,5582[3]). In 90 p. c. alcohol the oil is but imperfectly soluble, in absolute alcohol it is soluble in all proportions.

Composition. The principal constituent of nigella oil[4]) is the alkaloid *damascenine,* $C_{10}H_{13}O_3N$, which produces the characteristic fluorescence, and which was first prepared by A. Schneider[5]). By shaking the oil with tartaric acid and subsequent decomposition of the tartrate with soda[6]), as much as 9 p. c. can be isolated from the oil. The alkaloid can also be obtained by

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[1]) Berl. Berichte 24 (1891), 2459.

[2]) Report of Schimmel & Co. April 1895, 75.

[3]) H. Hænsel, Apotheker Ztg. 15 (1911), 28.

[4]) The statements found in the reports on earlier investigations are largely contradictory. This is due to the fact that in some instances the seeds of *Nigella damascena,* L., were examined, in others those of *Nigella sativa,* L. — H. G. Greenish, Pharmaceutical Journ. III. 12 (1882), 681. — Reinsch, Jahrbuch f. prakt. Pharm. II. 4 (1841), 385; Pharm. Zentralbl. 1842, 314. — Flückiger, *ibidem* III. 2 (1854), 161.

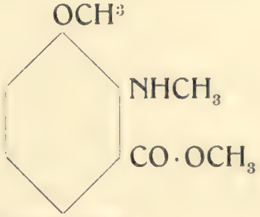
[5]) Pharm. Zentralh. 31 (1890), 173 and 191. Comp. also the inaug. dissertation by the same author, Erlangen 1890.

[6]) Report of Schimmel & Co. October 1899, 38.

percolating the comminuted seed with dilute hydrochloric acid, supersaturating the solution with soda and extracting with petroleum ether. From the petroleum ether solution the chlorhydrate of the base can be shaken out in a pure condition by means of hydrochloric acid. In this manner 18 kg. of seeds yielded 110 g. of hydrochlorate[1]).

Pure damascenine boils with slight decomposition at 270° (750 mm.)[2]) or in vacuum at 157° (10 mm.). It congeals in the cold and melts at 26°. According to A. Schneider it yields crystalline salts with acids. With platinum chloride, gold chloride, and mercuric chloride, crystalline double salts result. With the general alkaloidal reagents it produces characteristic precipitates: solution of iodine in potasium iodide produces a purplish-brown precipitate; potassium bismuth iodide, a brown precipitate; potassium mercuric iodide and phosphomolybdic acid yield white precipitates.

The problem of the constitution of damascenine has been attacked consecutively by Schimmel & Co.[3]), H. Pommerehne[4]) and O. Keller[5]). However, A. J. Ewins[2]) first succeeded in proving the constitutional formula of damascenine by its synthesis, thus demonstrating it to be the methyl ester of a 2-methylamino-3-methoxybenzoic acid.



Damascenine.

The synthesis of damascenine was accomplished in the following manner: with the aid of dimethyl sulphate, *m*-hydroxybenzoic acid was converted into *m*-methoxybenzoic acid. When nitrated, this yielded a mixture of nitro products from which the

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[1]) Arch. der Pharm. **237** (1899), 475.

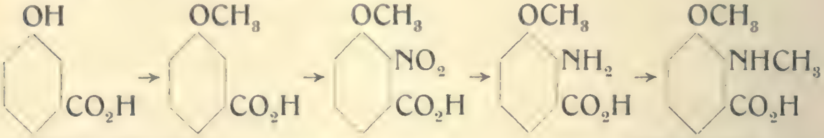
[2]) Journ. chem. Soc. **101** (1912), 544.

[3]) *Loc. cit.*

[4]) Arch. der Pharm. **238** (1900), 546; **239** (1901), 34; **242** (1904), 295.

[5]) *Ibidem* **242** (1904), 299; **246** (1908), 1.

2-nitro-3-methoxybenzoic acid could be isolated without difficulty. This was reduced to 2-amino-3-methoxybenzoic acid which, when heated with methyl iodide in a sealed tube, yielded the hydriodide of 2-methylamino-3-methoxy benzoic acid. By heating it with freshly precipitated silver chloride it was converted into the corresponding hydrochloride (m.p. 210 to 211°) which is identical with the hydrochloride of damasceninic acid. By passing hydrogen chloride into the methyl alcoholic solution of the hydrochloride, the hydrochloride of the methyl ester is produced. When hydrogen chloride is split off, this yields *methyl-2-methylamino-3-methoxybenzoate* or *damascenine* (m. p. 23 to 24°). Mixed with the natural product, this synthetic damascenine suffers no lowering of the melting point.



m-Hydroxybenzoic acid

Damasceninic acid

The seeds of other species of *Nigella* have also been examined for alkaloids by O. Keller[1]. In the seeds of *Nigella aristata* he is supposed to have found a new alkaloid, *methyldamascenine,* in addition to damascenine. According to Ewins, however, this is an error. The methyldamascenine of Keller, $C_{10}H_{13}O_3N$, is by him supposed to be identical with the damascenine of *Nigella damascena* to which the above formula should be assigned. Keller's attempts to isolate alkaloids from the seeds of *Nigella sativa, N. arvensis, N. orientalis, N. hispanica, N. Garidella, N. integrifolia* and *N. diversifolia* by extraction with dilute hydrochloric acid gave negative results.

242. Oil of Ranunculus Ficaria.

The dry herb (with few flowers) of *Ranunculus Ficaria,* L. (family *Ranunculaceæ*) yields upon distillation[2] 0,02 p.c. of a dark brown oil with a tobacco-like odor. d_{24° 0,9101; b.p. 150 to 310°. It contains *palmitic acid,* m.p. 61°.

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[1] *Loc. cit.*

[2] H. Hænsel, Apotheker Ztg. **24** (1909), 774.

Family: MENISPERMACEÆ.

243. Colombo Root Oil.

From the officinal root of *Jatrorrhiza palmata,* Miers (family *Menispermaceæ*), H. Hænsel[1]) obtained a volatile oil of a dark brown color: $d_{15°}$ 0,9307; α_D, so far as the dark color of the oil permitted observation, inactive; A.V. 24; S.V. 54; readily soluble in 96 p.c. alcohol, more difficultly soluble in 80 p.c. alcohol, with the separation of brown floccules. The yield amounted to 0,00568 p.c.

Family: MAGNOLIACEÆ.

244. Oil of Magnolia glauca.

According to F. Rabak[2]), the leaves of the North American tree *Magnolia glauca,* L. *(Magnoliaceæ)* contain 0,05 p.c. of a light yellow, ethereal oil: $d_{25°}$ 0,9240; $[\alpha]_D + 3,96°$; $n_{D25°}$ 1,4992; A.V. 1,8; E.V. 13; E.V. after acetylation 28; forms a turbid solution with 3½ vol. of 90 p.c. alcohol, insoluble in 80 p.c. alcohol.

245. Kobuschi Oil.

Origin and Production[3])[4])[5]). The oil distilled, with a yield of about 0,45 p.c., from the fresh leaves and twigs of the kobuschi tree, *Magnolia Kobus,* DC. (family *Magnoliaceæ*), which occurs in the interior of Japan, is light yellow in color and possesses the following properties: $d_{15°}$ 0,9432 to 0,9642; α_D —1° 6′ to —1° 32′; A.V. 0,7 to 1,5; E.V. 4,3 to 8,87; soluble in 1,2 to 10 vol. of 80 p.c. alcohol, the strongly diluted solution of which reveals opalescence; soluble in 0,5 to 1 vol. of 90 p.c. alcohol to a clear solution.

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[1]) Apotheker Ztg. **19** (1904), 46.

[2]) Midland Drugg. and pharm. Review **45** (1911), 486.

[3]) Report of Schimmel & Co. October **1903**, 78.

[4]) E. Charabot and G. Laloue, Compt. rend. **146** (1908), 183; Bull. Soc. chim. IV. **3** (1908), 381.

[5]) Report of Schimmel & Co. April **1908**, 61.

Composition. The oil, which boils between 190 and 230°, contains *cineol*[3] (resorcinol derivative), about 15 p.c. *citral*[1][2][3] and 16 p.c. *anethol*[2] (m.p. of anisic acid 184°; m.p. of anethol dibromide 66 to 67°). Probably *methylchavicol* is also present. Whereas the corresponding fraction could not be made to congeal at first, it solidified readily after boiling for two hours with strong alkali (re-arrangement to anethol)[3]. However, safrol, the presence of which was at first suspected[1], is not a constituent of the oil.

An oil distilled in the province Shizuoka from very young twigs and examined by Y. Asahina and H. Nakamura[4] differs in part from the oils described above. It was light yellow and possessed a citral-like odor: d_{15° 0,982; $\alpha_D + 6^\circ 8'$; A. V. 4,3; S.V. 19,1; E.V. after acetylation 56,48; soluble in 1,4 volume of 85 p. c. alcohol, the addition of more alcohol producing opalescence. Of its constituents the following were identified: *citral* (6 to 7 p. c.; m. p. of α-citryl-β-naphthocinchoninic acid 197 to 200°), *eugenol* (m. p. of benzoyl derivative 69°), *cineol* (m.p. of cineol-iodol 112 to 113°, m.p. of cineolic acid 195°), and *methylchavicol* as principal constituent. Upon oxidation with potassium permanganate it yielded homoanisic acid (m.p. 84 to 85°) and anisic acid (m.p. 184°). Possibly the oil also contains *pinene,* for fraction 150 to 160° yielded traces of a nitrosochloride which, however, could not be characterized because of the small amount. Of acids the presence of *caprinic acid* (silver salt 38,52 p.c. Ag) and *oleic acid* (silver salt 27,54 p.c. Ag) were ascertained. It is noteworthy that the oil examined by Asahina and Nakamura contained no anethol but *eugenol* which was wanting in the oils previously examined.

246. Magnolia Oil.

A Japanese oil designated as magnolia oil[5] but concerning the origin of which nothing was known, was a limpid liquid, light

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[1] Report of Schimmel & Co. October **1903**, 78.

[2] E. Charabot and G. Laloue, Compt. rend. **146** (1908), 183; Bull. Soc. chim. IV. **3** (1908), 381.

[3] Report of Schimmel & Co. April **1908**, 61.

[4] Journ. of the Pharm. Soc. of Japan No. 322 Dec. 1908, Tokyo; Report of Schimmel & Co. April **1909**, 59.

[5] Report of Schimmel & Co. October **1907**, 101.

yellow in color and possessed the following properties: d_{15° 0,9100; $\alpha_D + 14^\circ 10'$; soluble in about 7 vol. and more of 80 p.c. alcohol showing slight turbidity. Of its constituents the presence of *cineol* and *phellandrene* was demonstrated. Presumably *linalool* and *terpineol* are also present. These results would seem to exclude the identity of this oil with kobuschi oil from *Magnolia Kobus,* DC.

247. Champaca Flower Oil.

GENUINE CHAMPACA FLOWER OIL[1]).

The genuine champaca tree, *Michelia Champaca,* L. (family *Magnoliaceæ*), which is characterized by its yellow flowers, occurs throughout tropical Asia, particularly in Java and the Philippines. However, it does not occur so abundantly that the perfume can be obtained on a large scale from the fragrant flowers. Attempts to prepare the oil by steam distillation failed, on the one hand because of the small yield, and on the other hand because the oil thus obtained resembles the flowers but little as to odor.

R. F. Bacon[2]), however, has pointed out that the maceration of the flowers with paraffin oil, in which the flowers are allowed to remain 24 hours and which is used nine times over for the extraction of fresh flowers, and subsequent extraction of the hydrocarbon oil with strong alcohol yields an oil with a fine and strong odor. Later the same investigator[3]) describes a product, obtained with a yield of 0,2 p. c. (the method of preparation is not given) which upon standing separates a considerable amount of crystals. The oil, separated by filtration, congealed to a semi-solid mass upon standing, due to the separation of an amorphous mass (presumably resinified oil) which upon the addition of 70 p.c. alcohol was isolated as a brown odorless substance. The filtrate was evaporated in a vacuum at 40° until a brown oil had separated which possessed a fine cham-

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[1]) The oil of guaiac wood distilled from *Bulnesia Sarmienti* (which see), which enters commerce as champaca wood oil, has nothing in common with the genuine champaca oil. Report of Schimmel & Co. April 1893, 42.

[2]) Philippine Journ. of Sc. 4 (1909), A. 131.

[3]) *Ibidem* 5 (1910), 262.

paca odor. In this way oils were obtained that possessed the following properties: $d_{30^\circ}^{30^\circ}$ 0,9543 to 1,020; n_{D30° 1,4550 to 1,4830; S.V. 160 to 180. The optical rotation could not be determined because of the dark color of the oil. It was soluble in 70 p.c. and stronger alcohol, the solution having a neutral reaction.

Upon saponification the oil of champaca flowers loses its characteristic odor almost completely. From 50 g. of oil 1,5 g. = 3 p.c. of phenols, principally iso*eugenol* (m. p. of benzoylderivative 103°) were obtained. In addition the oil contained 15 g. = 30 p.c. of acids (none of which boiled below 140° under 40 mm. pressure, indicating the absence of methylethylacetic acid) and 23 g. = 46 p.c. of neutral substances the odor of which resembles that of bay oil.

Oils likewise distilled in Manila by B. T. Brooks[1]) had the following properties: $d_{30^\circ}^{30^\circ}$ 0,904 to 0,9107; n_{D30° 1,4640 to 1,4688; E.V. 124 to 146; E.V. after acetylation 199. They could not be fractionated in vacuum because they resinified. Brooks identified *cineol* (m. p. of the iodol compound 112 to 114°). Possibly *p*-cresol methylether is also present but it could not be identified. When the oil was shaken with sodium acid sulphite solution *benzaldehyde* could be isolated (m. p. of phenylhydrazone 149 to 151°). Presumably another aldehyde is present, but it was not further investigated. Of alcohols Brooks found *benzyl alcohol* which he characterized by oxidation to benzaldehyde, also *phenylethyl alcohol.* In the alkaline saponification liquid he found *benzoic acid.* The benzaldehyde content of the oil amounts to about 6 p.c. Of benzoic acid it contains but 0,5 p.c. Brooks is of the opinion that this may have resulted from the oxidation of the benzaldehyde or benzyl alcohol.

In the oil of champaca flowers there occurs a crystalline substance, which melts at 165 to 166°, to which Bacon assigns the empirical formula $C_{10}H_{20}O_5$. Contrary to the observations of Bacon, Brooks found that this substance reacts quantitatively with bisulphite solution. However, it cannot be regenerated from the bisulphite compound. It is a ketone the phenylhydrazone of which melts at 161°, the semicarbazone at 205 to 206°.

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[1]) Philippine Journ. of Sc. **6** (1911), A, 333. — Journ. Americ. chem. Soc. **33** (1911), 1763.

COMMERCIAL OILS.

From Bacon's investigations, to which reference has been made above, it becomes apparent that formerly the so-called champaca oils of commerce[1]) were either distillates of a mixture of ylang-ylang blossoms and champaca blossoms or of a mixture of the genuine yellow blossoms and of the white blossoms of *Michelia longifolia,* the latter being used rather freely.

An oil examined for its constituents by Schimmel & Co.[2]) which, according to the manufacturer in Java, had been distilled mainly from the white flowers to which few of the yellow ones had been added, had the following properties[3]): d_{15° 0,8861; α_D — 11° 10′; A.V. 10,0; E.V. 21,6; E.V. after acetylation 150,1; soluble in 2 vol. of 70 p.c. alcohol, the addition of 4 vol. and more, however, renders the solution decidedly turbid; soluble in 1 vol. and more of 80 p.c. alcohol, but the addition of more than 7 vol. produces opalescence due to the separation of paraffin. The oil was light brown in color and revealed a slight bluish fluorescence, particularly in alcoholic solution. It contained about 60 p.c. of l-*linalool* (m. p. of phenylurethane 65 to 66°) and small amounts of *geraniol* (m. p. of diphenylurethane 80 to 81°). Fraction 248 to 255° consisted of *eugenol methyl ether* as became evident from its oxidation to veratric acid (m. p. 179 to 180°; analysis of silver salt). Of terpenes mere traces only were present. The first fraction contained esters of *methylethylacetic acid* (b. p. of the free acid 176 to 177°; α_D — 16° 40′), apparently as esters of methyl and ethyl alcohols. It is not improbable that the higher boiling alcohols, found in the oil (linalool and geraniol), are in part combined with methylethylacetic acid. Furthermore, the presence of the acid in the *free state* was established, for when 250 g. of oil were shaken with 5 p.c. potassium hydroxide solution, methylethylacetic acid was obtained as well as a small amount of a phenol that was not further investigated.

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[1]) Schimmel's Bericht April 1882, 7; Report of Schimmel & Co. April 1894, 59; October 1894, 15; April 1897, 11.

[2]) *Ibidem* October 1907, 32.

[3]) *Ibidem* October 1906, 23.

Benzoic acid, which had previously been found in champaca oils, due presumably to the ylang ylang blossoms used in the distillation, could not be found in this oil.

According to Elze[1]), champaca oil also contains *nerol* (m. p. of the diphenyl urethane 50 to 50,5°). In what kind of oil this alcohol has been found cannot clearly be learned from the publication.

248. Oil of Michelia longifolia.

According to Schimmel & Co.[2]), the oil distilled from the fresh flowers of *Michelia longifolia,* Blume, a tree growing in Java, is almost water-white, very limpid, and its odor reminds vividly of that of basilicum: d_{15° 0,883; α_D — 12° 50′.

From the flowers of the same species Brooks[3]) obtained a dark product but does not record the method of preparation. It had the following properties: d 0,897; n_{D30° 1,4470; E. V. 180,0. It contains *linalool* (characterized by its boiling point and its oxidation to citral), *methyleugenol* (oxidation to veratric acid which melted at 179 to 180°), *methylethylacetic acid* (silver salt), *acetic acid,* also traces of a *phenol* that had the odor of thymol.

249. Staranise Oil.

Oleum Anisi stellati. — Sternanisöl. — Essence de Badiane[4]).

Origin. The several species of *Illicium* are native to the middle and northern portions of western Asia, Japan and the islands of the Chinese Sea and Indian Ocean. Owing to the similarity of the various species of this genus, the statements concerning the origin and the species from which the commercial fruits are derived have been conflicting until recently. Linné first named the tree, which belongs to the *Magnoliaceæ, Bada-*

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[1]) Chem. Ztg. 34 (1910), 857.

[2]) Report of Schimmel & Co. April 1894, 60.

[3]) Philippine Journ. of Sc. 6 (1911), A, 342. — Journ. Americ. chem. Soc. 33 (1911), 1763.

[4]) Originally staranise was known in Europe as *Anis de la Chine, de la Sibérie, Fœniculum sinense, Badian.* The latter name derived from the Arabic "*Bádiyán*" for fennel, was used by Pierre Pomet, the author of *Histoire générale des drogues* (livre 1, p. 43), and remained in use for a long time.

nifera anisata[1]), later *Illicium anisatum*[2]). A Japanese species, which is cultivated particularly in Buddhistic temple gardens, was described by Kæmpfer in 1690[3]), by Thunberg in 1781[4]) and again by Fr. von Siebold in 1825[5]). The last mentioned named it *Illicium japonicum,* which name he changed in 1837 to *Illicium religiosum.* In 1886 Jos. Hooker Jr.[6]) pointed out that the officinal staranise was not derived from the species designated *Illicium anisatum* by Linné, but from another species which he named *Illicium verum.*

Illicium verum, Hooker f., is an evergreen tree that grows 7 to 8 metres high (Radisson[7])), according to others 10 to 15 m. high (Eberhardt[8])). On account of its white bark it reminds one somewhat of the birch. The staranise tree, which yields a full crop only after 16 to 17 years, is propagated by means of seeds. The fruit known as staranise can be harvested three times a year, but the trees yield a full crop only once in three years. This is probably due to the bad treatment which the trees receive while the fruit is picked. On an average a tree is said to yield 30 to 35 kg. or even as much as 45 kg.[8]) of fruit.

Production. For the production of the fruit, the staranise tree is cultivated principally in the south-eastern province of China and the adjoining parts of Tonkin. A part of the fruits is dried and enters the market in this condition. Another part is distilled fresh on the spot for oil. In Tonkin the principal centers of distillation are Dong-Dang incl. Langson (see fig. 36, p. 383), Vinh-Rat, Halung, Nachan and Thatkhe. In China the areas of

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[1]) Linné, *Materia medica e regno vegetabile.* Stockholm 1750, *Lib.* 1, p. 180.

[2]) Linné, *Species plantarum.* Stockholm 1753, p. 664.

[3]) Kämpfer, *Amœnitates exoticæ.* Lemgo 1712, p. 880.

[4]) Thunberg, *Flora japonica.* Leipzig 1784, p. 235.

[5]) *Het gezag van Kämpfer, Thunberg, Linnæus en anderen, omtrent den botanischen oorsprong van den steranijs des Handels.* Leiden 1837, p. 19. — Rein, *Japan* 1886, vol. 2, p. 160 and 307.

[6]) Botanical Magazine. July 1888. — Watt's Dictionary of India. Calcutta 1890, vol. 4, p. 330. — E. M. Holmes, Americ. Journ. Pharm. **60** (1888), 503.

[7]) *Culture, Distillation et Commerce de la Badiane.* Rev. des cult. colon. **5** (1899), 65, 138.

[8]) Ph. Eberhardt, *L'Anis étoilé au Tonkin.* La Nature, 25 mai 1907; Journ. de Pharm. et Chim., VI. **26** (1907), Renseign. et Nouvelles XLII.

production are the provinces Kwantung and Kwangsi with distillation centers at Ping-Siang, Lung-Tschou (Lungchow, Long-Tcheou) and Pe-Se (identical with Pac-Sé[1]), Pak-se[2]), Po-sê, Pos-Seh[3]), Po-Seh?).

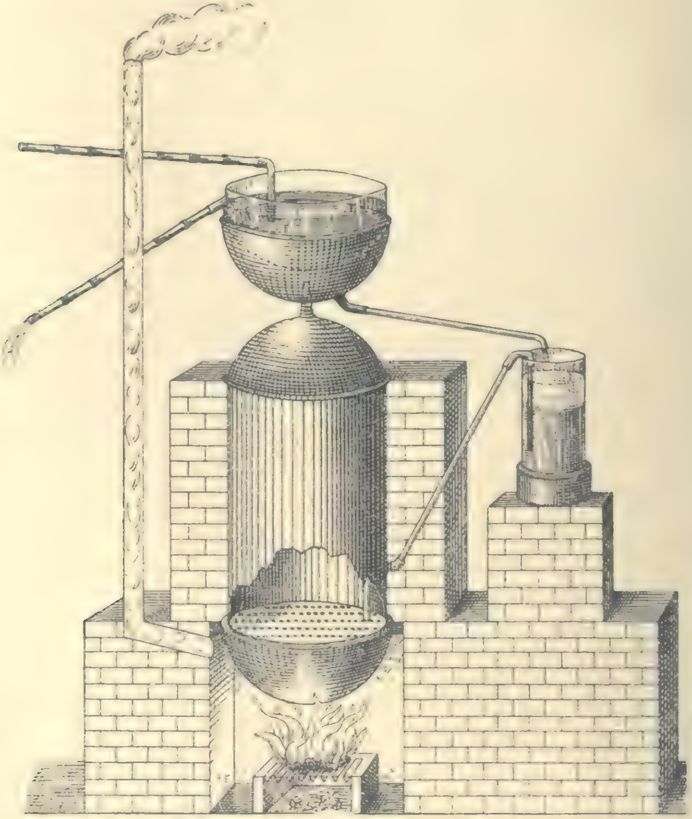

Fig. 34.

Tonkin Chinese apparatus for the distillation of staranise.

On account of the congealing point, which frequently is higher, the Tonkin oil is more highly esteemed than the Chinese article. Of particularly poor quality is the oil from the Pe-Se

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[1]) Report of Schimmel & Co. October **1911**, 85.

[2]) *Ibidem* April **1904**, 84.

[3]) *Ibidem* October **1898**, 48.

district. It has a very low congealing point and appears to consist in part of the distillate of the leaves.

At the present time the distillation of the staranise fruits is still conducted in a primitive manner. According to English[1]) and French reports the method of procedure is the same in Tonkin as in the Chinese provinces.

The body of the still (Fig. 34) consists of a strong, steam-tight, wooden vat or an iron cylinder the bottom of which is freely perforated. This body rests on an hemispherical or flat, iron kettle which in turn is supported on a masonry fire-place over direct fire. The upper part of the vat or cylinder is so constructed that charging and discharging can be effected and that when sealed the vapors must pass through a central opening which is provided with a tube that passes into the condenser above. The condenser mostly consists of a glazed earthenware vessel, on the top of which is placed a well fitting, flat, sheet-iron kettle which serves as cover. Into this kettle cold spring water is passed by means of a bamboo tube and is withdrawn by means of a siphon.

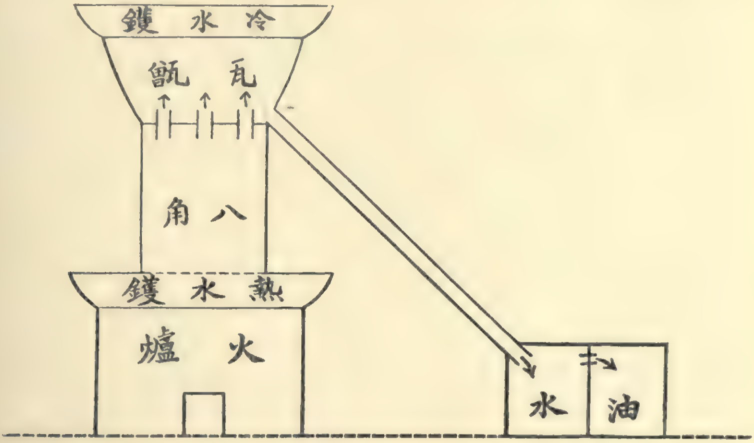

Fig. 35.

Chinese apparatus for the distillation of staranise.

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[1]) Decennial Reports on the trade, navigation and industries of the ports open to foreign commerce in China and Corea. Statistical series No. 6, 1882 to 1891. Published by the Inspector General of Customs. Shanghai 1893, 659.

The cylinder, which serves as body of the still, is filled with comminuted staranise. After all of the joints have been sealed the water in the lower boiler is heated over a direct fire. After the contents of the cylinder have been heated, the water vapors saturated with oil pass through the upper opening into the condenser where they are condensed by the flat or hemispherical kettle which serves as top. The distillate, as it drops, flows directly into a tube placed at the base of the condenser and is mostly conducted to a wooden tank lined with tin.

There is no essential difference in the apparatus employed in the neighboring Chinese provinces. However, the construction of the receiver is somewhat different. In China the receiver consists of two compartments. An opening near the top of the division wall admits of the overflow of the oil. The aqueous distillate is prevented from likewise overflowing by means of a siphon. (Fig. 35.)

In Tonquin a sort of Florentine flask is employed and the aqueous distillate is allowed to flow back into the still by means of a suitable tube.

As a rule, the stills have a capacity of 3 piculs = 180 kg. of staranise. The distillation requires about 45 hours[1]) of firing. The yield of oil, computed as to fresh fruits, amounts to 3 to 3½ p.c. (Radisson), according to another statement (Eberhardt) only 1,56 to 1,75 p.c.

The oil is shipped in lead canisters of 7,5 kg. capacity, of which 4 are packed in a case.

Composition. *Anethol* is the most important and valuable constituent of staranise oil. The determination of the congealing point reveals whether the oil is relatively rich in anethol or not. A more exact quantitative method for the determination of this substance is not known. Inasmuch as from 85 to 90 p.c. of pure anethol can be obtained from good oils by the freezing method, the actual content may be somewhat higher. Anethol was first recognized in staranise oil by A. Cahours[2]) who

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[1]) The method of distillation is criticised by von Rechenberg, *Theorie der Gewinnung und Trennung der ätherischen Öle.* Miltitz near Leipzig 1910, p. 458.

[2]) Compt. rend. 12 (1841), 1213. — Liebig's Annalen 35 (1840), 313.

Fig. 36.

Plantation of staranise trees in the vicinity of Langson (Tonquin).

established the identity of the stearoptenes of the oils of fennel, anise and staranise. Somewhat later J. Persoz[1]) obtained anisic acid upon oxidation of the oil with chromic acid and named the acid thus obtained badianic acid. For the properties and derivatives of anethol see vol. I, p. 476.

The 10 to 15 p.c. of non-anethol constituents of the oil consist of a mixture of not less than a dozen distinct substances. The lowest fraction, boiling between 157 and 175°, contains several terpenes.

1. d-*α-Pinene,* b. p. 155 to 158°; $\alpha_D + 24° 31'$ (m. p. of pinene nitrolbenzylamine 122 to 125°)[2]).

2. Fraction 163 to 168° had a distinct terebinthinate odor and the following constants: $d_{15°}$ 0,8551; $\alpha_D + 14° 7'$; $n_{D20°}$ 1,47343. Repeated attempts to identify *β-pinene* and *sabinene* by oxidation with permanganate in alkaline solution gave negative results[3]).

3. *Phellandrene.* In 1893, Schimmel & Co.[4]) demonstrated the presence of l-*α-phellandrene* in fraction 170 to 176° ($\alpha_D - 5° 40'$) by means of its nitrite (m. p. 102°). Somewhat later[5]) a similar fraction yielded not only *α*- but also l-*β-phellandrene* (m. p. of semicarbazone of tetrahydrocuminic aldehyde 202 to 205°; m. p. of cuminic acid 113 to 115°). During a third investigation[6]) the presence of d-*β-phellandrene* was also established. Hence three phellandrenes occur in the oil. Presumably all three occur together, but occasionally one or the other modification appears to predominate.

4. p-*Cymene*[7]) (m. p. of hydroxy*iso*propyl benzoic acid 156 to 157°; m. p. of *p*-propenylbenzoic acid 159 to 160°).

5. *Cineol*[7]) (m. p. of iodol compound 110 to 111°).

6. *Dipentene*[8]) (m. p. of tetrabromide 124°; m. p. of nitrol piperidide 153°).

7. l-*Limonene*[8]) (m. p. of tetrabromide 102 to 103°).

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[1]) Compt. rend. **13** (1841), 433. — Liebig's Annalen **44** (1842), 311.

[2]) Report of Schimmel & Co. April **1893**, 61; April **1910**, 99; October **1911**, 86.

[3]) *Ibidem* October **1911**, 86.

[4]) *Ibidem* April **1893**, 61.

[5]) *Ibidem* April **1910**, 99, 100.

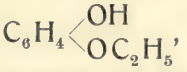
[6]) *Ibidem* October **1911**, 86.

[7]) Report of Schimmel & Co. April **1910**, 99, 100.

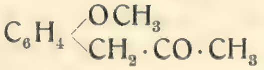
[8]) *Ibidem* October **1911**, 86.

8. *α-Terpineol.* According to E. J. Tardy[1]) fractions 216 to 218° or 218 to 224° are supposed to contain terpineol. By passing hydrogen chloride into two fractions boiling between 215 and 218° and 218 and 220° a good yield of dipentene dihydrochloride, m. p. 47 to 48°, was obtained. With nitrosyl chloride a smaller yield of a nitrosochloride, m. p. 113°, was obtained. With phenyl-*iso*cyanate a urethane, m. p. 110 to 111°, was obtained which showed no melting point depression with terpinylphenylurethane melting at 111 to 112°. When oxidized with dilute permanganate solution, the corresponding glycerol was obtained which, when treated with chromic acid, yielded the ketolactone melting at 62 to 63°, the semicarbazone of which melted at 200°.

9. *Methylchavicol* (*p*-methoxy allyl benzene)[2]). If staranise oil is freed from anethol by means of repeated exposure to low temperatures to such an extent that no crystals separate in a freezing mixture, a limpid oil results which is greatly altered when boiled with alcoholic potassium hydroxide (Eykman's method). The boiling temperature rises, the index of refraction increases and, on cooling, large amounts of anethol are again separated. This has been formed by the action of potassium hydroxide on methylchavicol.

10. *Hydroquinone ethyl ether,*  $C_6H_4\langle^{OH}_{OC_2H_5}$, is present only in traces and can be obtained by shaking out large amounts of staranise oil with caustic alkali. In a pure condition it consists of colorless laminæ with a pearly lustre, melting at 64°.

11. *Safrol.* The probability of the presence of this substance was demonstrated by F. Oswald[3]) who, upon oxidation with permanganate, obtained a substance that melted at 35 to 36° and had the odor of piperonal. Schimmel & Co.[4]) proved its identity by converting it into the piperonal semicarbazone melting at 224 to 225°.

12. *Anise ketone.* According to Tardy[1]), staranise oil contains a substance  $C_6H_4\langle^{OCH_3}_{CH_2\cdot CO\cdot CH_3}$ (b. p. 263; d 1,095) which

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[1]) Tardy, *Étude analytique sur quelques essences du genre anisique.* Thèse Paris (1902), p. 22; Report of Schimmel & Co. October **1902**, 79.

[2]) Report of Schimmel & Co. October **1895**, 7.

[3]) Arch. der Pharm. **229** (1891), 86.

[4]) Report of Schimmel & Co. April **1910**, 101.

he designated anise ketone *(acétone anisique)*, the oxime of which melts at 72° and the semicarbazone at 182°. Anise ketone combines with bisulphite, and upon oxidation with faintly alkaline permanganate solution yields acetic acid and anisic acid.

13. The highest boiling fraction consists of a *sesquiterpene:* b. p. 272 to 275°; $\alpha_D - 5°$[1]).

Two other substances should be mentioned which result upon exposure to air and which are always found in staranise oil as in every anethol-containing oil, *viz.*, anisic aldehyde and anisic acid. The older the oil, the more it contains of these substances.

Properties. Staranise oil is a colorless or yellowish, strongly refractive liquid which congeals in the cold because of its anethol content. Its odor is anise-like and its taste intensely sweet. $d_{20°}$ 0,98 to 0,99; α_D slightly lævogyrate to $-2°$, in isolated cases slightly dextrogyrate[2]) to $+0° 36'$; $n_{D20°}$ 1,553 to 1,556; congealing point +15 to +18°, mostly about +16°, in exceptional cases it drops to +14°[3]); soluble in 1,5 to 3 vol. and more of 90 p. c. alcohol.

Under certain conditions, more particularly when cooled slowly in sealed vessels, staranise oil can be cooled much below its congealing point without solidifying and it then acquires the property of remaining liquid for a long time. The congealing is usually started by some external stimulus, *e. g.* by a particle of dust or by some disturbance. It then takes place all the more quickly the more sub-cooled the oil was at the time. Most readily, however, such a sub-cooled oil is made to congeal by

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[1]) Foot noote 1, p. 385.

[2]) The dextro-rotation probably results from the admixture of the dextrogyrate leaf oils (see p. 390).

[3]) From time to time there appear in the market oils which, though they have a lower congealing point, are nevertheless unadulterated. The properties of five such oils were: $d_{15°}$ 0,988 to 0,998; $\alpha_D + 0° 11'$ to $+ 0° 32'$; cong. pt. + 8,75 to 13,75°; all soluble in 1,5 vol. of 90 p. c. alcohol. These oils, which are designated flower oils, are not distilled from the flowers as the name would indicate but from the unripe fruits. In order to facilitate the ripening of the remaining fruits, these are picked. Possibly these oils are nothing more or less than staranise leaf oils (see p. 390). It goes without saying that such "flower" oils are of inferior value and should be sold as staranise oil (Report of Schimmel & Co. October 1898, 42).

introducing a fragment of solid anethol or by scratching the inner wall of the container with a glass rod.

It is noteworthy that an oil which has been kept in half-filled bottles for a considerable time or which has been liquefied repeatedly in the presence of air, loses its capacity to congeal. This is due to the partial change of anethol to anisic aldehyde and anisic acid.

In order to distinguish staranise oil from anise oil, a color reaction[1]) with alcoholic hydrogen chloride has been recommended. However, it does not yield reliable results. With this reagent staranise oil is said to give a yellowish to brownish color, whereas anise oil is colored blue or red according to the degree of concentration of the hydrochloric acid.

Examination. For the detection of adulterations and in order to ascertain the presence of a normal anethol content, the determination of the specific gravity, solubility and congealing point are necessary.

Formerly adulterations were never observed. Occasionally, however, it occurs to the Chinese to add petroleum or some other mineral or fatty oil[2]). These cause a reduction of the specific gravity and congealing point. They also interfere with the solubility of the oil in 90 p.c. alcohol. Whereas a pure oil yields a perfect solution with 3 vol. of 90 p.c. alcohol which remains clear upon the addition of more alcohol, an oil adulterated with petroleum yields only turbid mixtures, from which drops of petroleum separate upon standing.

In order to isolate the petroleum, the oil is distilled with water vapor, the first fraction collected separately and treated with concentrated sulphuric acid, then with strong nitric acid. The volatile oil is destroyed when subjected to such treatment whereas the petroleum remains almost unchanged and can be recognized by its general behavior. High-boiling mineral oils are not volatile with water vapor, hence must be looked for in the residue.

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[1]) Eykman, Mitteil. d. deutsch. Gesellsch. f. Natur- und Völkerkunde Ostasiens. **23** (1881). — J. C. Umney, Pharmaceutical Journ. III. **19** (1889), 647. — P. W. Squire, *ibidem* III. **24** (1893), 104. — Umney, *ibidem* III. **25** (1894/95), 947.

[2]) Report of Schimmel & Co. October **1912**, 104.

In how far the properties of staranise oil are modified by an addition of from 5 to 10 p. c. of petroleum is indicated in the following table[1]):

	$d_{15°}$	Congealing point	Solubility in 90 p.c. alcohol
Pure oil	0,986	+ 18°	1 : 2,2 and more
The same with 5 % petroleum	0,978	+ 16°,25	not clearly soluble in 10 vol. of 90 p. c. alcohol
The same with 10 % petroleum	0,970	+ 14°,75	

From the above data it becomes evident that the adulteration of staranise oil with petroleum is more readily recognized by means of the specific gravity and solubility than by the congealing point. Hence it should invariably be demanded that an oil respond to the requirements specified under "Properties" as regards its solubility and specific gravity, even though the congealing point be satisfactory.

Occasionally oils have been observed, the low anethol content of which seemed to indicate adulteration. It was supposed[2]) that a camphor oil fraction had been added. Comparative experiments[3]), however, revealed the fact that oils of the same properties as the suspected ones are obtained when normal staranise oil is deprived of part of its anethol by freezing.

On the other hand, unadulterated oils with normal behavior as to specific gravity and solubility may be inferior because of their lower anethol content. Inasmuch as the value of the oil increases with its anethol content, and since the congealing point increases with the increased anethol content, the congealing point may be regarded as a direct measure of the value of the oil.

DETERMINATION OF THE CONGEALING POINT. The method of determination is described in vol. I, p. 563. When drawing the

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[1]) Report of Schimmel & Co. April 1897, 37.

[2]) E. J. Parry, Chemist and Druggist 77 (1910), 687. — J. C. Umney, Perfum. and Essent. Oil Record 1 (1910), 236. — H. R. Jensen, Pharmaceutical Journ. 85 (1910), 759.

[3]) Report of Schimmel & Co. April 1911, 110.

sample care must be taken to ascertain that the entire contents of the canister are molten and well shaken[1].

In order to obtain comparable results, the congealing should be induced when the thermometer registers + 10°.

Theoretically, the determination of the melting point of a staranise oil would be of like value as that of the congealing point. However, since the melting point of the staranise oil cannot be determined with anything like the same accuracy, the congealing point method is given preference.

The congealing point of a good staranise oil should not be below 15°. The Tonkin oil mostly has a higher congealing point.

Production and Commerce. The production of staranise is restricted to the Chinese districts Lungtschou (province Kwang-si), Pe-se (province Kwang-tung), on the border of Tonquin, and in the French colony Tonkin to the vicinity of Lang-son. Wutschou on the Si-kiang above Canton is the port of export for Chinese staranise[2], for Tonkinese staranise Haiphong in Tonkin. As to the output of the Chinese districts, no statistics are available for recent years. In the nineties of the past century the output varied materially. Thus, in 1895 it amounted to but 1922 piculs (of 60 kg. each), whereas in 1892 it reached 16138 piculs. The bulk of it is shipped via Wutschou to Hongkong which place is the world's market for staranise. The exports amounted to:

1908:	14 337	cwts.	valued	at	33 836	£
1909:	8 188	„	„	„	24 532	„
1910:	12 465	„	„	„	38 685	„
1911:	15 314	„	„	„	33 476	„

An even larger amount of staranise than is exported is utilized in the districts of production for the distillation of the staranise oil. The oil distilled in the Chinese districts[3], which is

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[1] Oils that are not perfectly clear can be cooled below their congealing point only with difficulty. The suspended particles cause the oil to congeal as soon as the temperature has dropped a few degrees below the congealing point.

[2] The Chinese harbor Pak-hoi which formerly exported almost exclusively staranise and staranise oil, appears to have turned over its entire trade in these articles to Wutschou.

[3] The Chinese revenue statistics lump cassia oil and staranise oil. Hence without a knowledge of the ratio of the two, detailed figures are valueless.

estimated at 2000 piculs (= 4000 cases of 30 kg. net content), is likewise shipped via Wutschou to Hongkong, which city is also the world's market for the oil. The oil distilled in Tonkin, which in recent years amounted to about 600 to 800 piculs, is shipped partly to China, partly sent by rail and steamer to Haiphong. The oil from the latter port is shipped principally to the mother country, France, being favored by special tariff regulations. The export of staranise oil from Tonkin amounted to[1]:

1908: 29000 kg. valued at 17950 £
1909: 50000 „ „ „ 22437 „

The average imports at Hamburg during the last 12 years amounted to 36171 kg. Of this amount 6000 kg. were again exported. Via Hamburg, Germany imported the following quantities[2]:

1897	28120 kg. staranise oil	1904	52400 kg. staranise oil[4]
1898	22320 „ „ „	1905	40165 „ „ „
1899	17110 „ „ „	1906	33640 „ „ „
1900	24990 „ „ „	1907	36920 „ „ „
1901	25500 „ „ „	1908	89920 „ „ „
1902	33330 „ „ „	1909	63470 „ „ „
1903	30000 „ „ „[3]		

250. Staranise Leaf Oil.

In the course of an investigation which Ph. Eberhardt[5] undertook with the object of rendering the staranise trees of Tonkin more productive, he studied the internal morphology of the tree. He found that the mesophyll cells of the leaves are as rich in oil as are the pericarp cells of the fruit in which the oil is especially secreted. Upon distillation of 1 kg. of leaves, Eberhardt obtained 200 drops (hence about 1 p.c.) of a pungent oil. It congealed at 13°, hence had a somewhat lower congealing point than the oil from the fruits which congeals between 16 and 18°.

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[1] Report of Schimmel & Co. April **1911**, 108.

[2] Tunmann, Apotheker Ztg. **26** (1911), 370.

[3] Value: 257670 ℳ

[4] Value: 460710 ℳ

[5] Compt. rend. **142** (1906), 407.

According to a communication by J. L. Simon[1]) an oil from the leaves and twigs of the staranise tree has been distilled in China for some time in the Pe-Se district. J. C. Umney[2]) has investigated such leaf oils and found the following constants: $d_{15,5^\circ}$ 0,9878; $\alpha_D + 1^\circ$. They congealed at a relatively low temperature (the exact congealing point was not determined by Umney). A comparison of the fractionation of such an oil with that of normal staranise oil revealed remarkable differences.

	Starnanise oil	Leaf oil
Below 225°	20 %	10 %
Between 225 and 230°	65 %	60 %
Above 230°	15 %	30 %

According to these results, the leaf oil contains less anethol but more of the high boiling portions, particularly anisic aldehyde. Whether the latter is characteristic for the leaf oil remains undecided, since the oil examined may have been exposed accidentally to air and thus become oxidized.

Remarkable is the dextro-rotation of the leaf oil. Hence it is not impossible that the poor oils previously mentioned[3]), which have been designated as flower oils, consisted entirely or in part of leaf oil.

251. Japanese Staranise Oil.

OIL OF THE FRUITS.

The poisonous fruits of the Japanese staranise tree *Illicium religiosum,* Sieb. contain 1 p.c. (with reference to the dry fruit[4])) of a volatile oil. Its odor is very disagreeable[5]) and has nothing in common with that of the true staranise. d_{15° 0,984[6]) to 0,985[7]); $\alpha_D - 0^\circ 50'$[7]) to $- 4^\circ 5'$[4]); A. V. 1,8[7]); E. V. 12,9[7]); soluble in 5 to 6 vol. of 80 p. c. alcohol with the separation of paraffin[7]).

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[1]) Chemist and Druggist **53** (1898), 875.

[2]) *Ibidem* **54** (1899), 323.

[3]) Foot note 3 on p. 386.

[4]) Report of Schimmel & Co. October **1893**, Table, p. 42.

[5]) Schimmel's Bericht September **1885**, 29.

[6]) Report of Schimmel & Co. October **1893**, 40.

[7]) *Ibidem* April **1909**, 52.

Tardy[1]) extracted dried and pulverized fruits with petroleum ether and obtained 0,4 p.c. of oil after evaporation of the solvent. The oil contained *eugenol* which was changed to vanillin. From the lower fractions of that portion of the oil which had not been taken up by caustic alkali solutions, Tardy obtained two terpene chlorhydrates. Fraction 170 to 177° consisted principally of *cineol* of which the bromide was prepared and from which the cineol was regenerated. Fraction 220 to 230° yielded upon oxidation anisic acid, thus revealing the presence of *anethol* or *methylchavicol.* Oxidation of fraction 230 to 235° yielded piperonylic acid melting at 228°, thus indicating the presence of *safrol.* The higher fractions contained mainly *sesquiterpenes.* The distillation residue, which was considerable, yielded upon saponification *palmitic acid* melting at 62°.

An oil examined by Schimmel & Co.[2]) congealed at —18° with separation of safrol. It also contained cineol (resorcinol compound). A higher fraction presumably contained *linalool.* Anethol, however, seemed to be wanting almost entirely.

OIL OF THE LEAVES.

The oil from the leaves of the Japanese staranise tree has been examined by J. F. Eykman[3]). Upon distillation of the leaves he obtained 0,44 p.c. of volatile oil with a specific gravity of 1,006 at 16,5° and a specific angle of rotation $[\alpha]_D - 8° 6'$. It contained a *terpene* boiling between 173 and 176° (d 0,855; $\alpha_D - 22,5°$) and 25 p.c. of *liquid anethol* (methyl chavicol?), which yielded nitroanisic acid melting at 174°.

According to a second communication by the same author[4]), the oil from the leaves and the unripe fruits contains *eugenol,* a terpene boiling between 168 and 172° named *"shikimene"* (d 0,865) and *"shikimol"* or *safrol.*

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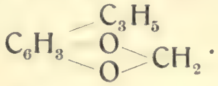
[1]) E. J. Tardy, *Étude analytique sur quelques essences du genre anisique.* Thèse, Paris 1902, p. 42.

[2]) Report of Schimmel & Co. April **1909**, 57.

[3]) Mitteilungen d. deutsch. Gesellsch. für Natur- u. Völkerkunde Ostasiens **23** (1881); Berl. Berichte **14** (1881), 1720.

[4]) Recueil trav. chim. des P.-B. **4** (1885), 32; Berl. Berichte **18** (1885), 281. Abstracts.

It is noteworthy that in connection with this shikimol Eykman determined the constitution of safrol



$$C_6H_3\begin{array}{l}\diagup C_3H_5\\ - O\\ \diagdown O\end{array}\!\!>CH_2 .$$

252. Winter's Bark Oil.

According to P. N. Arata and F. Canzoneri[1]) the genuine Winter's bark of *Drimys Winteri,* Forst (family *Magnoliaceæ*) contains 0,64 p. c. of a dextrogyrate volatile oil. In the main it consists of *"winterene",* a hydrocarbon boiling between 260 and 265°. According to the opinion of the investigators this is a triterpene. The boiling point, however, would indicate a sesquiterpene.

Family: ANONACEÆ.

253. Ylang-Ylang Oil and Cananga Oil.

Oleum Anonæ. — Oleum Canangæ. — Ylang-Ylangöl. — Canangaöl. — Essence d'Ylang-Ylang. — Essence de Cananga.

Origin[2]). *Cananga odorata,* Hook. f. et Thomson *(Uvaria axillaris,* Roxb.; *U. farcta,* Wall.; *U. odorata,* Lam.; *U. Cananga,* Vahl; *Unona odorata,* Dun.; *U. odoratissima,* Blanco; *U. leptopetala,* DC., family *Anonaceæ),* the ylang-ylang tree, is distributed throughout the tropical portion of eastern Asia. The tree which is 20 m. high[2]) is known in Manila as *ylang-ylang,* in most of the Philippine provinces as *Alangilang.* The meaning of the word is "something that hangs loosely, something fluttering". The name is apparently due to the fact that the flowers, also the twigs of the older trees are flabby and are readily moved by the wind. In the Moluccas and in Java the tree is known as *Tsjampa* or *Kananga,* from which Rumph has derived the genus name *Cananga.* In Burma the tree is known as *Kadapanam.*

In European literature the ylang-ylang tree was first described as *Arbor Saguisan* by the botanist John Ray[3]), shortly thereafter

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[1]) Jahresb. f. Pharm. 1889, 70.

[2]) To Mr. A. Loher of Manila I am greatly indebted for valuable information concerning the ylang-ylang tree.

[3]) John Ray, *Historia plantarum, Supplementum tomi 1 et 2. Historia stirpium insulæ Luzonensis et Philippinarum a* Georgio Jesepho Camello. London 1704, p. 83.

as *Cananga* by Rumph[1]) who also supplied an imperfect illustration of the plant. Lamarck[2]) named the plant *Uvaria* or *Unona odorata*. In 1797, Roxburgh[3]) became acquainted with the tree that had been transplanted from Sumatra to the botanical garden in Calcutta. The first correct illustration of the inflorescence and fruit was published by Blume[4]) in 1829.

According to Blume the flowers of the wild tree are almost odorless. For this reason all the commercial oils, ylang-ylang oil as well as cananga oil, are distilled almost exclusively from cultivated material. The differences in the quality of the two oils are due partly to differences in the method of production, partly, no doubt, to differences in the delicacy of the odor of the blossoms in different districts. Thus it is claimed that the flowers of the trees grown in Java have a much less delicate fragrance than those of the trees grown in Manila, although the plants show no botanical differences whatever; neither are cultural varieties of *Cananga odorata* known. Hence the differences in the oils from Java and the Philippines must be sought in conditions other than climate or soil, neither can they be explained by differences in distillation.

In Manila the ylang-ylang tree flowers almost all the year round but there are two principal periods which, however, are greatly dependent on rain and typhoons: the first period lasts from March to May, the second from July to October.

The fully developed flowers, which alone should be utilized for the distillation of a good oil, are yellow, the less developed flowers are green. The latter yield a less fragrant oil that is richer in terpenes, hence has a lower specific gravity[5]).

On account of the fragrance of the flowers and that of the oil distilled therefrom, the tree has been cultivated extensively outside of the Philippines. So far as the commercial oil is

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[1]) Rumphius, *Herbarium Amboinense, Amboinsch Kruidboek*. Amsterdam 1750, Cap. 19, fol. 195, Tab. 65.

[2]) Jean Baptiste de Lamarck, *Encyclopédie méthodique. Dictionnaire de botanique*, 1783, p. 595. — Junghuhn, *Java*. Leipzig 1852, p. 166.

[3]) William Roxburgh, *Flora indica*, 1832. Vol. II. p. 661.

[4]) Carl Ludwig Blume, *Flora Javæ*. Bruxellis 1828—1829, fol. 29, Tab. 9 and 14, B.

[5]) Report of Schimmel & Co. April 1899, 9.

concerned, the cultivation in Java[1][2]) and Réunion[3]) only need be considered. Attempts to distill of the oil have likewise been made in Cochinchina (Bangkok[4])), Madagascar[5]), Nossi Bé[6]), in the Seychelles[7]), in Mayotte and the other Comoro islands[8]), in Amani[9]), New Guinea[10]) and Jamaica. Samoa[11]) has supplied dried flowers from which, however, no satisfactory oil could be obtained.

Cultivation. Concerning the cultivation of ylang-ylang in Réunion, Flacourt[12]) gives detailed directions. In order to raise the trees from seeds, the ripe, fleshy berries are carefully deprived of every trace of pulp by repeated washing. Immediately after the last washing they are placed into the seed bed which is prepared in rich, highly fertilized soil. After 40 to 60 days the seedlings make their appearance and from 1 to 1½ months later they are transplanted into nurseries which must be arranged in a shady place.

In stead of transplanting the seedlings into nurseries, the planters of Réunion prefer another method. The seedlings are transplanted to so-called *tentes,* cup shaped forms readily made from the leaves of *Pandanus utilis.* Whether transplanted according to one method or the other, the transplanted plants require about two months to attain a height of about 25 to 30 cm. and to acquire a satisfactory development. In this stage they are best adapted for transplanting into plantations. For the next two years the plants must receive careful treatment but

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[1]) Report of Schimmel & Co. April **1899**, 9.

[2]) *Ibidem* April **1909**, 26; April **1911**, 39.

[3]) Flacourt, Rev. cultures coloniales **13** (1903), 366; **14** (1904), 16; Report of Schimmel & Co. April **1904**, 91; April **1909**, 94; October **1911**, 103; Report of Roure-Bertrand Fils April **1911**, 36.

[4]) Report of Schimmel & Co. April **1904**, 18; April **1908**, 119.

[5]) *Ibidem* October **1908**, 135; October **1911**, 102.

[6]) *Ibidem* October **1909**, 129.

[7]) Bull. Imp. Inst. **6** (1908), 110.

[8]) Report of Roure-Bertrand Fils April **1910**, 66.

[9]) Der Pflanzer, Ratgeber f. trop. Landwirtschaft **4** (1908), 257; Report of Schimmel & Co. April **1909**, 93; October **1911**, 102.

[10]) Berichte der deutsch. pharm. Ges. **19** (1909), 25.

[11]) Report of Schimmel & Co. October **1890**, 48.

[12]) Rev. cultures coloniales **13** (1903), 366; **14** (1904), 16.

produce nothing. From the third year on the trees produce flowers and the harvest can be estimated at from 150 to 200 francs per hectare. However, care must be taken not to allow the trees to attain a greater height than 2,5 to 3 m. This end is accomplished by cutting back the top. At the same time the lateral branches develop more strongly and flowers are produced more plentifully so that the results become very profitable.

In Réunion the flowering period of the ylang-ylang tree begins in January or February; however, a regular crop cannot be counted on before May to August. The fresh flowers yield a better quality of oil. 50 to 64 kg. of freshly picked flowers yield 1 kg. of oil, hence 1,56 to 2,0 p.c. From a hectare of a plantation, laid out according to the directions of Flacourt, 3 to 4 kg. of oil can be obtained annually.

Production. When the flowers are distilled, traces of terpenes and the more readily volatile oxygenated and ester constituents pass over first. These are the bearers of the fragrance, whereas the later distillate consists largely of sesquiterpenes. In Luzon and sometimes in Java the first distillate is collected separately and brought into the market as ylang-ylang oil. The later distillate and the total distillate are called cananga oil.

On account of the delicacy of their fragrance, the gathering and distillation of the flowers require considerable skill and care. Hence but few distillers have succeeded in producing a ylang-ylang oil of uniformly good quality.

But little is known concerning the distilling apparatus used in Manila. The first requisite for the production of a superior oil are perfectly developed, fresh flowers. According to R. F. Bacon¹) 350 to 400 kg. of flowers yield 1 kg. of oil of prime quality and $^3/_4$ kg. of oil of second grade.

In Manila the oil which is distilled in the interior, *viz.,* in Camarins, Mindoro and Albay is universally regarded as of inferior quality. However, this is due only to the primitive method of distillation. The flowers are in no way inferior to those raised in Manila. Indeed, some of the Manila firms distil oil in the interior for which they obtain the same price as for their other

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¹) Philippine Journ. of Sc. 3 (1908), A, 65 ff.; Report of Schimmel & Co. October 1908, 128 to 136.

product. The distiller in the interior enjoys the great advantage of less competition, hence is in a position to buy the flowers at a lower price and to reject those of an inferior grade. With the use of modern apparatus and the application of rational methods of distillation, the ylang-ylang industry in the interior ought to be susceptible of considerable development.

The production of cananga oil in Java is described by A. W. K. de Jong[1]). Inasmuch as the distilleries are not located on the plantations, the flowers have to be carted to the stills. Previous to distillation the flowers are pounded. The body of the still consists of a copper boiler. It is provided with a pipe for the replacement of water during distillation. A copper helmet connects it with the condenser. The copper condensing tube which is about 15 cm. in diameter passes in a diagonal direction through a large earthenware jar filled with water. The condensation water is not replaced by fresh water when warm, but merely replenished upon evaporation. In place of a Florentine flask, a wine bottle with a small hole at the bottom is used for collecting the distillate. This bottle is placed into a copper vessel, filled with water, in such a manner that the neck of the bottle projects over the side of the vessel. The copper vessel in turn is placed in an earthenware pan into which the aqueous distillate is allowed to flow during the operation. The aqueous distillate is poured back into the still. A charge of flowers is distilled uninterruptedly for two days, but the condensation during the second day is imperfect.

This irrational method, which has been criticised in detail by C. von Rechenberg[2]), can yield but an inferior oil.

Composition. As already pointed out, ylang-ylang oil consists of the lower boiling portions of the oil rich in esters, whereas in the cananga oil the sesquiterpenes predominate. Hence the differences between the two oils are quantitative rather than qualitative.

The first investigation of ylang-ylang oil was conducted by H. Gal[3]) in 1873. From the saponification liquid he separated

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[1]) Teysmannia 1908, 578. Batavia; Report of Schimmel & Co. April 1909, 26.

[2]) *Gewinnung und Trennung der ätherischen Öle.* Miltitz b. Leipzig 1910, p. 450.

[3]) Compt. rend. 76 (1873), 1482.

benzoic acid which occurs in the oil as ester. Later A. Reychler[1]) showed that *acetic acid* occurs in the oil likewise in the form of ester.

Of alcoholic constituents, presumably partly combined with the two acids, l-*linalool*[1]) (b. p. 196 to 198°; $d_{20°}$ 0,874; α_D —16° 25′) and *geraniol*[1]) (b. p. 230°; $d_{20°}$ 0,885), the latter separated by means of its calcium chloride compound from the corresponding fraction, have been isolated. In addition to these two alcohols, p-*cresol methyl ether*[1]) $CH_3 \cdot C_6H_4 \cdot OCH_3$ (b. p. 175°; m. p. of anisic acid 178°) contributes to the characteristic odor of the oil.

The high boiling fractions contain *cadinene*[1]) (m. p. of dichlorhydrate 117°) which is found in larger amounts in cananga oil. This sesquiterpene is accompanied by an odorless and colorless substance[2]) which crystallizes in needles melting at 180° and which apparently belongs to the class of the *sesquiterpene hydrates.* Additional investigations have been conducted by Schimmel & Co. These constitute the basis of an artificial ylang-ylang oil[3]) which has been placed upon the market. In the lowest boiling fractions they found *d*-α-pinene[4]) (m. p. of nitrol benzylamine 123°).

An important part, as bearers of the perfume, is played by several phenols[5]), *viz., eugenol* (m. p. of benzoate 70 to 71°), iso*eugenol*[6]) (m. p. of benzoate 103 to 104°; m. p. of acetate 79 to 80°) and probably *creosol*[6]). Eugenol is present not only as such but also as *eugenol methyl ether*[7]) (m. p. of veratric acid 180°).

In addition to the two acids already mentioned, *viz., acetic acid* and *benzoic acid* (m. p. 122°)[8]), *salicylic acid*[9]) has been found, combined with *methyl alcohol* (methyl iodide)[8]) and *benzyl alcohol* (m. p. of phenyl urethane 78°)[8]). They constitute valuable constituents of the oil. Hence of esters there are

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[1]) Bull. Soc. chim. III. **11** (1894), 407, 576 and 1045; **13** (1895), 140.

[2]) Compt. rend **76** (1873), 1482.

[3]) G. I. P. 142859.

[4]) Report of Schimmel & Co. October **1901**, 53.

[5]) F. A. Flückiger, Arch. der Pharm. **218** (1881), 24.

[6]) Report of Schimmel & Co. October **1901**, 53 and 54.

[7]) *Ibidem* April **1903**, 79.

[8]) *Ibidem* April **1902**, 67.

[9]) *Ibidem* April **1900**, 48.

Fig. 37.

Distillation of cananga flowers in Java.

present: *methyl benzoate, methyl salicylate*[1]), *benzyl acetate, benzyl benzoate,* besides free *benzyl alcohol*[2]).

The presence of the following substances may be assumed, although it has not yet been definitely established; *viz., anthranilic acid methyl ester* which causes the slight fluorescence of the oil, and *creosol* (3-methyl ether of the homopyrocatechol)[3]). In the saponification liquid, G. Darzens[4]) found methyl alcohol and *cresol* (m. p. of benzoate 70 to 71°). Of the latter he thinks that it is contained in the original ylang-ylang oil as *acetyl-p-cresol.*

R. F. Bacon[5]) identified formic acid and either *safrol* or iso*safrol* as constituents of the oil. It has not been definitely decided which of these two phenol ethers is present. Inasmuch as the odor of heliotropin was produced during the oxidation with potassium bichromate, the presence of *iso*safrol may be assumed. Contrary to the observation of Flückiger[6]), Bacon did not obtain a decided color reaction with ferric chloride. He draws the inference that upon ageing the phenol ethers may be hydrolized. However, with fuchsine sulphurous acid the characteristic color reaction for aldehydes was obtained, although it was not possible to isolate aldehyde-like constituents either with phenyl hydrazine or bisulphite. Hence, they can be present in traces only[7]), if at all. Possibly, small amounts of *valeric acid* are also present.

From Javanese cananga oil Elze[8]) has isolated about 0,2 p.c. of *nerol* (m. p. of diphenyl urethane 50 to 50,5°) and about 0,3 p.c. of *farnesol* (b. p. 145 to 146°; d_{15° 0,895; α_D inactive) by means of the acid phthalic ester.

Properties. As already pointed out under "Production" on p. 396, in the distillation of the ylang-ylang oils of better quality the more fragrant constituents that come over first are collected

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[1]) Report of Schimmel & Co. April 1900, 48.

[2]) *Ibidem* April 1902, 67.

[3]) *Ibidem* October 1901, 57.

[4]) Bull. Soc. chim. III. 27 (1902), 83.

[5]) Philippine Journ. of Sc. 3 (1908), A, 65.

[6]) Arch. der Pharm. 218 (1881), 24.

[7]) These reactions are possibly due to traces of benzaldehyde.

[8]) Chem. Ztg. 34 (1910), 857.

separately. Inasmuch as this separation is controlled merely by the sense of smell, it is not surprising that the products differ greatly. Hence the physical constants fluctuate within wide limits. Consequently it is often impossible to place a certain oil merely by its physical constants into one of the two grades of commercial oils, *viz.,* ylang-ylang oil and cananga oil.

PROPERTIES OF YLANG-YLANG OIL.

With Manila oils the following observations have been made in the laboratory of Schimmel & Co.: d_{15° 0,930 to 0,945; α_D — 37 to — 57°; n_{D20° 1,491 to 1,500; A. V. up to 1,8; E. V. 75 to 120; E. V. after acetylation 145 to 160°.

In alcohol the oil is difficultly soluble. Ordinarily it yields a clear solution with ½ to 2 vol. of 90 p.c. alcohol which, however, as a rule becomes turbid again upon the addition of more alcohol. Similar is the behavior of the oil toward 95 p.c. alcohol. With ferric chloride the alcoholic solution of the oil yields a more or less pronounced violet color reaction.

In connection with 23 samples of Manila oils, Bacon[1] established the following limit values: $d_{4^\circ}^{30^\circ}$ 0,911 to 0,958; α_{D30° — 27 to — 49,7°; n_{D30° 1,4747 to 1,4940; E. V. 90 to 150, in one instance 169. He arrived at the conclusion that, as a rule, the ester value is 100 or more, n_D is rarely over 1,4900 and α_D more than — 45° and that, as a rule, the latter fluctuates between — 32 and — 45°. In a general way it may be said that oils with a low ester value are inferior and that a high ester value is an indication of a good oil. The other properties vary: specific gravity, optical rotation and index of refraction are independent of the ester value. At times they are high, at other times low and do not afford a criterion as to the value of the oil. However, a high specific gravity and a high ester content as a rule cause a high index of refraction and such oils may be regarded as specially good.

Qualitatively, the ylang-ylang oil from Réunion is greatly inferior to that from Manila[2]. So far as the hitherto not very

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[1] *Loc. cit.* and Philippine Journ. of Sc. 5 (1910), A, 265.

[2] In their report of October 1910, 63 Roure-Bertrand Fils make the following statement: "It would be better by far if less but better oil were produced".

numerous observations admit of a conclusion, the physical constants do not differ materially from those of the Manila oil[1]).

d_{15° 0,932 to 0,962; α_D — 34 to — 64°; E. V. 96 to 134. An older oil[2]) had the high density of 0,974 at 15°.

In connection with other oils, which, however, play no commercial role as yet, the following constants have been established:

Jamaica[3]) (from the botanical garden at Kingston): d_{15° 0,9407; α_D — 38° 6′; n_{D20° 1,50510; A. V. 1,0; E. V. 57,6.

Madagascar[4]): d_{15° 0,9577; α_D — 49° 55′; n_{D20° 1,51254; A. V. 1,8; E. V. 113,2; E. V. after acetylation 160,2.

Nossi-Bé[5]): d_{15° 0,9622 to 0,9737; α_D — 39° 15′ to — 43° 14′; n_{D20° 1,50689 to 1,50974; A. V. 0,9 to 1,4; E. V. 134,5 to 159,1; soluble in 0,5 to 1 vol. of 90 p.c. alcohol. The addition of more solvent causes turbidity.

Seychelles[3])[6]): d_{15° 0,9201; α_D — 29° 6′; n_{D20° 1,49157; A. V. 1,8; E. V. 40,2; also d_{15° 0,924; α_D — 18° 46′ and d_{15° 0,958; α_D — 45° 27′.

Amani[7]): The following constants were observed in connection with an oil distilled from fresh flowers, *i. e.* one obtained in a normal way: d_{15° 0,9366; α_D — 17° 0′; n_{D20° 1,48451; A. V. 1,1; E. V. 136,3; soluble in 8 vol. and more of 70 p.c. alcohol with opalescence.

Mayotte[8]): d_{15° 0,9324 to 0,9651; α_D — 4° 4′ to — 53° 56′; n_{D20° 1,48451; A. V. 1 to 1,4; E. V. 129,7 to 136,3; E. V. after acetylation 167 to 180,8.

It should be added that Bacon[9]) has made experiments with the object of extracting ylang-ylang oil with various volatile

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[1]) Comp. also Berichte von Roure-Bertrand Fils April **1910**, 67; E. Tassilly, Bull. Sciences pharmacol. **17** (1910), 1; Report of Schimmel & Co. April **1910**, 122.

[2]) Report of Schimmel & Co. October **1890**, 60.

[3]) Observations made in the laboratory of Schimmel & Co.

[4]) Report of Schimmel & Co. October **1908**, 135.

[5]) Observations made in the laboratory of Schimmel & Co.

[6]) Bull. Imp. Inst. **6** (1908), 110; Report of Schimmel & Co. October **1908**, 135.

[7]) Report of Schimmel & Co. October **1911**, 102.

[8]) Berichte von Roure-Bertrand Fils April **1910**, 66; October **1911**, 43.

[9]) Philippine Journ. of Sc. **4** (1909), A, 127.

solvents and that he obtained the best results with petroleum ether. The yield varied between 0,7 and 1 p.c. A rather dark oil containing considerable resin resulted. Undiluted, it did not have an extraordinarily pleasant or strong odor, but when greatly diluted the floral odor became very marked. The constants of this oil were: $d_{4°}^{30°}$ 0,940; $n_{D30°}$ 1,4920; E.V. 135; E.V. after acetylation 208. It will be seen that these properties agree with those of first class oils. The somewhat different odor of the extracted oil (which is said to have the advantage that it cannot be reproduced synthetically and, therefore, should fetch a higher price) is attributed to the presence of small amounts of unknown constituents that are readily decomposed by heat. If the extracted oil be shaken with water fairly considerable amounts of resin are separated which have the characteristic odor of the flowers, whereas the odor of this oil itself then reminds of that of p-cresol methyl ether.

PROPERTIES OF CANANGA OIL.

As already pointed out, the name cananga oil is applied both to higher fractions which are obtained as a by-product in the distillation of cananga oil (Manila), and to the total distillate of the flowers (Java). Hence it will be readily understood that the properties of the oil vary even more than those of the ylang-ylang oil: $d_{15°}$ 0,906 to 0,950; α_D — 17 to — 55°; $n_{D20°}$ 1,495 to 1,510; A.V. up to 2,0; E.V. 10 to 35. In 90 p.c. alcohol most of the cananga oils are not completely soluble: in 95 p.c. alcohol they dissolve at first, but the addition of more than 1 to 2 vol. commonly produces turbidity.

In connection with 36 samples of second grade ylang-ylang oils from Manila, Bacon¹) observed the following constants: $d_{4°}^{30°}$ 0,896 to 0,942; $\alpha_{D30°}$ — 27,4 to — 87°; $n_{D30°}$ 1,4788 to 1,5082; E.V. 42 to 94; E.V. after acetylation 96 to 141. Dried cananga flowers from Samoa²), which are known as *Mosoi,* yielded upon distillation 1 p.c. of oil, which, while it differed as to odor from the oil distilled from fresh flowers, nevertheless had the same general character. Like the ordinary cananga oil it contained benzoic acid: $d_{15°}$ 0,922.

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¹) *Loc. cit.*

²) Report of Schimmel & Co. October 1890, 60.

The distillate varies according to whether "green" (not fully developed) or yellow (fully developed) flowers are used. Experiments along this line were conducted in the municipal pharmacy in Samarang¹).

1. Oil from green flowers: d_{15° 0,930; α_D — 19° 21′; S.V. 24,31; insoluble in 10 vol. of 95 p.c. alcohol.

2. Oil from yellow flowers: d_{15° 0,956; α_D — 25° 11′. Solubility same as under 1. It contained 12 p.c. eugenol.

Oil from Bangkok²). Distilled from fresh and dried flowers: d_{15° 0,920; α_D — 51° 40′; n_{D20° 1,50510; A.V. 1,82; E.V. 34,17.

Oil from the Seychelles³): d_{15° 0,954; α_D — 43° 10′.

Adulteration. Adulteration with cocoa-nut fat has been observed repeatedly in connection with cananga oil⁴). Such an addition is readily recognized. While both specific gravity and optical rotation are influenced but little, the saponification value is greatly increased and the oil is no longer soluble in 95 p.c. alcohol. Cocoa-nut fat can also be recognized readily by placing a sample of the questionable oil into a freezing mixture of ice and salt. Whereas the pure oil remains liquid, an oil to which much cocoa-nut fat has been added congeals to a butyraceous mass.

Smaller amounts of fat, also fatty oils that do not congeal in the cold, remain in the residue when the oil is distilled with steam and can thus be detected. It should be noted, however, that even unadulterated oils leave a residue of up to 5 p.c. when distilled with water vapor. Hence, in an approximately quantitative determination of the added fat or oil 5 p.c. should be deducted from the amount of residue found. Comp. also vol. I, p. 613.

Among other adulterants occasionally employed in the Philippines, Bacon mentions turpentine oil, alcohol and petroleum.

For this purpose the turpentine oil is sprinkled over the flowers and distilled along with them. Inasmuch as pinene is a normal though minor constituent, the detection of such an

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¹) Report of Schimmel & Co. April 1899, 9.

²) *Ibidem* April 1904, 18.

³) Bull. Imp. Inst. 6 (1908), 111.

⁴) Report of Schimmel & Co. October 1897, 8; April 1905, 19.

adulteration, when practised moderately, is scarcely possible. Moreover, the presence of terpenes in ylang-ylang oil may be due to the utilization of immature flowers. In 100 cc. of an oil that had been distilled from good flowers, Bacon could not detect pinene or other terpenes. The distillation of imperfectly developed flowers, however, yielded an oil the odor of which resembled that of turpentine and bananas and which, without doubt, contained terpenes. A turpentine oil that had been obtained for the purpose of adulterating ylang-ylang oil revealed itself as a carefully purified dextrogyrate product to which a trace of peppermint oil had been added. The addition of appreciable amounts of turpentine oil imparts a pungent odor to ylang-ylang oil. In addition the specific gravity, optical rotation and index of refraction are lowered. If upon fractionation of 100 cc. of oil under 10 mm. pressure more than 1 cc. passes over below 65°, the addition of turpentine oil or some other low boiling substance may be assumed. The identification of pinene is accomplished in the usual manner by means of its nitrosochloride.

For the detection of alcohol and petroleum see vol. I, pp. 612 and 614.

Physiological Action. P. Kettenhofen¹), who has investigated the action of ylang-ylang oil on micro-organisms, on the white blood corpuscles, upon cold-blooded and warm-blooded animals, its influence on the amplitude of respiration and on the blood pressure, also its action during normal and stimulated irritability, has arrived at the following conclusions. Ylang-ylang oil harms or kills micro-organisms and prevents decay and fermentation as a result of its paralysing action on the protoplasm of organisms of putrefraction and decay. Toward the white blood corpuscles it exerts an analogous action; the corpuscles are paralysed and are prevented from leaving the blood vessels, thus suppressing any incipient suppuration. In the organism of cold-blooded animals, ylang-ylang oil produces, even in small doses, a general paralysis, which results in death when the dose is increased. In warm-blooded animals a temporary diminution of the functions results, however, without appreciable

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¹) Inaug. Dissert. Bonn 1906.

detriment to the organism. The frequency of pulse and breathing are diminished, both breathing and blood pressure become fainter. The animals show a somewhat apathetic behavior. If the reflex activities be stimulated by cramp poisons, they are moderated by ylang-ylang oil and the cramps cease. If inferences from these results be drawn with regard to man, Kettenhofen assumes that with moderate doses, aside from the symptoms mentioned above, no serious illness will be caused. The normal reflex activity is at first diminished and, with sufficiently large doses, ceases altogether.

In the treatment of malaria it might be applied as a substitute for quinine wherever this is incompatible or cannot be administered for other specific reasons.

Production and Commerce. According to the official U. S. A. statistics, the values of ylang-ylang oil exported from Manila are as follows[1]):

1902/3	103789 £
1903/4	103247 „
1904/5	100349 „
1905	93918 „
1906	99009 „
1908	181638 „

According to English consular reports, the export diminished during the following years until the normal had been reached. The quantities by weight recorded in the American statistics for ylang-ylang oil are gross weights, hence are misleading, since in the case of ylang-ylang oil the net weight is about one tenth of the gross weight.

According to French statistics the following amounts were exported from Réunion: —

1906	118 kg.	at a value of 51630 fr.
1907	523 „	an annual average of: 1237 kg. at a value of 418437 fr.
1908	1126 „	
1909	1792 „	
1910	2373 „	at a value of 579094 fr.

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[1]) The statistical sources do not indicate whether the last three years are calendar years or fiscal years which run from July 1 to June 30.

As regards exports of cananga oil from Java, no statistical data are available.

254. Oil of Monodora Myristica.

The seeds of *Monodora Myristica,* Dunal (family *Anonaceæ*), which are esteemed as spice and medicament by the natives of the west coast of Africa, contain, in addition to fat, a volatile oil of which 5,3[1]) to 7 p.c.[2]) are obtained by steam distillation. It is yellow in color, shows a greenish-yellow fluorescence and has a very pleasant odor. An oil distilled by H. Thoms[2]) had $d_{20°}$ 0,896; $[\alpha]_D$ — 64,96°. The oil deprived of its free acids and traces of phenols was fractionated in vacuum. The terpene fraction ($d_{20°}$ 0,842) consisted principally of l-*limonene* (b.p. 74 to 76° under 16 mm. pressure; α_D — 105,68°; m.p. of nitrosochloride 103 to 105°). In the third fraction, which constituted 20 p.c. of the oil and which boiled at 110 to 116° (16 mm.), the presence of a substance $C_{10}H_{16}O$ was established which, according to H. Thoms, is probably identical with myristicol[2]).

An oil distilled by Schimmel & Co.[1]) had the following properties: $d_{15°}$ 0,859; α_D — 117° 40′; A.V. 1,36; E.V. 3,4; E.V. after acetylation 27,11; soluble in about 4 vol. or more of 90 p.c. alcohol.

In the main it consisted of *phellandrene.* The melting point of the nitrite, re-crystallized from acetic ether, was found at 114 to 115°.

255. Oil of Monodora grandiflora.

Upon the distillation of the seeds of *Monodora grandiflora* (author?) (family *Anonaceæ*), which grows wild in Africa, R. Leimbach[3]) obtained about 30 p.c. of oil with the following constants: $d_{15°}$ 0,8574; α_D — 46° 15′; A. V. 3,9; S.V. 7 to 12; soluble in $3\frac{1}{2}$ vol. of 90 p.c. alcohol. It is a mobile, light yellow liquid, has an odor of cymene, and its taste is at first aromatic, then bitter.

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[1]) Report of Schimmel & Co. April 1904, 62.

[2]) Berichte d. deutsch. pharm. Ges. 14 (1904), 24. — Later investigations revealed that the myristicol of nutmeg oil (see p. 411) was not a unit but a mixture of three alcohols.

[3]) *Wallach-Festschrift,* Göttingen 1909, Vandenhoeck & Ruprecht, p. 502.

In the lowest fraction the presence of l-*phellandrene* (m.p. of nitrosite 108 to 110°) was established. This fraction probably also contained a small amount of camphene. In fraction 70 to 85° (20 mm.) the presence of cymene was established by its oxidation to hydroxy isopropyl benzoic acid. The highest boiling fractions contain *palmitic acid* and probably some *carvacrol*. The principal constituent, however, is a *compound* $C_{10}H_{16}O$, a light yellow oil (b.p. 130 to 154° under 30 mm. pressure; d_{15° 0,9351; $\alpha_D - 9^\circ 14'$) to which the aromatic odor of the oil is partly due. In addition they contain a *sesquiterpene* (b.p. 260 to 270°; d_{15° 0,9138; $\alpha_D + 24^\circ$; n_{D16° 1,50513) that has not been further characterized and a solid substance of unknown composition melting at 160 to 163°.

Family: MYRISTICACEÆ.

256. Oil of Mace. Oil of Nutmeg.

Oleum Macidis. Oleum Nucis moschati. — Macis- und Muskatnußöl. — Essence de Macis. Essence de Muscade.

Origin. The nutmeg tree *Myristica fragrans,* Houtt. (*Myristica officinalis,* L. fil.; *M. moschata,* Thbg.; *M. aromatica,* Lam.), which belongs to the family *Myristicaceæ* is indigenous to the Moluccas, more particularly to the Banda and Sunda islands. By means of cultivation it has been distributed¹) throughout these islands and in other parts of the world, *e.g.* Brazil and the West Indies. The fruits obtained from the Indian Archipelago are preferred. The principal ports of export at the present time are Batavia and Singapore.

For distilling purposes injured and imperfectly developed nutmegs which are not suitable as spice are used. The yield amounts to from 7 to 15 p.c. The mace or arillus of the nutmeg, which yields from 4 to 15 p.c. of oil, is rarely used for distillation. Commercially no distinction is made between nutmeg oil and mace oil.

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¹) The cultivation of the nutmeg tree in Java has been described by Gillavry in Rev. cult. coloniales 14 (1904), 342; Report of Schimmel & Co. October 1904, 66.

Properties of Nutmeg Oil. Nutmeg oil is a limpid, colorless liquid which thickens with age, owing to the absorption of oxygen, and which has the characteristic odor of nutmeg and a spicy taste. According to the condition of the raw material, the specific gravity of the distillate varies considerably, fluctuating between 0,865 and 0,925; $\alpha_D + 8$ and $+ 30°$; $n_{D20°}$ 1,479 and 1,488; soluble in 0,5 to 3 vol. of 90 p.c. alcohol. When distilled in a fractionating flask, about 60 p.c. pass over up to 180°. When evaporated on a water bath, a good oil leaves but a slight residue. When making this test, it should be remembered that nutmeg oil evaporates but slowly. As has been observed by Schimmel & Co. in connection with their own distillates, 5 g. of oil require 12 to 15 hours before the residue becomes of constant weight. This residue amounts to from 1 to 1½ p.c.

The properties of the oil distilled by de Jong[1]) from fresh nutmegs were as follows: $d_{26°}$ 0,940; $\alpha_{D26°} + 10° 20'$; boiling temperature: 155 to 175° 9,5 p.c., 175 to 200° 3 p.c., 200 to 250°, 22 p.c., 250 to 280°, 27 p.c.

Properties of Oil of Mace. In all its properties oil of mace closely resembles nutmeg oil and cannot be distinguished from the latter. It is colorless or yellowish and later acquires a reddish color. It has an agreeable, yet strong, mace odor which in old oils becomes unpleasant and terebinthinate. Its aromatic taste, mild at first, later becomes pungent. $d_{15°}$ 0,890 to 0,930; $\alpha_D + 10$ to $+ 22°$. With 2 to 3 vol. of 90 p.c. alcohol the oil forms a clear solution.

An oil distilled from fresh mace by de Jong[1]) had the following properties: $d_{26°}$ 0,942; $\alpha_{D26°} + 7°$; upon distillation 30,5 p.c. passed over between 155 and 180°, 15 p.c. between 180 and 200°, 20 p.c. between 200 and 250° and 27,5 p.c. between 250 and 285°.

Composition. Because of the similarity of mace and nutmeg oils no distinction is made between the two oils in commerce. Hence it is impossible to distinguish at the present time between

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[1]) Teysmannia, Batavia 1907, No. 8; Report of Schimmel & Co. October 1908, 89.

the oils that have been investigated. For this reason the two oils are discussed together. Inasmuch as no difference in their composition has been revealed thus far, this method of procedure does not appear to be objectionable[1]).

Although numerous older investigations of these oils are on record[2]), a clear insight into their composition has been obtained only recently, more particularly through the investigations of O. Wallach[3]), F. W. Semmler[4]), H. Thoms[5]), F. B. Power and A. H. Salway[6]), and Schimmel & Co.[7]).

Arranged according to their boiling points, the following constituents have been isolated:

1. *α-Pinene* was found by Wallach[3]) in the lowest fraction (m.p. of nitrolbenzylamine 123°). It is an almost inactive mixture of *d*- and *l*-*α*-pinene. As early as 1862 Schacht had isolated it, had named it "macene", and prepared the solid hydrochloride (pinene hydrochloride).

2. The presence of *camphene* was first established by Power and Salway who converted it into *iso*borneol (m.p. 207 to 212°; m.p. of phenylurethane 138°).

3. *β-Pinene* is present in small amounts only (m.p. of nopinic acid 126 to 128°)[7]).

4. *Dipentene* (m.p. of tetrabromide 124 to 125°)[3])[6])[7]).

5. p-*Cymene*. With the aid of concentrated sulphuric acid Wright had indicated the presence of this hydrocarbon. Inas-

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[1]) K. T. Koller declares both oils identical (N. Jahrb. Pharm. **23** [1864], 136; Vierteljahrsschr. f. Pharm. **13**, 507; Jahresb. f. Chem. **1864**, 536).

[2]) John, Chemische Schriften **6** (1821), 61; Journ. f. Chem. u. Phys. von Schweigger und Meinecke **33** (1821), 250. — G. J. Mulder, Journ. f. prakt. Chem. **17** (1839), 102 and Liebig's Annalen **31** (1839), 71. — C. Schacht, Arch. der Pharm. **162** (1862), 106. — J. Cloëz, Compt. rend. **58** (1864), 133. — J. H. Gladstone, Journ. chem. Soc. **25** (1872), 1; Jahresb. f. Chem. **1872**, 816. — C. R. A. Wright, Journ. chem. Soc. **26** (1873), 549; Jahresb. f. Chem. **1873**, 369. — Pharmaceutical Journ. III. **4** (1873), 311.

[3]) Liebig's Annalen **227** (1885), 288 and **252** (1889), 105.

[4]) Berl. Berichte **23** (1890), 1803; **24** (1891), 3818.

[5]) *Ibidem* **36** (1903), 3446.

[6]) Journ. chem. Soc. **91** (1907), 2037. The oil examined by P. and S. had been specially distilled for this investigation from unlimed Ceylon nutmegs. It had the following properties: d_{15° 0,8690; $\alpha_D + 38^\circ 4'$; A.V. 0,81; E.V. 315; soluble in 3 parts of 90 p.c. alcohol.

[7]) Report of Schimmel & Co. April **1910**, 80.

much, however, as this method is not reliable in the presence of terpenes, the proof was first established by Schimmel & Co.[1]) who prepared *p*-hydroxy *iso*propyl benzoic acid (m.p. 155 to 156°) from the corresponding fraction without previous treatment.

6. d-*Linalool* (oxidation to citral, m.p. of citrylnaphthocinchoninic acid 200°)[2]).

7. *Terpinenol-4.* The alcohol which occurs in fraction 205 to 215° yields terpinene (m.p. of dihydrochloride 50 to 52°) when heated with concentrated formic acid. When oxidized with dilute permanganate it yields a glycerol melting at from 112 to 115° which, upon boiling with hydrochloric acid, loses water and yields *p*-cymene and carvenone. This identifies the original alcohol with terpinenol-4[1]) (See vol. I, p. 382). In agreement with this result is an observation by Power and Salway who, upon the oxidation of a corresponding fraction with chromic acid mixture, obtained a diketone, the dioxime of which melted at 140°. The diketone which thus results from terpinenol-4 is identical with ω-dimethylacetonylacetone. This same compound, the dioxime of which melts at 137°, was obtained by Wallach[3]) upon further oxidation of the glycerol from terpinenol-4, mentioned above, to α,α'-dihydroxy-α-methyl-α'-*iso*propyladipinic acid.

8. *Borneol.* In the oxidation liquid of fraction 205 to 215° mentioned under 7, Power and Salway found camphor (m.p. of semicarbazone 238°) the formation of which is probably due to borneol present in the original oil.

9. α-*Terpineol* (m.p. of dipentene dihydriodide 80°; oxidation to the ketolactone $C_{10}H_{16}O_3$ which melted at 62 to 63°)[2]).

Hence, it would appear that the alcohol described as myristicol by Wright[4]) and which boiled between 212 and 218° was a mixture of α-terpineol, borneol and terpinenol-4.

10. *Geraniol*[2]) (m.p. of diphenyl urethane 81 to 82°).

11. *Safrol*[2]) (oxidation to piperonal, m.p. 34 to 35°).

12. An *aldehyde* with the odor of citral and characterized merely by its β-naphthocinchoninic acid melting at 248°.

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[1]) Report of Schimmel & Co. April **1910**, 80.

[2]) Footnote 6, p. 410.

[3]) *Terpene und Campher,* Leipzig 1909, p. 486. Report of Schimmel & Co. October **1908**, 179.

[4]) *Loc. cit.*

13. *Myristicin*[1]), $C_{11}H_{12}O_3$, 4-allyl-6-methoxy-1,2-methylene dihydroxy benzene, is contained in the highest boiling fraction of the oil. Wright[2]) first assigned to it the formula $C_{10}H_{13}O_2$ and Semmler[3]) regarded it originally as a butenyl derivative of the formula $C_{12}H_{14}O_3$[4]). The constitutional formula, the properties and derivatives of this interesting phenol ether are recorded in vol. I, p. 489.

In the saponification liquor of the oil the following acids have been found:

14. *Formic acid* (Ba-salt)[5]).

15. *Acetic acid* (Ba-salt)[5]).

16. *Butyric acid*[5]).

17. *Caprylic acid* (*n*-Octylic acid) (Ag-salt)[5]).

18. A non volatile, *monocarboxylic acid* $C_{12}H_{17}OCO_2H$, that melts at 84 to 85° and is insoluble in water[5]).

19. *Myristic acid,* m. p. 54°, occurs both free and as ester. According to the duration of the distillation the oil contains more or less. Occasionally it separates in crystalline form[1]). Upon evaporation of the oil it remains behind.

Of phenols Power and Salway[5]) found the following:

20. *Eugenol* (m. p. of benzoate 69°; m. p. of diphenyl urethane 107 to 108°).

21. Iso*eugenol* (m. p. of benzoate 105°).

As to the quantitative composition of oil of nutmeg, Power and Salway record the following percentages:

Eugenol and iso*eugenol* (about 0,2 p. c.), d-*pinene* and d-*camphene* (abt. 80 p.c.), *dipentene* (abt. 8 p.c.), d-*linalool,* d-*borneol,* i-*terpineol* and *geraniol* (abt. 6 p.c.), small amounts of a new alcohol *(terpinenol-4),* traces of a citral-like *aldehyde, safrol* (abt. 0,6 p.c.), *myristicin* (abt. 4 p.c.), *myristic acid* free

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[1]) This should not be confounded with "myristicin", the stearoptene of John and Mulder, which occasionally crystallizes out of old oils and which, as Flückiger (Pharmaceutical Journ. III. **5** [1874], 136) has shown, consists of myristic acid.

[2]) Footnote 2, p. 410.

[3]) Berl. Berichte **23** (1890), 1803; **24** (1891), 3818.

[4]) *Ibidem* **36** (1903), 3446.

[5]) Footnote 6, p. 410.

(abt. 0,3 p.c.) and small amounts as esters, finally small amounts of *formic acid, acetic acid, butyric acid, octoic acid* and a new *monocarboxylic acid* $C_{13}H_{18}O_3$ all as ester.

As Power and Salway point out, these figures may not have any general import since they must vary considerably according to the conditions of the material employed. From the low specific gravity and the exceptionally high rotation it must be supposed that Power and Salway worked with an oil particularly rich in terpenes. Many of the nutmeg oils presumably have a larger content of oxygenated constituents than recorded above.

Physiological Action. Toxic action has been observed repeatedly as the result of the use of large amounts of nutmeg. According to the experiments made by Power and Salway[1]) this is doubtless due to the volatile oil, more particularly to the myristicin. The poisonous character of the latter had already been ascertained experimentally by F. Jürss[2]).

257. Nutmeg Bark Oil.

In Buitenzorg[3]) an oil has been distilled from the bark of the nutmeg tree, *Myristica fragrans,* Houtt. with a yield of 0,14 p.c. Its density was 0,871 (26°), its optical rotation — 12° 14′ in a 10 cm. tube. S.V. 14; E.V. after acetylation 37,5. It contains no aldehydes.

258. Nutmeg Leaf Oil.

The oil from the leaves of *Myristica fragrans,* Houtt. (d_{27° 0,861 to 0,863) boils principally at 165°[4]). According to P. van Romburgh[5]) it contains *α-pinene* (m.p. of nitrosochloride 108°).

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[1]) Chemical examination and physiological action of nutmeg. Americ. Journ. Pharm. **80** (1908), 563.

[2]) *Über Myristicin und einige ihm nahestehende Substanzen.* Bericht von Schimmel & Co. April **1904**, 157.

[3]) Jaarb. dep. Landb. in Ned.-Indië, Batavia **1909**, 64; **1910**, 49.

[4]) Verslag 's Lands plantentuin, Buitenzorg 1895, p. 38.

[5]) Koninklijke Akademie van Wetenschappen te Amsterdam **1900**, 446.

Family: MONIMIACEÆ.

259. Paracoto Bark Oil.

Origin. Paracoto bark of commerce is the bark of an unknown species of the *Monimiaceæ* from Bolivia[1]). The oil, which is obtained as a byproduct in the production of cotoin, was first examined by J. Jobst and O. Hesse[2]), later by O. Wallach and T. Rheindorff[3]).

Properties. Paracoto bark oil is a very mobile, colorless liquid of an extremely pleasant odor. Sp. gr. 0,9275; $\alpha_D - 2,12°$[2]).

Composition. 1. According to Jobst and Hesse, fraction 160° (d 0,8727; $[\alpha]_D + 9,34°$) consists of a hydrocarbon $C_{12}H_{18}$ which they named *α-paracotene.*

2. Fraction 170 to 172° (d 0,8846; $[\alpha]_D - 0,63°$) yielded upon elementary analysis figures for the formula $C_{11}H_{18}$. This hydrocarbon was named β-paracotene.

Both these fractions, which evidently consisted of not quite pure terpenes, were lacking almost entirely in the oil examined by Wallach and Rheindorff.

3. The bulk of paracoto bark oil consists of lævogyrate *cadinene*[3]) (m.p. of dibromhydrate 121°, of dichlorhydrate 118°).

4. The mother liquid that remains after saturation with hydrogen bromide and the removal of the crystalline compound contains *methyleugenol* (m. p. of bromide 78°; m. p. of veratric acid 179 to 180°).

According to Wallach, the α-, β- and γ-paracotol of Jobst and Hesse, to which they assigned the formulas $C_{15}H_{24}O$ and $C_{28}H_{24}O_2$, are not chemical units but essentially mixtures of lævogyrate sesquiterpenes and inactive methyleugenol. As to the α-paracotol, the possibility of its being a natural hydrate

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[1]) Möller *(Anatomie der Baumrinden)* is of the opinion that the bark belongs to a tree of the *Monimiaceæ,* whereas Vogl *(Kommentar zur österreich. Pharmakopöe)* believes that it belongs to a lauraceous plant.

[2]) Liebig's Annalen **199** (1879), 75.

[3]) *Ibidem* **271** (1892), 300.

of cadinene is not excluded. In this case, however, its formula should be $C_{15}H_{26}O$ and not $C_{15}H_{24}O$.

260. Coto Bark Oil.

A bark which, like the genuine coto bark, is obtained from Bolivia, is known as new coto bark[1]). Its botanical origin is likewise unknown. According to O. Hesse[2]), it contains *methyl benzoate* to which ester the agreeable odor of the bark is due.

261. Boldo Leaf Oil.

The dried boldo leaves which are obtained from *Peumus Boldo,* Mol. (family *Monimiaceæ*)[3]), a fragrant tree that is native to Chili, yielded about 2 p.c. of a volatile oil upon distillation. Its odor is cymene-like and also recalls that of the Baltimore wormseed oil.

Properties. d_{15° 0,915 to 0,9567; α_D — 1° 40′ to + 0° 28′; n_{D20° 1,47928; A.V. 2,4; E.V. 11,2; soluble in 8 to 9 vol. of 70 p.c. alcohol. Occasionally the solution is slightly turbid, due to the separation of paraffin.

Composition. The presence of the following substances was demonstrated by Schimmel & Co.[4]): p-*cymene* (m.p. of hydroxy *iso*propyl benzoic acid 154 to 156°; m.p. of *p-iso*propenyl benzoic acid 253 to 255°), *cineol* (m.p. of iodol compound 119 to 120°), and *ascaridol*, $C_{10}H_{16}O_2$. For the properties and constitution of this substance see Baltimore wormseed oil, p. 362. Cymene and cineol constituted about 30 p.c. of the oil, ascaridol about 40 to 45 p.c. In addition there are present a *terpene* that boils at about 170° but which has not been characterized, also traces of a *phenol* which, in alcoholic solution, gives a dirty green color with ferric chloride.

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[1]) The bark of *Cryptocaria pretiosa* is also known as new coto bark.

[2]) Journ. f. prakt. Chem. II. 72 (1905), 243.

[3]) The genuine boldo leaves are frequently confounded with those of *Cryptocaria Peumus,* Nees. F. W. Neger, Pharm. Zentralh. 42 (1901), 461.

[4]) Schimmel's Bericht April 1888, 43; Report of Schimmel & Co. October 1907, 19.

Very different in properties and composition, and hence in all probability of different botanical source, was an oil prepared and investigated by E. Tardy[1]; yield almost 2 p. c.; d 0,876; α_D — 6° 30′. The following constituents were ascertained: *α-pinene* (m.p. of chlorhydrate 125°), *dipentene* (m.p. of dichlorhydrate 50°), *terpineol, cuminic aldehyde, eugenol, sesquiterpenes* and an ester of acetic acid.

262. Laurel Leaf Oil.

The strongly fragrant leaves of *Laurelia aromatica,* Juss. (*Laurelia sempervirens,* Tul.) (family *Monimiaceæ*), a tree which is known in Chile as laurel, is utilized in that country as a kitchen spice. It seems probable that an oil sent from southern Chile to Schimmel & Co.[2] in 1889 under the designation *Essencia de Hojas de Laurel,* was obtained from this species. Its properties were: d_{15° 1,063; b. p. 185 to 236°; the bulk of the oil distilling between 230 and 236°. In a freezing mixture it solidified, showing that it consisted principally of *safrol.*

263. Atherosperma Oils.

The bark of *Atherosperma moschatum,* Lab. (family *Monimiaceæ*) yields 1 p.c. of volatile oil upon distillation[3]. Because of its sassafras-like odor, the tree is also known as sassafras of Victoria or Australian sassafras. According to J. H. Gladstone[4], the oil has a yellowish-brown color; specific gravity 1,0386 at 20°; optical rotation in a 10 inch tube + 7°. It begins to boil at 221° and distills over almost completely at 224°. The oil probably contains *safrol*[5].

The leaves have been examined by M. E. Scott[6]. Distilled a few days after collection, they yield 1,7 to 2,65 p.c. of oil.

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[1] Journ. de Pharm. et Chim. VI. **19** (1904), 132.

[2] Schimmel's Bericht April **1890**, 49.

[3] J. H. Maiden, Useful native plants of Australia. London and Sydney 1889, p. 254.

[4] Journ. chem. Soc. **17** (1864), 5; Jahresb. f. Chem. **1863**, 545. — Chem. News **24** (1871), 283.

[5] Flückiger, Pharmaceutical Journ. III. **17** (1887), 989.

[6] Journ. chem. Soc. **101** (1912), 1612.

The first portion of the distillate (about 30 p. c.) was lighter, the remainder of the oil, heavier than water. The yellowish, unrectified oil had a distinct odor of sassafras; d 1,027; $[\alpha]_D + 7,5°$; n_D 1,5211. Of its constituents the following were determined: 15 to 20 p. c. of *α-pinene* (b. p. 157 to 158°; m. p. of hydrochloride 130°; of nitrosochloride 103°), 15 to 20 p. c. of d-*camphor* (m. p. 174,5 to 176°; $[\alpha]_D + 40,66°$), 50 to 60 p. c. of *methyleugenol* (b. p. 251,7° under 755 mm. pressure; m. p. of bromide abt. 75°) and 5 to 10 p. c. of *safrol* (m. p. 8 to 12°; b. p. 233°).

264. Oil of Citrosma oligandra.

Citrosma oligandra, Jul. (*Siparuna obovata,* A. DC.) is a tree of the family *Monimiaceæ.* Because of its disagreeable odor it is known in Brazil as *Negra mina, Catinga de negra* or *Catingueira.* The leaves, which have a goat-like odor yield 0,54 p. c. of oil upon distillation. It is light yellow in color with a greenish fluorescence and its odor recalls distantly that of bergamot. Sp. gr. 0,899[1]).

265. Oil of Citrosma cujabana.

In Brazil *Citrosma cujabana,* Mart. (*Siparuna cujabana,* A. DC.) is known as *Limoeiro domato* and *Limoeiro bravo* or wild lemon tree. The fresh leaves yield 0,18 p. c. of volatile oil, the fresh twigs 0,07 and the fresh bark 0,22 p. c. The oil is limpid and has a pleasant odor resembling that of a mixture of bergamot and lemon oils. Sp. gr. 0,894[1]).

266. Oil of Citrosma Apiosyce.

Citrosma Apiosyce, Mart. (*Siparuna Apiosyce,* A. DC.) is known in Brazil as *Limoeiro bravo,* as *Cidreira Melisse* or as *Café bravo,* wild coffee tree. All parts of the shrub, more particularly the leaves and unripe fruits, have an odor strongly resembling that of balm or lemon. From the fresh leaves Peckolt obtained 0,14 p. c.; from the twigs, 0,06 p. c. of volatile oil[1]).

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[1]) Th. Peckolt, Berichte d. deutsch. pharm. Ges. 6 (1896), 93.

Family: LAURACEÆ.

267. Ceylon Cinnamon Oil.

Oleum Cinnamomi zeylanici. — Ceylon-Zimtöl. — Essence de Cannelle de Ceylan.

Origin and Production. The genus *Cinnamomum* of the family *Lauraceæ* consists of evergreen, aromatic trees and shrubs. Several of the species yield volatile oils that are much used. Both the underground as well as the overground portions of the Ceylon cinnamon shrub *Cinnamomum zeylanicum,* Nees, contain volatile oil. Whereas in the case of the cassia shrub, *Cinnamomum Cassia,* Blume, the oils obtained from the different parts of the plant are almost identical, in the case of the Ceylon cinnamon shrub the oil from the bark is very different from that of the leaves also from that of the roots.

Cinnamomum zeylanicum is a tree indigenous to the forests of Ceylon. Formerly the bark was collected from the trees that grew wild. At present it is collected principally from the cultivated plants which are grown shrub-like in the cinnamon gardens¹).

For the distillation of the oil the shavings and fragments which result in the peeling and which since 1867 have been exported as "chips" are used. The distillation of the oil from chips was introduced into Germany by Schimmel & Co., in 1872. The yield of oil from the chips amounts to between 0,5 and 1,0 p. c. It should be noted, however, that both yield and properties of the oil depend largely on the method of distillation²).

The oil distilled in Ceylon is rarely the pure distillate of the bark. As a rule it contains much leaf oil. Either the leaves are distilled with the bark or the cheaper and inferior leaf oil is added to the bark oil.

In recent years much cinnamon bark, likewise from *Cinnamomum zeylanicum,* Nees, is obtained in the Seychelles. It however, enters the market in thick pieces and represents the

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¹) The cultivation, production and packing of Ceylon cinnamon is described in detail by A. Tschirch in his *Indische Heil- und Nutzpflanzen.* Berlin 1892, p. 86. — Comp. also: Der Pflanzer 8 (1912), 611.

²) Comp. Report of Schimmel & Co. April 1909, 32; October 1910, 34.

bark of the wild trees[1]). On the average a tree yields 20 lbs. of bark. Especially large trees yield as much as 100 lbs.

In the Seychelles the bark oil is likewise distilled[2]). However, compared with the pure Ceylon cinnamon oil (*i. e.* the oil distilled without leaves) it has a less pleasant odor, hence must be pronounced as inferior. (See below under Properties and Composition.)

Properties. Ceylon cinnamon oil is a light yellow liquid possessing the agreeable, delicate odor of Ceylon cinnamon and a spicy, sweet and burning taste.

d_{15° 1,023 to 1,040; slightly lævogyrate, up to -1°, rarely higher; n_{D20° 1,581 to 1,591; aldehyde content 65 to 76 p. c.; eugenol content, determined with 3 p. c. sodium hydroxide solution, 4, commonly 6 to 10 p. c.; soluble in 2 to 3 vol. or more of 70 p. c. alcohol.

In connection with 5 Seychelles cinnamon oils that were distilled in the islands, the following constants were observed[3]): d_{15° 0,943 to 0,967; $\alpha_D - 2^\circ 30'$ to $-5^\circ 10'$; n_{D20° 1,52843 to 1,53271; aldehyde content 21,7 to 35 p. c.; eugenol content 6 to 15 p. c.; with 10 vol. of 70 p. c. alcohol it does not form a clear solution but it is soluble in 0,6 to 5 vol. of 80 p. c. alcohol, becoming opalescent upon the additon of more alcohol.

Composition. R. Blanchet[4]) had already observed that upon distillation of Ceylon cinnamon two oils separate in the receiver, one of which is lighter, the other heavier than water, whereas Chinese cinnamon yields only a heavy oil. The older chemists studied only the heavier oil. J. Dumas and E. Péligot[5]) ascertained that, as is the case with cassia oil, *cinnamic aldehyde* is the principal constituent of Ceylon cinnamon oil. That the heavy oil of Ceylon cinnamon also contains *eugenol* was ascertained later. The amount of eugenol in the bark oil, as contrasted with that of the leaf oil, is small. It amounts to but 4 to 10 p. c.

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[1]) Brit. and Colon. Druggist **54** (1908), 152; Report of Schimmel & Co. April **1909**, 33.

[2]) Bull. Imp. Inst. **6** (1908), 111; Report of Schimmel & Co. Oct. **1908**, 41.

[3]) Report of Schimmel & Co. October **1908**, 41.

[4]) Liebig's Annalen **7** (1833), 163.

[5]) Ann. de Chim. et Phys. **57** (1834), 305. — Liebig's Annalen **14** (1835), 50.

All of the other constituents that have become known thus far have been found in the laboratories of Schimmel & Co.

Methyl-n-*amyl ketone*[1]). Upon treating fraction 163° with bisulphite a crystalline addition product was obtained from which pure methyl-*n*-amyl ketone was separated. (M. p. of semicarbazone 122 to 123; comp. vol. I, p. 434.)

Furfurol[1]). Its presence was indicated by means of the characteristic reaction with aniline hydrochloride.

l-*α-Pinene*[1]) (m. p. of nitrosochloride 102 to 103°; of nitrolbenzylamine 122 to 123°).

l-*Phellandrene.* Fraction 170 to 174° (α_D — 5° 4′) yielded a nitrite that melted at 102°[2]). After repeated re-crystallization from acetic ester and methyl alcohol the melting point could not be raised above 103 to 104° ($[\alpha]_D + 11° 39'$)[1]). The inference to be drawn is that the phellandrene of Ceylon cinnamon oil is a mixture of *l-α-* and *β*-phellandrene in which the latter predominates.

Cymene[1]) (m. p. of hydroxy*iso*propyl benzoic acid 154 to 156°; of propenyl benzoic acid 161 to 162°).

Benzaldehyde[1]) (m. p. of phenylhydrazone 156°; of semicarbazone 213 to 214°).

Nonylic aldehyde[1]) (oxidation to pelargonic acid, silver determination).

Hydrocinnamic aldehyde (phenyl propylic aldehyde)[1]). This aldehyde had previously not been found in nature. Being mixed with the nonylic aldehyde mentioned above, it could only be characterized by its semicarbazone melting at 126°. When the semicarbazone was heated with dilute sulphuric acid it developed the odor of phenyl propylic aldehyde. The melting point of the semicarbazone prepared from synthetic phenyl propylic aldehyde was found to be at 130 to 131°.

Cuminic aldehyde[1]) (m. p. of semicarbazone 201 to 202°; m. p. of cuminic acid 114 to 116°).

l-*Linalool*[1]) (oxidation to citral; m. p. of citryl-*β*-naphthocinchoninic acid 197°).

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[1]) Report of Schimmel & Co. April **1902**, 14. — H. Walbaum and O. Hüthig, Journ. f. prakt. Chem. II. **66** (1902), 47.

[2]) Report of Schimmel & Co. October **1892**, 47.

Linalyl iso*butyrate*[1]) is probably present. Fraction 80 to 111° (6 to 7 mm.), after having been treated with bisulphite, yielded a saponification number of 20,4. Upon saponification it yielded, in addition to a pungent acid (possibly formic acid), one with a distinct odor of St. John's bread. However, the silver determination of the silver salt did not agree with the silver content computed for silver *iso*butyrate. This discrepancy may be attributable to admixed silver formate or silver acetate.

Eugenol[1]) (m. p. of benzoate 69 to 70°).

Caryophyllene is contained in the highest boiling fractions (m. p. of caryophyllene alcohol 95°; of the phenylurethane 136 to 137°).

The Seychelles cinnamon oil has a composition similar to that of the Ceylon cinnamon oil. It differs merely by the presence of camphor. An oil with the following properties was examined by Schimmel & Co.[2]), d_{15° 0,9670; $\alpha_D - 4° 44'$; aldehyde content 32 p. c. The following substances were found: *cinnamic aldehyde* (m. p. of semicarbazone 211°), *eugenol* (m. p. of benzoate 69 to 70°), l-*β-phellandrene* (m. p. of nitrite 103°), *cymene* (m. p. of *p*-hydroxy*iso*propyl benzoic acid 156 to 157°; of propenyl benzoic acid 255 to 260°), and *camphor* (m. p. of oxime 116 to 118°).

In the first fractions of a Seychelles cinnamon oil Schimmel & Co.[3]) also found the following substances: Small amounts of a *hydrocarbon* that boiled below 155° the nitrosochloride of which was decomposed instantaneously at 86 to 87°, *camphene* (m. p. of *iso*borneol 209 to 210°), *β-pinene* (m. p. of nopinic acid 125 to 126°), traces of l-*limonene* (m. p. of nitrosochloride 103 to 104°; of nitrolpiperidide 93°), *benzaldehyde* (m. p. of semicarbazone 212 to 214°), *linalool* (m. p. of phenylurethane 59 to 62°), and mere traces of a higher aldehyde that had the odor of *nonylic aldehyde.*

Adulteration and Examination. Ceylon cinnamon oil is very frequently adulterated with the cheaper cinnamon leaf oil. From Ceylon, apparently, no pure bark oils enter the market, for all the oils from this source were found, upon examination, to

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[1]) Footnote 1, p. 420.

[2]) Report of Schimmel & Co. October 1908, 41.

[3]) *Ibidem* April 1913.

contain leaf oil. Naturally, it cannot be decided whether the leaf oil has been added to the finished bark oil, or, what is perhaps more probable, whether the leaves have been distilled together with the chips.

Inasmuch as the admixture of leaf oil increases the eugenol content appreciably, thereby decreasing the cinnamic aldehyde content in like proportion, the detection of such sophistication is not difficult. All that is necessary is to make an approximate quantitative determination of both substances.

After the determination of the specific gravity, which is increased by the addition of appreciable amounts of leaf oil, the cinnamic aldehyde content is determined in the well known manner. If this amounts to less than 65 or more than 76 p. c. the oil is suspicious. If less than 65 p. c. are found the amount of eugenol in the oil deprived of its cinnamic aldehyde is determined. For this purpose one of several methods may be followed. The best results are obtained by the rather complicated method of Thoms, according to which the eugenol is weighed as benzoyl eugenol (see Vol. I, p. 596). It suffices, however, to determine the phenol content by shaking with three percent. caustic alkali as directed in Vol. I, p. 590. In a pure oil the eugenol content does not, as a rule, exceed 10 p. c. If more be found, this generally is indicative of adulteration with leaf oil.

To what extent the adulteration with leaf oil is carried on becomes apparent from the reports by Umney[1]) and by Schimmel & Co.[2]). The results of the examination of seven oils that were imported directly from Ceylon and bought in London are dealt with. All of these oils were heavily adulterated with leaf oil: three samples contained at least 30 p. c. of leaf oil and four not less than 50 p. c.

The four last mentioned oils had the following properties: —

	Spec. Gr.	α_D	Cinnamic aldehyde content	Eugenol content (according to Thoms)
1.	1,039	—0° 55′	29 %	41,9 %
2.	1,040	—0° 28′	28 %	39,1 %
3.	1,041	—0° 57′	29 %	47,7 %
4.	1,049	—0° 22′	24 %	45,7 %

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[1]) Pharmaceutical Journ. III. **25** (1895), 949.

[2]) Report of Schimmel & Co. October 1895, 65.

Ceylon cinnamon oils that have been adulterated with cassia oil have a higher specific gravity, and, as a rule, a higher cinnamic aldehyde content. Oils with more than 76 p.c. aldehyde are suspicious. At least they are inferior, for cinnamic aldehyde is not the constituent that imparts to the cinnamon oil its value as it does to cassia oil. In the case of cinnamon oil, the non-aldehydic constituents are of greater value, a circumstance that is readily demonstrated by the fact that several times the price of cassia oil is paid for cinnamon oil though the latter contains less aldehyde[1]).

Statistics. The amount of cinnamon oil exported from Ceylon is comparatively small. Considerable, however, is the amount of waste bark which, in the form of chips, is annually exported for the purpose of distillation.

The following quantities of chips were exported:—

1896	808502	lbs.	1904	2135220	lbs.
1897	1067051	„	1905	2235395	„
1898	1414165	„	1906	2531614	„
1899	1829127	„	1907	2835936	„
1900	1863406	„	1908	2785824	„
1901	1521149	„	1909	2941578	„
1902	1763679	„	1910	3022858	„
1903	2253269	„	1911	2644598	„

By way of comparison, the amounts of quills exported during the last two years may be mentioned: in 1910, 3283202 lbs., in 1911, 3128542 lbs.

The price of chips averages 40 to 45 shillings per hundredweight (= 112 lbs. = 50,8 kg.), whereas that of the quills is higher, 4 to 5 times as great.

268. Cinnamon Leaf Oil.

Oleum foliorum Cinnamomi. — Zimtblätteröl. — Essence de Feuilles de Cannelle de Ceylan.

Origin. For a time the oil from the leaves of the genuine cinnamon shrub, *Cinnamomum zeylanicum,* Nees, entered the market as cinnamon root oil. When, however, in 1892 Schimmel & Co. found that the oil distilled by them from Ceylon cinnamon

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[1]) Compare herewith Report of Schimmel & Co. October **1910**, 35.

leaves (yield 1,8 p.c.) corresponded in all its properties with the so-called cinnamon root oil, this erroneous designation could be upheld no longer. Two oils, correctly labelled as cinnamon leaf oil, which resembled their own distillates in every particular had previously been obtained from the Seychelles and from the Botanical Garden at Buitenzorg in Java[1]).

As cinnamon leaf oil there was exported at that time a viscid oil of the consistency of West Indian sandalwood oil. Since then this oil has disappeared from the market and nothing definite is known as to its origin.

Properties. Cinnamon leaf oil is light in color, rather limpid, and has an odor reminding one of cloves and cinnamon: d_{15° 1,044 to 1,065; $\alpha_{\mathrm{D}} - 0^\circ 15'$ to $+ 2^\circ 20'$ (mostly dextrogyrate); n_{D} 1,531 to 1,540; eugenol content 65 to 95 p.c.; aldehyde content up to 25 p.c. With 1 to 3 vol. of 70 p.c. alcohol it yields a clear solution, but occasionally the solution becomes turbid upon the addition of more alcohol.

Several oils obtained from the Seychelles had the following properties: d_{15° 1,0206 to 1,0604; $\alpha_{\mathrm{D}} - 1^\circ 43'$ to $+ 0^\circ 27'$; phenol content 78 to 94 p.c.; aldehyde content (determined for an oil of 78 p.c. eugenol) about 5 p.c.; soluble in 1 to 1,5 vol. or more of 70 p.c. alcohol.

Composition. J. Stenhouse[2]) found that cinnamon leaf oil contained large amounts (70 to 90 p.c.) of *eugenol.* E. Schær[3]) later confirmed this statement. In the above-mentioned oil distilled by themselves, Schimmel & Co. proved the presence of cinnamic aldehyde (0,1 p.c.).

A more detailed investigation of two different oils was conducted by J. Weber[4]). The first, from the Seychelles, had $d_{18,5^\circ}$ 1,0552 and contained *eugenol* (m. p. of benzoyl eugenol 69 to 70°), *cinnamic aldehyde* (m. p. of phenylhydrazone 167°) and *terpenes* that were not identified.

The other oil, imported by Schimmel & Co. under the erroneous designation of cinnamon root oil, was also leaf oil,

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[1]) Report of Schimmel & Co. April **1892**, 58 and October **1892**, 47.

[2]) Liebig's Annalen **95** (1855), 103.

[3]) Arch. der Pharm. **220** (1882), 492.

[4]) *Ibidem* **230** (1892), 232.

$d_{19°}$ 1,041. Its composition differed somewhat from that of the previous oil. Weber found *eugenol, safrol* (m. p. of piperonylic acid 226 to 227°), *terpenes* and *benzaldehyde* (m. p. of phenyl hydrazone 150 to 151°). Cinnamic aldehyde could not be identified.

Stenhouse had found *benzoic acid* which was presumably combined with an alcohol. Later investigators do not mention this constituent. Whether the benzaldehyde found by Weber was contained in the original oil, or whether it resulted as an oxidation product of cinnamic aldehyde remains undetermined.

Schimmel & Co.[1]), found l-*linalool* in the oil (oxidation to citral; m.p. of citryl-β-naphthocinchoninic acid 198°), also *safrol.*

269. Cinnamon Root Oil.

The oil distilled from the root bark of the cinnamon shrub is a colorless liquid with a strong odor of camphor. Upon standing, even at room temperature, some of the *camphor*[2]) separates out. This is identical with the ordinary laurus camphor. This fact has long been known, having been mentioned by Trommsdorff[3]) as well as by Dumas and Péligot[4]). A further constituent of the oil is *cinnamic aldehyde*[5]).

The latest examination of the oil was conducted by A. A. L. Pilgrim[6]). The properties of the oil distilled from the fresh root bark were as follows: $d_{15°}$ 0,99366 and $\alpha_D + 50{,}2°$ (?). The presence of the following constituents was established: *pinene, dipentene, phellandrene, cineol, camphor, eugenol, safrol, caryophyllene* and *borneol.*

Cinnamomum zeylanicum affords the interesting example of a plant of which roots, leaves and bark yield oils very different in composition. In the root oil camphor is found as characteristic constituent, leaf oil contains principally eugenol, whereas in the the bark oil cinnamic aldehyde predominates.

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[1]) Report of Schimmel & Co. October **1902**, 27.

[2]) *Ibidem* October **1892**, 47.

[3]) Trommsdorff's *Handbuch der Pharmacie.* 1827, p. 666.

[4]) Liebig's Annalen **14** (1835), 50.

[5]) Holmes, Pharmaceutical Journ. III. **20** (1890), 749.

[6]) Pharm. Weekblad **46** (1909), 50; Chem. Zentralbl. **1909**, I, 534.

270. Cassia Oil.

Oleum Cinnamomi Cassiæ. — Cassiaöl, Chinesisches Zimtöl, Zimtblütenöl. — Essence de Cannelle de Chine.

Origin and Production. Although the plant, the *Cinnamomum Cassia,* Blume, from which the cassia oil is obtained has been known for a long time, considerable uncertainty existed until recently as to the part of the plant from which the oil is distilled. Thus it was supposed that the oil was distilled from the unripe fruits which are sold as *Flores cassiæ,* hence it was called *Zimtblütenöl.* It was not until 1881¹) that it became known that the leaves of the cassia shrub were used in the distillation of the oil at In-lin, north of Pak-hoi. However, this oil was reported to be more viscid, darker and less fragrant than the cassia oil. In the description of his trip into the cassia district, undertaken by H. Schrœter²) in 1886, he also mentions the production of oil from leaves. It was supposed, however, at that time that the leaves produced but little oil, and that of an inferior quality. In order to ascertain the properties of the leaf oil, Schimmel & Co., secured, through the aid of Melchers & Co. of Canton, not only leaves, but all parts of the cassia shrub that are utilized in the production of the oil³). Upon distillation, bark, flowers, flower stems, branches and leaves yielded oils that were much alike in properties and aldehyde content. Inasmuch, however, as bark, flowers and parts of flowers are out of the question because of their high price, leaves and branches only can come into consideration as far as the production of the commercial cassia oil is concerned. As a matter of fact, aside from waste bark, only leaves are probably used for distillation purposes, as was ascertained by O. Struckmeyer, who, in 1895, undertook a trip⁴) into the cassia district for the firm of Siemssen & Co., of Hongkong.

The distillation is conducted in the valleys of the provinces Kwang-si and Kwang-tung, in places where abundant water for condensation is available.

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¹) Deutsches Handels-Archiv for Sept. 2nd, 1881, 262.

²) H. Schrœter, *Bericht über eine Reise nach Kwang-si. Im Herbst 1886 unternommen.* Hongkong 1887.

³) Report of Schimmel & Co. October 1892, 13.

⁴) *Ibidem* October 1896, 19.

The distilling apparatus used in that locality[1] (fig. 38) consists of a brick furnace with an iron pan mounted in masonry. On this rests a wooden cylinder coated on the inside with sheet iron and open at the top. After the cylinder has been charged with cassia twigs and leaves and filled half with water, it is closed with a peculiarly shaped helmet of sheet iron. The apparatus is sealed by means of wet clothes pressed between the joints. On the inside of the lower margin, the helmet is provided with a gutter in which collects the condensed distillate that has gathered on the cooled walls. By means of a tube it is conveyed from this gutter to the receiver. The condensation

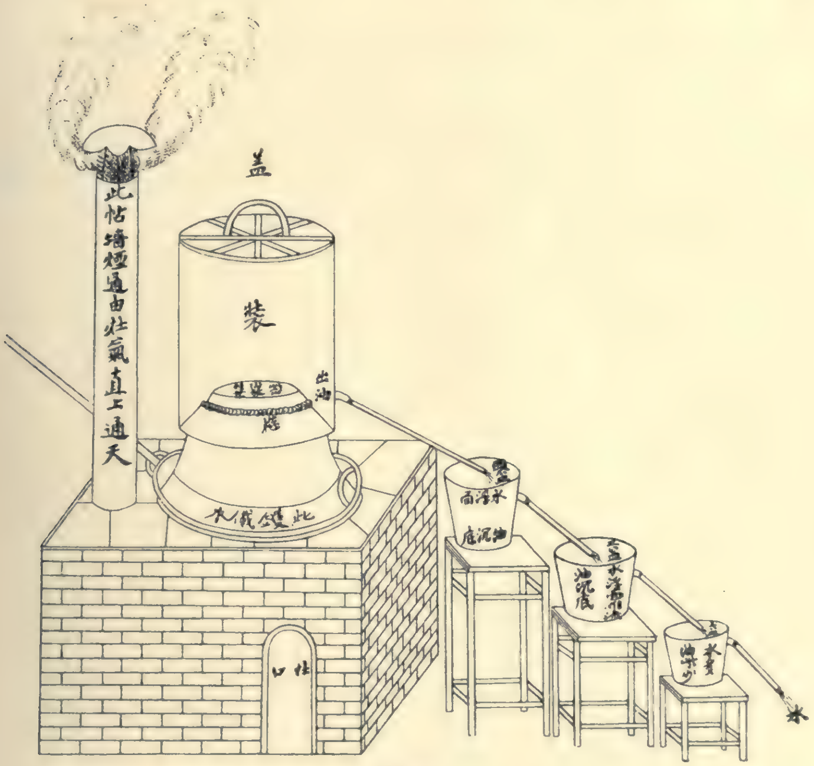

Fig. 38.
Chinese still for cassia oil.

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[1] Report of Schimmel & Co. April 1893, 11 and October 1896, 13.

is effected from without. The distillate from the gutter flows into a series of receivers arranged as a cascade, the oil collecting at the bottom. The water from the last receiver is used for the next distillation.

Cassia oil is shipped in lead canisters each containing $16\frac{2}{3}$ lb. net, four of which are put into a case. The spaces between the canisters are tightly packed with rice chaff.

The labels on the canisters have remained unchanged for a long time, both as to style and color.

Properties. When pure, Chinese cinnamon or cassia oil is a rather limpid oil, yellow or brownish in color and with high refractive power. Its odor is cinnamon-like, its taste burning and intensely sweet, without the exceedingly grating after-taste that becomes apparent in oils adulterated with rosin. d_{15° 1,055 to 1,070. Inasmuch as the specific gravity of cinnamic aldehyde is almost the same as that of the other constituents of the oil, differences in the aldehyde content find no expression in changes of density. $\alpha_D - 1$ to $+ 6^\circ$; n_{D20° 1,602 to 1,606; A.V. 6 to 15, exceptionally up to 20.

In 1 to 2 vol. of 80 p.c. alcohol cassia oil is readily soluble. Its behavior toward 70 p.c. alcohol differs in this respect that whereas most oils are soluble in 2 to 3 vol. of this solvent to a clear solution, other oils, otherwise equally good, yield opalescent, turbid solutions. This behavior is perhaps attributable to lead cinnamate which is frequently present in the oil.

The oil boils between 240 and 260° with partial decomposition and splitting off of acetic acid. In the distillation flask there remain 6 to 8 p.c. of a viscid residue. For further details see under adulterations and their detection.

If to a small amount of cassia oil (4 drops) cooled with ice water, an equal volume of nitric acid be added, the two liquids congeal to a crystalline mass. This reaction, which was formerly given by the German Pharmacopœia as a test for identification, depends on the formation of a loose addition product of cinnamic aldehyde and nitric acid, which is again resolved into its components by water. As a test for purity this reaction is of no use since even strongly adulterated oils yield these crystals. It should be observed, however, that the reaction mixture should be carefully cooled, otherwise oily products only result.

The principal constituent of the oil, which determines its value, is the cinnamic aldehyde, of which good oils contain 75 to 90 p.c.

Rectified cassia oil has $d_{15°}$ 1,053 to 1,065. Inasmuch as it contains no lead cinnamate, it forms a clear solution with 2 vol. of 70 p.c. alcohol.

Composition. Cassia oil, like cinnamon oil, contains cinnamic aldehyde as principal constituent. The chemists who, during the first half of the past century, examined cinnamon oil were acquainted with the differences between the two oils as being due to their secondary constituents. Thus Blanchet[1]) points out that the odor of cassia oil is much more pungent than that of Ceylon cinnamon oil. Dumas and Péligot[2]) also referred to the different kinds of cinnamon oil. In connection with the oils distilled by themselves, the details of which need not be mentioned here, they arrived at the important conclusion that the cinnamic acid obtained upon oxidation of the oil is related to the latter or cinnamyl hydride as is benzoic acid to bitter almond oil or benzoyl hydride. In other words, they recognized that cinnamon oil consists principally of the aldehyde of cinnamic acid, *viz., cinnamic aldehyde.*

The same investigators also discovered the unstable compound $C_9H_8ONO_3H$ mentioned above, which results upon the addition of nitric acid to cinnamic aldehyde in the cold and which is characterized by its crystallization capacity.

Of other investigations of the same period those of Mulder[3]) and Bertagnini[4]) should be mentioned.

Bertagnini studied the addition products of the acid sulphites of alkalies to cinnamic aldehyde, the exact composition of which was later ascertained by F. Heusler[5]).

The properties and derivatives of cinnamic aldehyde have been described in Vol. I, p. 424.

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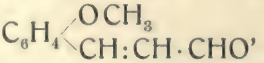
[1]) Liebig's Annalen **7** (1833), 164.

[2]) Ann. de Chim. et Phys. **57** (1834), 305; Liebig's Annalen **12** (1834), 24; **13** (1835), 76; **14** (1835), 50.

[3]) Liebig's Annalen **34** (1840), 147. — Journ. f. prakt. Chem. **15** (1838), 307; **17** (1839), 303 and **18** (1839), 385.

[4]) Liebig's Annalen **85** (1853), 271.

[5]) Berl. Berichte **24** (1891), 1805.

The *"Cassia stearoptene"* is a crystalline substance which was discovered jointly by F. Rochleder, H. Hlasiwetz and R. Schwarz[1]. It is observed but rarely, separating from old oils. Its constitution was determined in 1895 by J. Bertram and R. Kürsten[2]. The stearoptene that served as a basis for this investigation had separated from the last fractions in the rectification of a cassia oil. In the pure state it consists of well-developed six-sided yellow plates that melt at 45 to 46° and have a very persistent but not very pleasant odor. This substance is identical with *methyl*-ortho-*cumaric aldehyde*  $C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CH:CH\cdot CHO\end{matrix}$, a substance that can be obtained synthetically by condensation of methyl salicylic aldehyde and acetaldehyde.

Cinnamyl acetate, which was discovered in 1889 by Schimmel & Co.[3], is essential but exerts no favorable influence on either odor or taste of the cassia oil. It boils between 135 and 140° (11 mm.) and possesses a rather unpleasant odor and a grating taste.

In addition to this ester there appears to be present a small amount of another, *viz.,* the *acetate of phenylpropyl alcohol.* Its presence has been inferred from the boiling point of an alcohol that accompanies the cinnamyl alcohol after saponification.

On account of the ease with which cinnamic aldehyde oxidizes, oil of cinnamon always contains *cinnamic acid;* however, the amount, about 1 p.c.[4], is less than might be assumed from the changeability of the pure aldehyde.

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[1] Rochleder and Schwarz, Ber. d. Academ. d. Wissensch. zu Wien, mathem. phys. Kl., June **1850**, 1. *Ibidem* vol. **12**, 190 to 199; Pharm. Zentralbl., **1851**, **46**; **1854**, 701.

[2] Journ. f. prakt. Chem. II. **51** (1895), 316.

[3] Schimmel's Bericht October **1889**, 19.

[4] Apparently the cinnamyl acetate acts as a preservative to a high degree. A very old cassia oil, containing 77,7 p.c. of aldehyde, was exposed or a year in a shallow dish, covered with perforated filter paper, in a place where warmth, light and air had free access. After the expiration of this time, the cinnamic acid content, which in the original oil had amounted to 0,7 p.c., had increased to 8,5 p.c. A real resinification had not taken place, for the distillation residue (see under Examination) was but little greater at the end of this period than at the beginning. Under like conditions, pure cinnamic aldehyde would soon have been changed to lumps of cinnamic acid. (Report of Schimmel & Co. October **1890**, 16.)

Free cinnamic acid has the undesirable property of attacking the lead of the canisters in which the oil is shipped, thus imparting to the oil a decided lead content. A crystalline sediment observed by Hirschsohn[1]) in a cassia oil consisted of lead cinnamate. Following up this observation with the examination of 12 commercial oils, he found that 11 of these contained lead. The detection of the lead is accomplished by shaking a few drops of the oil with hydrogen sulphide water. According to the lead content the oil is colored red to black.

If cassia oil is used for medicinal or culinary purposes, the lead-free, rectified oil only should be used.

Adulterations and their Detection. Formerly cassia oil was adulterated only with fatty oils, cedarwood oil and gurjun balsam oil. The detection of these adulterants was very simple since they lowered the specific gravity and interfered with the solubility in 80 p.c. alcohol. Because of their decided lævorotation, cedarwood oil and gurjun balsam oil could readily be detected by means of the polariscope. Less simple was the recognition of an adulteration, practiced extensively in Macao and Hongkong toward the close of the eighties. It consisted in the addition of colophony and petroleum. At first the Chinese may have used colophony only. But, inasmuch as larger additions of rosin made the oil too thick and also increased the specific gravity, this fault was corrected with the aid of petroleum. Since this mode of adulteration did not alter the specific gravity or, remarkable though it may seem, the solubility in 80 p.c. alcohol, it remained undetected for some time. Detection was brought about only when the additions of rosin gradually became too great. The commercial oils of that period had an exceedingly unpleasant odor, a dark brown color, and a thick, varnish-like consistence. The slightly sweetish taste soon gave way to a nauseating, persistent grating sensation in the mouth. Upon rectification with water vapor, as much as 40 p.c. of a hard resinous mass remained in the still. The distillate separated in the Florentine flask in two layers: one sank under water, the other floated. The latter consisted of petroleum, as was shown upon examination.

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[1]) Pharm. Zeitschr. f. Russland **30** (1891), 790.

The desirability of being able to detect this mode of adulteration rapidly and on a small scale resulted in Schimmel & Co.'s distillation test[1]). It consists in distilling a weighed or measured amount of oil in a fractionating flask over a free flame and weighing the residue. The test is carried out in the following manner: Into a tared fractionating flask of 100 cc. capacity (Vol. I, p. 565, fig. 70), the exit tube of which is not too high, 50 g. of cassia oil are weighed. After the flask has been connected with a tube 1 m. long that serves as condenser, the contents are distilled over a Bunsen burner or alcohol lamp. At first some water passes over with a cracking noise, then the thermometer rises rapidly to 240° and the bulk of the oil distils over between 240 and 260°. The end of the distillation is indicated by the formation of white fumes that result from the decomposition of the residue. The thermometer then rises to 280 and 290°.

After cooling, the flask with the residue is weighed. In the case of good oils, the latter is thick, of tough consistence and amounts to from 6 to 8, or at most 10 p.c. of the original oil. The residue of oils adulterated with colophony is hard, vitreous and brittle and is correspondingly larger.

Instead of weighing the oil, 50 cc. can be measured in a pipette and the distillate can be collected in a graduated cylinder. The amount of residue can be ascertained with sufficient accuracy by deducting the number of cc. of distillate from 50.

The presence of petroleum can be shown in the distillate. In the case of pure oils this forms a clear solution with 70 and 80 p.c. alcohol. If petroleum be present, solution is not complete[2]). The liquid is milky at first but becomes clear on standing. The petroleum floating on the surface can be decanted and recognized by its behavior toward sulphuric and nitric acids. (Comp. Vol. I, p. 614).

According to H. Gilbert[3]) the test for colophony can be carried out without much loss of substance by evaporating a

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[1]) Schimmel's Bericht October 1889, 15.

[2]) As previously mentioned, cassia oil which contains petroleum as well as colophony, is soluble in 80 p.c. alcohol, whereas the petroleum added to pure cassia oil is separated in the form of oily drops by 80 p.c. alcohol.

[3]) Chem. Ztg. **13** (1889), 1406.

few grams of oil on a watchglass in a drying oven at a temperature of from 110 to 120° until of constant weight and computing the amount of residue.

Also, according to Gilbert, the determination of the acid value yields results that can be utilized for the detection of colophony. An oil with an evaporation-residue of 6 p.c. yielded an acid value of 13. After 20 p.c. of colophony (A. V. 150) had been dissolved in the oil the acid value had risen to 40. A cassia oil with 28 p.c. residue had an acid value of 47.

Inasmuch as an alcoholic solution of lead acetate yields a precipitate with solutions of colophony, Hirschsohn[1]) has proposed this reagent for the detection of rosin in cassia oil. For this purpose a solution of 1 vol. of cassia oil in 3 vol. of 70 p.c. alcohol is prepared. To it a freshly prepared solution of lead acetate in 70 p.c. alcohol, saturated at room temperature, is added drop by drop. If a precipitate results, the oil has been adulterated with colophony. In this manner as little as 5 p.c. of colophony can be detected.

Aldehyde Determination. Inasmuch as the value of cassia oil depends on its cinnamic aldehyde content, the quantitative determination of this substance is of the greatest importance. The directions for carrying out the bisulphite method, as suggested by Schimmel & Co.[2]) and as now generally practised in commercial transactions[3]), are given in vol. I, p. 582.

Stricktly speaking this method yields percentages by volume, not weight percentages. Inasmuch, however, as the specific gravities of the aldehyde and the non-aldehyde constituents of the oil are almost the same, the percentage by weight and volume are practically the same.

The chemical changes that come into consideration in the aldehyde test can be expressed by the following equations[4]):

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[1]) Pharm. Zeitschr. f. Russl. 29 (1890), 255.

[2]) Report of Schimmel & Co. October 1890, 15.

[3]) In an account of his trip to the cassia district, O. Struckmeyer states that he found the implements recommended for the aldehyde determination by Schimmel & Co. in the interior of China, *viz.*, on a cassia plantation in the neighborhood of Lotingchow. Report of Schimmel & Co. October 1896, 20.

[4]) F. Heusler, Berl. Berichte 24 (1891), 1805; Schimmel's Bericht April 1890, 13.

First, a non-soluble addition product of 1 mol. cinnamic aldehyde and 1 mol. sodium bisulphite is formed.

$$\underset{\text{Cinnamic aldehyde}}{C_6H_5\cdot CH:CH\cdot CHO} + \underset{\text{Sodium bisulphite}}{NaHSO_3} = \underset{\text{Cinnamic aldehyde sodium sulphite}}{C_6H_5CH:CH\cdot CHO\cdot NaHSO_3}$$

This addition product decomposes on boiling with water, and from two molecules there is formed one molecule each of cinnamic aldehyde and of sulphocinnamic aldehyde sodium sulphite.

$$\underset{\text{Cinnamic aldehyde sodium sulphite}}{2\,C_6H_5\cdot CH:CH\cdot CHO\cdot NaHSO_3}$$

$$= \underset{\text{Cinnamic aldehyde}}{C_6H_5\cdot CH:CH\cdot CHO\cdot} + \underset{\text{Sulphocinnamic aldehyde sulphite of sodium}}{C_6H_5CH_2\cdot CH(SO_3Na)\cdot CHO\cdot NaHSO_3}$$

Hence, in order to convert the entire aldehyde into the water-soluble compound an excess of sodium acid sulphite (2 mol.) must be used.

The salts of the sulphocinnamic aldehyde sulphonic acid are readily soluble in water and are stable when boiled. They are decomposed only when subjected to destructive distillation or when heated with caustic soda solution or sulphuric acid.

Suitable for the determination of the cinnamic aldehyde is also the sulphite method described in Vol. I, p. 584.

The cinnamic aldehyde content of good cassia oils amounts to at least 80 p.c., but is rarely greater than 90 p.c. However, oils have been obtained from China which contained no more than 35 to 50 p.c. aldehyde and yet no adulteration could be detected. According to statements made by the Chinese, these oils had been obtained from young leaves, a claim the correctness of which, naturally, cannot be verified.

Of such oils as contain less than 40 p.c. of cinnamic aldehyde only 5 cc. should be taken for an assay, otherwise a flask should be used the neck of which has a capacity of more than 10 cc. and the calibration of which ranges from 0 to 10.

OILS OBTAINED FROM THE SEVERAL PARTS OF THE CASSIA SHRUB.

All parts of the cassia shrub yield oils with a high aldehyde content[1]). The differences in specific gravity, though but

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[1]) Report of Schimmel & Co., October 1892, 14.

small, indicate that the non-aldehyde constituents vary somewhat. For the production of cassia oil, as already indicated, the leaves and branches alone come into consideration, since the bark and the so-called flowers are too expensive, whereas of flower stems no sufficient quantities can be collected. It is not impossible, however, that occasionally all these parts are utilized.

1. *Oil of cassia bark,* the *Cassia lignea* of commerce. Yield 1,2 p.c.; d_{15° 1,035; aldehyde content 88,9 p.c.

2. *Oil of so-called cassia buds,* the *Flores cassiæ* of commerce. Yield 1,9 p.c.; d_{15° 1,026; aldehyde content 80,4 p.c.

3. *Oil of the floral stems.* Yield 1,7 p.c.; d_{15° 1,046; aldehyde content 92 p.c.

4. *Oil of the leaves.* Yield 0,54 p.c.; d_{15° 1,056; aldehyde content 93 p.c.

5. *Oil of the twigs.* Yield 0,2 p.c.; d_{15° 1,045; aldehyde content 90 p.c.

6. *Oil from a mixture of leaves, floral stems and young twigs.* Yield 0,77 p.c.; d_{15° 1,055; aldehyde content 93 p.c.

7. *The oil of the root bark* also contains cinnamic aldehyde[1]).

Inasmuch as the commercial oil is distilled from the same material as that used in experiment No. 6, it ought to approximate this oil as to properties. However, the commercial oils never attain this high quality. This is probably due to the crude method of distillation over direct fire, which is customary in China.

Production and Commerce. The important spice cassia, which, in order to distinguish it from other cinnamon varieties of commerce, is commonly known as *Cassia lignea,* is produced in a relatively limited territory in the provinces of Kwang-si and Kwang-tung. This cassia territory lies between the 110th and 112th degree of eastern longitude, is bordered in the north by the Si-kiang or West river and extends southward as far as 23° 3′ northern latitude. The principal plantations are in the neighborhood of Tai-wo, Yung and Sih-leong on the Sang-kiang, also near Lotingchow on the Lintan river. In commerce the drug from Tai-wo is given preference. The amount of cassia produced annually fluctuates between

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[1]) Verslag 's Lands Plantentuin te Buitenzorg 1895, 39.

50000 and 80000 piculs or 3000000 and 4800000 kilos. The principal markets are Canton and Hongkong. From the latter place 54032 piculs were exported in 1896.

The distillation of cassia oil is carried on in the territory mentioned above. For the purpose of distillation the waste materials resulting from the production of *Cassia lignea* are used, *viz.,* the leaves, the floral stems and the twigs of the cassia shrub. Whereas the cassia bark is carried to Canton in junks on the natural water route, the Si-kiang, the cassia oil is carried in the well-known lead containers across the hills to Pak-hoi and thence by water to Hongkong, the principal exporting centre. This route is taken because of the high toll demanded at the likin stations on the way to Canton. It is reported that the entire cassia trade is controlled by a trust of Chinese merchants in the province of Kwang-tung who also control the export of *Cassia lignea.* How much cassia oil is produced cannot be stated with exactness. Even the amounts exported can only be estimated since, as mentioned on p. 389, footnote 3, the Chinese export statistics do not discriminate between cassia oil and staranise oil. American experts estimate the annual output in Kwang-tong and Kwang-si at from 200000 to 260000 lbs. The total output for all China is reported to have been 1577000 lbs. in 1907, representing a value of $ 560400 in gold. The total amount of cassia oil exported in 1911 was valued at £ 28964.—, half of which was exported via Honkong. From which ports the remaining half was exported is not mentioned. That there should be another port of export is news. It is also reported that in 1911, 2200 cases of a net content of 30 kg. each, passed through Hongkong as against 1400 cases in 1910. The value of the cassia oil shipped to the United States in 1911 is reported at £ 5560.—, as against £ 4880.— for the previous year.

Following the precedent set by Schimmel & Co., the cinnamic aldehyd content is regarded as the standard of value for the oil. The more important firms at Hongkong are equipped to carry out the determination and have acquired considerable skill therein, the result of several years of experience.

The fluctuations in the price of the best commercial grades of cassia oil with 80 to 85 p.c. aldehyde content are shown in the following table. The quotations are for September 1st of each year.

1886	ℳ 7.—	pro 1 kg.	1900	ℳ 9.10	pro 1 kg.
1887	,, 5.80	,, ,,	1901	,, 7.70	,, ,,
1888	,, 7.10	,, ,,	1902	,, 6.30	,, ,,
1889	,, 9.-	,, ,,	1903	,, 7.20	,, ,,
1890	,, 8.80	,, ,,	1904	,, 7.40	,, ,,
1891	,, 8.60	,, ,,	1905	,, 7.—	,, ,,
1892	,, 7.70	,, ,,	1906	,, 10.15	,, ,,
1893	,, 7.40	,, ,,	1907	,, 12.60	,, ,,
1894	,, 7.60	,, ,,	1908	,, 10.90	,, ,,
1895	,, 12.—	,, ,,	1909	,, 7.90	,, ,,
1896	,, 17.-	,, ,,	1910	,, 6.95	,, ,,
1897	,, 14.40	,, ,,	1911	,, 7.55	,, ,,
1898	,, 13.40	,, ,,	1912	,, 8.30	,, ,,
1899	,, 11.50	,, ,,			

271. Japanese Cinnamon Oil.

The various parts of *Cinnamomum Loureirii,* Nees[1]) are used in Japan as cinnamon. The tree, known as *Nikkei,* grows in the hottest part of Japan, namely in the provinces Tosa and Kii. Oils have been distilled from both overground and underground parts of the tree.

1. OIL FROM THE LEAVES AND YOUNG TWIGS.

The oil, obtained with a yield of 0,2 p.c., is light yellow in color and possesses an agreeable odor reminding one of citral and Ceylon cinnamon oil. The properties of an oil examined by Schimmel & Co.[2]), were as follows: d_{15° 0,9005; $\alpha_{\mathrm{D}} - 8^\circ 45'$; A. V. 3,01; E. V. 18,6. It is soluble in 2 to 2,5 vol. or more of 70 p. c. alcohol, the solution being opalescent. However, it forms a clear solution with an equal volume or more of 80 p.c. alcohol. The oil contained 27 p. c. of aldehydes, mostly *citral* (m.p. of α-citryl-β-naphthocinchoninic acid 199°). Upon fractionation of

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[1]) According to E. Perrot and P. Eberhardt (Bull. Sciences pharmacol. **16** [1909], No. 10 and 11; Report of Schimmel & Co. April **1910**, 31) the cinnamon produced in Tonquin and Annam which, according to former statements (Comp. Cayla, Journ. d'Agriculture tropicale **9** [1909], 164; Report of Schimmel & Co. October **1909**, 39), was supposed to be derived form *C. Loureirii,* is obtained form varieties of *C. obtusifolium,* Nees.

[2]) Report of Schimmel & Co. October **1904**, 96.

the non-aldehydic constituents *cineol* and *linalool* ($d_{15°}$ 0,8724; α_D — 17°; $n_{D20°}$ 1,46387) were found. Of the latter compound the oil probably contains at least 40 p.c.

K. Keimatsu[1]) found *eugenol* as well as *citral* in the leaf oil.

2. OIL OF THE STEMS.

According to K. Keimatsu[1]) the oil contains *cinnamic aldehyde* as principal constituent, also small amounts of *eugenol.*

3. OIL OF THE ROOTS.

Upon distillation of the root bark, known as *Komaki,* Shimoyama[2]) obtained 1,17 p. c. of a light yellowish, strongly refractory oil with $d_{15°}$ 0,982. Like the genuine cinnamon oil it contains *cinnamic aldehyde.* The portion of the oil which does not react with potassium bisulphite has an odor of lavender and boils between 175 and 176°. According to analysis it contains 87,78 p. c. C and 11,33 p.c. H, hence consists of a *terpene.*

In addition, Keimatsu[1]) found *camphene, cineol* and *linalool* therein.

272. Oil of the Bark of Cinnamomum Kiamis.

From massoy bark from *Cinnamomum Kiamis,* Nees (*C. Burmanni,* Blume), Bonastre[3]) distilled an oil which separated into a light and a heavy oil and from which a camphor separated. The light oil was almost colorless, limpid, and had an odor resembling that of sassafras. The heavy oil was more viscid and less volatile. Its odor was fainter but it had a decided taste of sassafras. The *massoy camphor,* which was also heavier than water, consisted of a white soft powder which was odorless and almost tasteless, and which dissolved in hot alcohol and ether.

From two barks received from Timor and Celebes, Schimmel & Co.[4]), obtained upon distillation 0,5 p.c. of a brownish-yellow oil which possessed an odor similar to that of Ceylon cinnamon but

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[1]) Journ. pharm. Soc. of Japan **1906**, 105; Apotheker Ztg. **21** (1906), 306.

[2]) Mitt. der med. Fak. Tokio, Bd. III. No. 1; Apotheker Ztg. **11** (1896), 537.

[3]) Journ. de Pharm. **15** (1829), 204.

[4]) Report of Schimmel & Co. October **1911**, 106.

less delicate. The constants also differed from those of cinnamon oil: d_{15° 1,0198; $\alpha_D - 1^\circ 50'$; n_{D20° 1,58282; soluble in 0,8 vol. or more of 80 p.c. alcohol; not soluble to a clear solution in 10 vol. of 70 p.c. alcohol. With the aid of neutral sodium sulphite the amount of cinnamic aldehyde present was found to be 77 p.c., whereas a determination with bisulphite yielded 80 p.c. However, in the latter test the results were inaccurate, probably because of the presence of other aldehydes, the bisulphite compounds of which separated from the solution and thus prevented accurate reading. A phenol determination carried out with a 3 p.c. sodium hydroxide solution yielded about 11 p.c. Upon shaking with the sodium hydroxide solution part of the oil was emulsified, thus preventing accurate reading in this instance also. Hence the figures are but approximately correct.

273. Culilawan Oil.

The oil from culilawan bark from *Cinnamomum Culilawan,* Blume, was first prepared by Schloss¹) in 1824. He describes it as an oil the odor of which resembles that of cloves and cajeput.

The yield amounted to 4 p.c. d_{15° 1,051; soluble in 3 vol. or more of 70 p.c. alcohol¹).

The principal constituent²) is *eugenol* (m.p. of benzoyl eugenol 70 to 71°). One oil, assayed according to Thoms' method, yielded 62 p.c. A second constituent of the oil is *methyleugenol* which boils between 249 and 252° (m.p. of monobrom methyleugenol dibromide 78 to 79°; m.p. of veratric acid 179 to 180°). Fraction 100 to 125° (10 mm.) possibly contains *terpineol.*

274. Oil of Cinnamomum Wightii.

The bark of *Cinnamomum Wightii,* Meissn. which grows in the mountainous regions of Southern India yielded 0,3 p.c. of oil upon distillation. It boiled between 130 and 170° and had a specific gravity of 1,010 at 15°. The plant from which this bark is obtained was at first erroneously named *Michelia nilagirica*³).

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¹) Trommsdorff's Neues Journ. der Pharm. 8, II (1824), 106.

²) E. Gildemeister and K. Stephan, Arch. der Pharm. 235 (1897), 583.

³) Schimmel's Bericht October 1887, 36 and April 1888, 46.

275. Oil of Cinnamomum Oliveri.

From the bark of *Cinnamomum Oliveri,* Bail., a tree known in Australia as black, brown or white sassafras, R. T. Baker[1]) obtained 0,75 to 1 p.c. of oil upon distillation with steam. The oil had a golden yellow color and a very pleasant odor. d 1,001; $\alpha_D + 22$ to $+ 22,3°$. Upon distillation the oil passed over between 213 and 253°, 54 p.c. distilling between 230 and 253°.

The lowest boiling fraction afforded the iodol-*cineol* reaction. With caustic alkali a small amount of phenol, which turned ferric chloride a blue color — presumably *eugenol* — was isolated. Bisulphite extracted about 2 p.c. of an aldehyde with the odor of cinnamon, presumably *cinnamic aldehyde.*

When cooled to — 12° the oil separated crystals which, however, melted as soon as the oil was removed from the freezing mixture *(safrol?).* The leaves of this tree, formerly erroneously named *Beilschmiedia obtusifolia,* yielded an oil[2]) (770 oz. from a ton) with a decided sassafras odor. According to Baker[3]) it contains a relatively large amount of *camphor*[4]).

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[1]) Proceed. Linnean Soc. of N. S. W. 1897, Part 2, p. 275; Pharm. Ztg. 42 (1897), 859.

[2]) Bericht von Schimmel & Co. April 1887, 38.

[3]) Journ. Soc. chem. Industry 20 (1901), 169.

[4]) The *Cinnamomum* species of Australia have been described by R. T. Baker in vol. 13 of the Australasian Association for the Advancement of Science (May 1, 1912). Baker bases his classification not only on morphological characteristics, but also on the anatomy of the bark and the chemistry of the oils obtained from the wood, the leaves and the bark. As had previously been pointed out by Baker and Smith in connection with the species of *Eucalyptus,* Baker found that in the case of the *Cinnamomum* species relations between the ribs of the leaves and the chemical composition of the leaf oils exist that are of great practical importance. In connection with the *Cinnamomum* species thus far examined in Europe and Australia, it was observed that those which contain camphor are penniveined, whereas the species with trinerved leaves yield oils free from camphor. The importance of this distinction is apparent. In its *Cinnamomum* trees Australia possesses a domestic source for camphor that has not yet been utilized. Thus the leaves of *C. Olivieri* yielded a large amount of camphor. The wood also contains this substance. The oil from the bark still awaits examination. *C. Laubatii* (see footnote 1, p. 442), a species little known as yet, also several other species appear to contain camphor. These observations have led to the planting of *Cinnamomum* trees along the northern coast for the production of camphor and oil. As yet no reports have been received as to the success of this experiment. Report of Schimmel & Co., April 1911, 38.

According to the same author[1]), the bark of *Beilschmiedia obtusifolia* is odorless.

276. Oil of Cinnamomum pedatinervium.

According to E. Goulding[2]), the bark of *Cinnamomum pedatinervium,* Meissn., a tree[3]) that is indigenous to the Fiji islands, yields upon distillation 0,92 p. c. of a yellowish-brown oil of an agreeable spicy odor. $[\alpha]_D - 4{,}96°$; $n_{D15°}$ 1,1963. Under ordinary pressure it distills between 180 and 255°. S. V. 4,4. After acetylation the saponification value of the oil had risen to 115,8, thus showing that it contains about 30,75 p.c. of free alcohols of the formula $C_{10}H_{18}O$. From the results of a methoxyl determination an OCH_3 content of 1,16 p.c. was computed.

The principal constituent of the oil, about 50 p.c., is *safrol* (piperonal; piperonylic acid; m.p. of safrol-α-nitrosite[4]) 129 to 130°). 30 p. c. of the oil consists of *linalool* (citral; citryl-β-naphthocinchoninic acid), 1 p.c. of *eugenol* (m.p. of benzoyl eugenol 70°) and probably about 3 p. c. of *eugenol methyl ether.* There are also present 10 to 20 p.c. of unknown terpenes which boil between 167 and 172° and which yield a liquid dibromide.

277. Oil of Cinnamomum Tamala.

Like other *Cinnamomum* species, *Cinnamomum Tamala,* Nees et Eberm., a medium-sized tree widely distributed throughout Southern Asia, yields the so-called *Mutterzimt,* the *Cassia lignea, Xylocassia* or *Holzcassia,* known as cassia in the retail trade. The leaves formerly entered commerce as narrow *Folia Malabathri,* but are now obsolete. However, they are still used for medicinal purposes in the East Indies. They contain a volatile oil which was distilled by J. H. Burkill in Calcutta and examined by Schimmel & Co.[5]). The oil was lemon-yellow in color and

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[1]) Pharmaceutical Journ. **63** (**1899**), 330 and 326.

[2]) The constituents of the volatile oil of the bark of *Cinnamomum pedatinervium* of Fiji. Thesis, London 1903.

[3]) The tree has been described by Berthold Seemann in his *Flora Vitiensis* p. 202.

[4]) A. Angeli and E. Rimini, Gazz. chim. ital. **25** II. (1895), 200.

[5]) Report of Schimmel & Co. April **1910**, 122.

possessed a clove-like and at the same time faintly pepper-like odor. It had the following constants: d_{15° 1,0257; $\alpha_D + 16^\circ 37'$; n_{D20° 1,52596; phenol content 78 p.c.; soluble in 1,2 or more vol. of 70 p.c. alcohol. The oil contains *eugenol* (m. p. of benzoyl derivative 69°). The oil deprived of phenols had a high optical rotation ($\alpha_D + 66^\circ 40'$) and yielded a solid nitrite which, after distillation from acetic ether, melted at 113 to 114°. Hence d-*α-phellandrene* was present. So far as its high eugenol content is concerned, the oil is closely related to the common cinnamon leaf oil.

According to Baker[1]) the leaves contain *camphor.*

278. Oil of Cinnamomum mindanaense.

Cinnamomum mindanaense, Elmer, which is closely related to *Cinnamomum zeylanicum,* is fairly common in the vicinity of Mindanao, Philippine Islands[2]). The bark yields 0,4 p.c. of volatile oil with the following properties: $d\frac{30^\circ}{30^\circ}$ 0,960; α_{D30° 7,9° (+?); n_{D30° 1,5300; the aldehyde content amounted to 60 p.c.

279. Oil of Cinnamomum Parthenoxylon.

From 15,82 kg. of the wood of *Cinnamomum Parthenoxylon,* Meissn. 124 cc. of oil were distilled in Buitenzorg[3]). The oil was heavier than water and, as ascertained by van Romburgh, it consisted principally of *safrol.* In Java the wood is called *Selasian*-wood.

A sample of this oil distilled by de Jong[4]) in Buitenzorg had the following constants: d_{15°1,0799; $\alpha_D + 1^\circ 22'$; n_{D20° 1,53229; soluble in 2,6 vol. or more of 90 p. c. alcohol. It was light yellow in color and showed a decided safrol odor. According to de Jong, the *bark* of this *Cinnamomum* species contains no volatile oil.

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[1]) Report of Schimmel & Co. April 1911, 38. Baker uses the name *Cinnamomum Laubatii;* according to the Index Kewensis *C. Laubatii,* F. v. Müll. = *C. Tamala,* Nees et Eberm.

[2]) R. F. Bacon, Philippine Journ. of Sc. 5 (1910), A, 257; Report of Schimmel & Co. April 1911, 43.

[3]) Jaarb. dep. Landb. in Ned.-Indië, Batavia 1909, 64.

[4]) Report of Schimmel & Co. April 1911, 43.

In one of the earlier annual reports of Buitenzorg[1]) there occurs a description of an oil also distilled from the wood. Its density was 1,074 (at 28°) and it consisted principally of *safrol.* The safrol was identified by conversion into *iso*safrol, which furnished its characteristic nitrite. Upon oxidation safrol yielded piperonylic acid and its homologue, melting at 126°.

A third oil also distilled in Buitenzorg from saw dust had the following properties[2]): d 1,067; $\alpha_D + 1° 3'$; S. V. 8,4; E. V. after acetylation 11,8.

280. Oil of Cinnamomum glanduliferum.

OIL OF THE LEAVES.

From the leaves of the Nepal sassafras or Nepal camphor tree, *Cinnamomum glanduliferum,* Meissn., a lauraceous tree growing in the southern districts of the Himalaya mountains, R. S. Pearson, of Dehra Dun, obtained a camphor which is identical with the Japanese drug. The crude product sent to Schimmel & Co.[3]) melted at 175°. Upon recrystallization from dilute alcohol the melting point rose to 176°. The specific angle of rotation of the purified camphor was $[\alpha]_D + 46{,}32°$ (in a 55,55 p.c. solution in 90 p.c. alcohol). In a 43,91 p.c. xylene solution it was $[\alpha]_D + 49{,}12°$ and after the solution had stood ten days it dropped to $[\alpha]_D + 48{,}72°$. The oxime melted at 118° and, as was to be expected, showed a reversed optical rotation, it being lævogyrate. Upon boiling the crude product with acetic acid anhydride the presence of alcoholic substances, *e. g.* borneol, could not be ascertained, hence it consisted of d-*camphor* only.

The leaves of a tree, the later investigation[4]) of which proved it to be *Cinnamomum glanduliferum,* Meissn., and which grew in the Villa Rothschild at Cannes, yielded upon distillation 0,52 p.c. of a volatile oil which was characterized by a decided cardamom odor. $d_{15°}$ 0,9058 and 0,9031; $\alpha_D - 26° 12'$

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[1]) Verslag 's Lands Plantentuin te Buitenzorg **1895**, 39.

[2]) Jaarb. dep. Landb. in Ned.-Indië, Batavia **1910**, 49.

[3]) Report of Schimmel & Co. October **1910**, 145.

[4]) *Ibidem* April **1905**, 83. This reference erroneously quotes *Laurus Camphora* as the plant from which the oil in question is derived. Comp. also *ibidem* April **1913**, 41.

and —24° 57′; A.V. 0,34 and 0,9; E.V. 8,82 and 18,4; E.V. after acetylation 46,9 and 55,3; soluble in 1 to 1,5 vol. or more of 80 p.c. alcohol.

The first-mentioned oil has been examined as to its constituents. Under a pressure of 4 mm. it boils between 35 and 95°. In the lowest boiling portion the presence of *α-pinene* was demonstrated (m.p. of nitrolbenzylamine 123°). The presence of camphene is probable, but its definite characterization by means of conversion into *iso*borneol was not accomplished. Furthermore the oil contained much *cineol* (m.p. of the iodol compound 112°).

Upon further fractionation in vacuum, of those portions of the oil which had passed over above 76° under 4 mm. pressure, the principal fraction which came over between 85 and 86° (5 mm.; α_D —58° 23′) and which constituted about 10 p.c. of the original oil, consisted of l-*α-terpineol*. This alcohol was characterized by its phenylurethane (m.p. 113°), as well as by its nitrosochloride (m.p. 112°). Upon inoculation of the strongly cooled fraction with solid terpineol, prolonged standing in the cold resulted in the separation of crystalline terpineol that melted at 35°. It is noteworthy that this oil contained no camphor, whereas the oil examined by Pearson consisted almost entirely of this substance.

OIL OF THE WOOD.

The oil from the wood of this plant has been distilled by S. S. Pickles[1]). The crude material used consisted of short pieces of the wood deprived of its bark. From the saw dust 2,95 p.c. of oil, computed with reference to the non-comminuted wood, were obtained. Computed with reference to the saw dust itself, the yield was 4,16 p.c. This difference is attributed to the loss of moisture which the wood suffered during the process of comminution. The oil constitutes a light yellow liquid, the odor of which reminds one distinctly of safrol, also of anise: $d_{15^\circ}^{15^\circ}$ 1,1033; α_{D20° — 0° 4′; S.V. 2,8; E.V. after acetylation 7,0; soluble in 5 vol. or more of 80 p.c. alcohol and in one-half vol. of 90 p.c. alcohol. Terpenes, acids, alcohols, esters, aldehydes and ketones are either absent, or present in very small quantities only. The bulk of the oil boils between 245 and 280°

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[1]) Journ. chem. Soc. **101** (1912), 1433. — Bull. Imp. Inst. **10** (1912), 298.

and contains very much *safrol.* This has the following properties: m.p. 9°; d_{15° 1,1059; $\alpha_D \pm 0$. It was characterized by its oxidation to piperonal (m.p. 37°) and by its α-nitrosite (m.p. 130 to 131°). In fraction 152 to 157° (12 mm.) Pickles found *myristicin* which he converted into dibromomyristicin dibromide (m.p. 129°) and dibromomyristicin (m. p. 52°). In order to convert the allyl group into the propenyl group, the fraction containing myristicin was heated with alcoholic potassa. The fraction was then oxidized with potassium permanganate, resulting in the formation of myristicinic aldehyde (m. p. 130°) and myristicinic acid (m. p. 212,3°), also of trimethyl gallic acid (m.p. 167 to 168°). The formation of trimethyl gallic acid indicates the presence of *iso*elemecin in the fraction treated with potassium hydroxide. It may, therefore, be assumed that the original oil contains *elemicin.* The other constituents of the oil are free *palmitic acid* (m. p. 62,5°), a phenol-like substance and a mixture of esters of low molecular fatty acids.

281. Oil of Cinnamomum Mercadoi.

According to Bacon[1]), *Cinnamomum Mercadoi,* Vid. is widely distributed in the Philippine islands. *Calingag* is the Tagaloc name of the tree. 25 kg. of the bark of a tree from the Lamao region, Bataan province, yielded after comminution 260 g. = 1,04 p. c. of a light yellow oil with an odor of sassafras; it had the following constants: $d_{4^\circ}^{30^\circ}$ 1,0461; $\alpha_{D30^\circ} + 4^\circ$; n_{D30° 1,5270. Neither bisulphite nor phenylhydrazine revealed the presence of aldehydes. Upon distillation under 10 mm. pressure the following fractions were obtained: fraction I (77 g.): b. p. 119 to 124°; n_{D30° 1,5333; fraction II (9,2 g.): b. p. 124 to 130°; n_{D30° 1,5320; residue: 11,5 g.; n_{D30° 1,5278. After distillation under ordinary pressure, fraction I had the following properties: b. p. 235 to 238° (760 mm.); $d_{4^\circ}^{30^\circ}$ 1,0631; $\alpha_{D30^\circ} + 0{,}9^\circ$; n_{D30° 1,5335. Oxidation with chromic acid yielded piperonylic acid, m. p. 227°. When heated with alcoholic potassa and subsequently oxidized with permanganate, piperonal resulted. This shows that the oil of this species of *Cinnamomum* contains much *safrol.*

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[1]) Philippine Journ. of Sc. 4 (1909), A, 114.

282. Oil of Cinnamomum pedunculatum.

The volatile oil of the stem bark of *Cinnamomum pedunculatum,* Presl. (Nees) (*C. japonicum,* Sieb.), which tree is known in Japan as *Yabunikkei,* has been examined by Keimazu and Asahina[1]). The oil which differs decidedly from ordinary cinnamon oil has the following properties: d 0,917; $[\alpha]_D$ — 280,54′ (— 4° 40′?); A. V. 0; S. V. 0; S. V. after acetylation 84,6. The oil is rich in *α-phellandrene* (m. p. of nitrite 110°). In addition, it contains a small amount of *eugenol* (m. p. of benzoyl compound 69°), also *methyl eugenol* (m. p. of veratric acid 179°).

An oil examined by Schimmel & Co.[2]), was light yellow in color and revealed the following constants: d_{15° 0,9316; α_D —14°32′; it was not completely soluble in 10 vol. of 70 p. c. alcohol, but soluble in 1,2 vol. or more of 80 p. c. alcohol. The oil contains about 6 p. c. of phenols with a cresol-like odor. The nonphenol portion contains *phellandrene* and probably *linalool.*

283. Oil of Cinnamomum Sintok.

From the stem bark of *Cinnamomum Sintok,* Blume[3]) there has been obtained by distillation a good yield of volatile oil, the odor of which reminds one of cloves and nutmeg; $d_{27,5^\circ}$ 1,008. After removal of 13 p. c. of *eugenol* (benzoyl compound) the remaining oil, which has an odor of nutmeg, boiled at 250°.

The oil of the root bark has an odor recalling more that of camphor.

284. Lawang Oil.

From the bark which is exported from Dutch East India under the name of *Lawang,* E. W. Mann[4]) obtained 0,5 p. c. of an oil the odor of which reminded one of nutmeg, sassafras and cloves, and which had the following properties: $d_{15,5}$ 1,0104; α_{D20° — 6,97°; n_{D20° 1,5095; A. V. 1,15; E. V. 4178, S. V. after acetylation 121,91; soluble in 2 vol. of 80 p. c. alcohol. When

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[1]) The Oriental Druggist 1 (1906), No. 3, Yokohama; Report of Schimmel & Co. April 1907, 28.

[2]) Report of Schimmel & Co. October 1907, 34.

[3]) Verslag 's Lands plantentuin te Buitenzorg 1895, 39. The question mark after the botanical name presumably indicates that the botanical origin of the plant has not been definitely ascertained.

[4]) Pharmaceutical Journ. 89 (1912), 145.

heated with metallic sodium, the oil reacted violently, forming a semisolid mass. Extracted with ether it yielded a substance which became blue on exposure to air. The portion insoluble in ether was readily soluble in water. Upon acidulation of the aqueous solution a white substance was precipitated which melted at 51 to 52° after recrystallization from alcohol. The nature of this substance is still unknown.

As to the botanical origin of the bark, Mann makes no definite statements. He records that, as Holmes supposes, it is probably derived from a species of *Cinnamomum* or *Litsea*. Schimmel & Co.[1]), suspected that *Cinnamomum iners,* Reinw. might be the source, since de Clercq[2]) records the Malay name *Lawang* for this plant.

This supposition, however, has not been verified by the botanical-pharmacognostical examination of the bark. Although its origin from a species of *Cinnamomum* may be regarded as established, the arrangement of the stone cells would seem to indicate some other species than *C. iners*.

285. Camphor Oil.

Campheröl. — Essence de Camphre.

Origin. The camphor laurel, *Cinnamomum Camphora,* Nees et Ebermayer *(Laurus Camphora,* L., family *Lauraceæ)* is a stately forest tree, the home of which is in southern China, Formosa and Japan.

In Formosa, which at present is the principal seat of production of camphor and camphor oil, the camphor tree does not grow in dense forests, but invariably in isolated specimens. This is more particulary true of the large trees suitable for distillation. The circumference of these, at the base, often is from 7 to 12 m. The quantity of wood which such a giant yields, suffices to supply one of the old Chinese distilleries, such as are still occasionally in operation, for several years with the necessary raw material for the production of camphor. Moreover, the operators prefer to utilize only the lower 3 or 4 m. of the trunk;

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[1]) Report of Schimmel & Co. October 1912, 77.

[2]) *Nieuw plantkundig woordenboek voor Nederlandsch-Indië.* Amsterdam 1909, p. 199.

the branches and the leaves, being less rich in camphor, are allowed to decay[1]. In accordance with recent regulations, trees less than 50 years of age may no longer be cut down. Inasmuch as the groves of wild trees have been thinned out to a considerable extent, endeavors are under way in Japan and Formosa to replace the loss by planting. Stimulated by the high camphor prices during recent years, a beginning has been made to cultivate camphor trees in all those parts of the world that seem suited to its cultivation. However, the trees are still too young to pass judgement as to the outcome. More or less detailed reports on such undertakings refer to the following countries: Ceylon[2], India[3], Farther India[4] (Annam, Burma, Assam), the Federated Malay States, Quelpart[5], East Africa[6],

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[1] Interesting details concerning the camphor industry in Formosa may be found in James W. Davidson's comprehensive treatise "The Island of Formosa", London and New York 1903, p. 397 to 443.

[2] Report of Schimmel & Co. April **1906**, 11; *Ibidem* October **1906**, 18. — Chemist and Druggist **69** (1906), 536; Report of Schimmel & Co. April **1907**, 23. — Journ. d'Agriculture tropicale **7** (1907), 58; Report of Schimmel & Co. April **1907**, 24. — J. K. Nock, Circul. and Agric. Journ. of the Roy. bot. Gardens, Ceylon, **4** (1907), No. 3; Report of Schimmel & Co. October **1907**, 25; April **1908**, 23. — Oil, Paint and Drug Reporter **74** (1908), No. 23, p. 52; Report of Schimmel & Co. April **1909**, 22. — Diplomatic and Consular Reports No. 4240, June 1909; Report of Schimmel & Co. October **1909**, 30.

[3] Report of Schimmel & Co. October **1906**, 19. — Chemist and Druggist **70** (1907), 540; Report of Schimmel & Co. October **1907**, 26.

[4] C. Crévost, Journ. d'Agriculture tropicale **6** (1906), 105; Report of Schimmel & Co. October **1906**, 20. — Nachrichten f. Handel u. Industrie **1908**, No. 45, p. 5; Report of Schimmel & Co. October **1908**, 34. — Journ. Soc. chem. Industry **26** (1907), 889; Report of Schimmel & Co. October **1907**, 26. — Journ. d'Agriculture tropicale **10** (1910), 8; Report of Schimmel & Co. April **1910**, 27. — Agricultural Bulletin of the S., and F. M. S. Aug. 1909; Report of Schimmel & Co. April **1911**, 37.

[5] Report of Schimmel & Co. April **1907**, 22. — Journ. d'Agriculture tropicale **8** (1908), 96; Report of Schimmel & Co. October **1908**, 33.

[6] Usambara-Post, Jan. 9. 1904, No. 9; Report of Schimmel & Co. October **1904**, 15. — Report of Schimmel & Co. October **1906**, 20 — Der Pflanzer **2** (1906), 333; Report of Schimmel & Co. April **1907**, 23. — Chemist and Druggist **70** (1907), 974; Report of Schimmel & Co. October **1907**, 27. — Der Pflanzer **3** (1907), 317; Report of Schimmel & Co. April **1908**, 25. — Seifenfabrikant **28** (1908), 280; Report of Schimmel & Co. October **1908**, 34. — Der Pflanzer **6** (1910), 86; Report of Schimmel & Co. October **1910**, 27. — Chemist and Druggist **79** (1911) 18; Report of Schimmel & Co. October **1911**, 27.

Algeria[1]), southern France, North America[2]) (Texas, Florida, Michigan, California), the West Indies[3]) and finally Italy[4]), the climate of which is regarded as still suitable for the cultivation of the camphor tree.

The propagation of the camphor tree is best brought about by means of seeds. It should be remembered, however, that they lose their capacity to germinate after 5 months. Propagation by means of buried branches and roots is also recommended[5]).

The formation of the oil in the several organs of the plant has been studied by A. Tschirch and Homi Shirasawa[6]), partly in connection with living, partly with dead material. According to these investigations, camphor is the product resulting from the change of a volatile oil that is formed in special cells. Such cells are to be found in all parts of the tree. They are formed very early during the development of the organs, but at first they contain no volatile oil. This is formed gradually and possesses a yellow color which it retains for a long time. Later, sometimes only years after the formation of the secretion, the yellow oil becomes colorless. It is then much more readily volatile than in the first stages. In addition it has acquired the capacity to crystallize. Frequently irregular, light crystalline masses of camphor separate. The very volatile, colorless oil, which has been formed in the oil cells, now apparently penetrates the entire body of wood. Thus the vapors also pass into the hollow spaces and fissures. Here the conditions for crystallization are particularly favorable, hence abundant deposits of

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[1]) Journ. de Pharm. et Chim. VI. **25** (1907), 182; Report of Schimmel & Co. April **1907**, 24. — Bull. Sciences pharmacol. **14** (1907), 259. — Journ. d'Agriculture tropicale **7** (1907), 335; Report of Schimmel & Co. April **1908**, 23.

[2]) Report of Schimmel & Co. October **1906**, 19. — *Ibidem* April **1907**, 20. — Oil, Paint and Drug Reporter **71** (1907), 25; Report of Schimmel & Co. October **1907**, 26. — Chemist and Druggist **72** (1908), 915; Report of Schimmel & Co. October **1908**, 34. — Journ. d'Agriculture tropicale **8** (1908), 360; Report of Schimmel & Co. April **1909**, 23. — Oil, Paint and Drug Reporter **79** (1911), No. 22, p. 41; Report of Schimmel & Co. October **1911**, 26.

[3]) West Indian Bulletin **9** (1908), 275; Report of Schimmel & Co. April **1909**, 25.

[4]) I. Giglioli, *La canfora italiana.* Rome 1908 (300 pages); Report of Schimmel & Co. October **1908**, 35.

[5]) J. K. Nock, Circult. and Agricult. Journ. of the Roy. bot. Gardens Ceylon **4** (1907), No. 3, p. 13; Report of Schimmel & Co. October **1907**, 25; April **1908**, 23.

[6]) Arch. der Pharm. **240** (1902), 257.

camphor crystals are found especially in the wood fissures. However, they have not been formed *in situ,* these formations being secondary deposits, for the actual formation of camphor takes place only in the oil cells.

The number of the oil cells depends on climatic conditions and locality. Thus the specimens of the camphor tree grown in the green-houses of the botanical garden at Bern contained decidedly less oil cells than those obtained from Java. Particularly striking was this difference in the petioles, for the leaf stalks of the camphor tree, as of all other *Lauraceæ,* are the organs richest in oil cells.

In the older trees camphor occurs in crystalline condition in the crevices of the trunk. Principally, however, it occurs dissolved in a volatile oil that permeates all parts of the plant. This oil occurs most abundantly in the underground roots, less abundantly in the trunk, and still less so in the branches, twigs and leaves. Moreover, the camphor oil content varies with the height in the tree, diminishing upwards. The older the trees and the firmer their wood, the higher the camphor content.

The proportion of solid camphor and camphor oil appears to vary with the age of the tree, the season of the year and the temperature. Young trees yield upon distillation more camphor oil and less camphor. The same is true with higher temperature, the yield of oil in summer being greater than in winter. At summer temperature, moreover, more camphor is dissolved in the oil than in winter time.

The amount of oil contained in the several parts of the plant have been determined by Professor Moriya[1]) of the College of Agriculture of the Imperial University.

Twigs	2,21 p.c.
Branches	3,70 „
Upper part of the stem	3,84 „
Lower part of the stem	4,23 „
Upper part of the stump	5,49 „
Lower part of the stump	5,74 „
Root	4,46 „ [2])

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[1]) J. W. Davidson, The Island of Formosa. London and New York 1903, 425.

[2]) Schimmel & Co. determined the oil content of the root at 4 p.c. Report of Schimmel & Co. October 1892, 11.

Hence the average is 4,22 p.c. These data reveal the fact that the lower portions of the tree are richer in oil than the upper portions. In addition it was ascertained that in winter the tree yields more camphor, in summer more oil.

With regard to the yield from the leaves, omitted in the above tabulation, a large number of data have been recorded which vary between 0,23 and 3 p.c. However, they are not directly comparable since some of them refer to the amount of camphor that had been separated in a variety of ways, others to the amount of oil. Hence they are not recorded in detail.

Upon the distillation of dried leaves, Schimmel & Co.[1]) obtained a yield of 1,8 p.c. The oil consisted of a liquid permeated with camphor crystals. D. Hooper[2]) reports a yield of 1 p.c. from fresh leaves .from the Government gardens at Ootakamund, India. V. Lommel[3]) distilled comminuted fresh leaves and twigs on a larger scale and obtained 1,2 p.c. of an oil rich in camphor.

Later, the same author[4]) contributed an interesting communication on the distillation of dried camphor leaves. He reports first on the distillation of leaves that had been obtained from a small cinchona grove, shortly before the rainy season. They had been spread out to dry but were not dried completely. The yield of camphor was so small that the percentage was not even calculated. Indeed the experiment was regarded as a failure.

For a second experiment the dry leaves that had accumulated on the ground between the hedges of a plantation were used. Their distillation yielded 0,06 p.c. of a crude camphor and 0,19 p.c. of camphor oil. Hence long lying on the ground with alternation of rain and sunshine had caused them to lose almost all of their volatile substance.

Finally, a young plantation was trimmed moderately, the fresh leaves were dried on the cleaned ground under the shade of cultivated cinchona trees. After 14 days the leaves had dried

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[1]) Report of Schimmel & Co. October 1892, 11.

[2]) Pharmaceutical Journ. 56 (1896), 21.

[3]) Der Pflanzer 6 (1910), 86; Report of Schimmel & Co. October 1910, 27.

[4]) Der Pflanzer 7 (1911), 441.

to such an extent that they could be stripped from the twigs without difficulty. They were packed in sacks and shipped to the place of distillation. This experiment yielded favorable results. The yield amounted to 1,55 p.c. of crude camphor and 0,49 p.c. camphor oil. It might have been larger, but for the fact that the condensation water at one time during the distillation became hot, thus allowing an appreciable amount of camphor to be lost.

Inasmuch as past experience seems to indicate that the trees may be trimmed twice annually, an annual crop of 9354 kg. of dried leaves per hectare may be expected from a 5 year old plantation. This would correspond to about 145 kg. of camphor and about 46 kg. of camphor oil.

In Jamaica experiments have also been made in the distillation of camphor leaves. H. W. Emerson and E. R. Weidlein[1]) found that the production of oil from the leaves may be carried on to advantage. 56,940 kg. of green leaves yielded 1353,8 gr. = 2,35 p.c. of distillate (1,32 p.c. of camphor, 0,54 p.c. of camphor oil and 0,49 p. c. of water). From 67 kg. of dried leaves they obtained 1719,5 gr. = 2,54 p.c. of distillate consisting of 1,57 p.c. of camphor, 0,46 p.c. of camphor oil and 0,51 p.c. of water. The green twigs yielded 0,58 p.c. camphor and 0,26 p.c. of camphor oil; the dried twigs contained 0,54 p.c. of camphor and the wood yielded upon distillation 0,61 p.c. of camphor.

Fairly extensive experiments on the production of camphor in the Federated Malay States have been described by B. J. Eaton[2]) in which he principally used leaves.

The cultivation of camphor trees in the Malay States was begun in 1904 in Batu-Tiga, Selangor. For this purpose the seeds had been obtained from Yokohama. The plants flourished and in 1909 the first camphor was distilled. The distillation material consisted of the shoots of five year old trees. The results of the experiment are shown in the following table:—

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[1]) Journ. Ind. Eng. Chem. 4 (1912), 33; Journ. Soc. chem. Industry 31 (1912), 149.

[2]) Camphor from *Cinnamomum Camphora* (The Japanese camphor tree), cultivation and preparation in the Federated Malay States. Department of Agriculture. Bulletin No. 15. February 1912.

Material	Yield computed with reference to fresh material.
Cut leaves, green	1,17 to 1,22 p.c.
Small stems, green	0,06 „ 0,45 „
Mouldy leaves	1,25 „ 1,47 „
Fresh leaves and stems	1,25 „ 1,58 „
Air-dried leaves	1,10 „ 1,16 „
„ „ mouldy leaves	1,54 „

In all cases the distillate consisted of camphor with very little oil.

The experiments were repeated on a larger scale with a larger apparatus. As material for distillation the parts of an entire 5 year old tree were used.

Material	Yield in p.c.
Leaves	1,00
Stems less than 1,3 cm. in diameter	0,22
„ more „ 1,3 „ „ „	0,61
Roots	1,10

In the main the distillate consisted of camphor, the roots, however, yielded an oil that had a mixed odor of camphor and lemons. Later, numerous further experiments were conducted, partly with modified apparatus. All of these have been accurately described by Eaton, who gave several illustrations of the apparatus.

In Java also leaves have been distilled on an experimental scale[1]). From 3560 kg. of fresh leaves 31,15 kg. of camphor and 14,1 liters of oil were obtained. 376 kg. of branches (presumably without leaves) yielded but a trace of oil. The vapors were passed into a box of galvanized iron, inside of which 3 cylindrical condensers, filled with water, were placed. In addition, the bottom and sides were flooded with water to effect better condensation. The bottom of the box was provided with a stopcock for drawing the water off. The distillation being concluded, the condensers were withdrawn from the box and the distilled camphor collected.

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[1]) A. W. K. de Jong, Teysmannia, Batavia 1912, No. 2, p. 125; Report of Schimmel & Co. October 1912, 29.

In order to give a clearer idea, the results of the principal experiments for the production of camphor are tabulated below.

Distillation conducted		Material	Yield in p.c.	Properties of the distillate
in	by			
Leipzig	Schimmel & Co.	dry leaves	1,8	—
Ceylon	Willis and Bamber	leaves and small stems	1,0	—
India	Hooper	—	1	The distillate contained from 10 to 75 p.c. of camphor
German East Africa	Lommel	branches and twigs	0,06 to 1,5	Camphor and oil
		shoots	0,22	
		dry leaves	1,55	Camphor
			0,49	Oil
Jamaica	Duncan	wood	0,61	Crude camphor
		branches	0,05	
		green leaves	2,37	
		dry leaves	2,52	
		dead leaves	1,39	
Jamaica	Emerson and Weidlein	green leaves	1,32	Camphor
			0,54	Oil
		dry leaves	1,57	Camphor
			0,46	Oil
		green branches	0,58	Camphor
			0,26	Oil
		dry branches	0,54	Camphor
		wood	0,61	Camphor
West Indies	Watts and Tempany	wood	0,5	Camphor and oil
		leaves and branches	0,5	
		leaves and branches	0,7	
Italy	Giglioli	green leaves	1,2 to 1,5	Camphor
		dry leaves	2,4 to 3,0	
		branches	0,02 to 0,25	
North America	Hood and True	fallen leaves	2	Camphor and oil
		trees grown in shady places	0,7	
		trees grown in poor soil in shady places	2,77	
Malay States	Eaton	green leaves	1,17 to 1,22	Camphor and very little oil
		thin green stems	0,06 to 0,45	
		mouldy leaves	1,25 to 1,47	
		fresh leaves and stems	1,25 to 1,58	
		air-dried leaves	1,10 to 1,16	

The oil from the leaves appears to differ in composition from the oils obtained from other parts of the tree. At all events the absence of safrol in the leaf oil has been definitely proved several times[1]. An oil distilled in Amani from leaves and twigs (yield 1 to 1,3 p. c.) contained appreciable amounts of camphor but no safrol[2]. Whether this technically important substance is always absent in the leaf oil, further investigations will have to demonstrate.

Production. At the present time by far the largest percentage of camphor and camphor oil is produced in Formosa. Japan occupies the second position, China the third. Whereas in times of high camphor prices China produced considerable quantities, it now either consumes its own product or, at most, exports some of it to India, and hence does not come into consideration so far as the European and American markets are concerned.

In Japan the production of camphor stands on a higher plane technically than the former industry in Formosa or in China to-day. The method is described in a most comprehensive manner by Grassmann[3].

On the slope of a hill near a supply of water a sufficient area is levelled. On this a stove is erected with crude stones having a height of about 1 m. and an inner diameter of 0,70 m. The opening for the fuel supply is rather small, 0,40 × 0,30 m., and is covered with a roof. On this roof the distilled chips (fig. 39, *b*) are dried to be used later as fuel. A shallow pan provided with a strong, perforated wooden cover is placed on top of the stove (fig. 40, *b*) and over this a barrel or tub. This has the shape of a truncated cone (fig. 39, *c*) and is 1,15 m. high: the upper diameter being 0,30 m., the lower 0,87 m. The cover of the pan fits as a bottom to the tub. On one side, just over the cover of the pan there is a rectangular opening in the tub, 0,30 m. high and 0,25 m. wide (fig. 40, *e*). The head-piece of the barrel or tub consists of a removable, well fitting cover provided with an opening that can be closed by a plug. The tub is coated with a layer of clay 0,15 m. thick and held together by a net work

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[1] Comp. *e.g.* Report of Schimmel & Co. October 1906, 21.

[2] Observation made in the laboratory of Schimmel & Co.

[3] D. E. Grassmann, *Der Campherbaum.* Mitteilungen der Deutschen Gesellschaft für Natur- u. Völkerkunde Ostasiens, Tokio, 6 (1895), 277 to 328.

of bamboo. Near the top a bamboo tube *(f)* 2 m. long is carefully inserted air-tight and connected with a condenser further up on the slope. This condenser, in its simplest form (fig. 41), consists of two boxes, one placed within the other, of which the upper one serves for the condensation of the camphor and the lower receptacle for the cooling water. The upper box is 1,60 m. long, 0,90 m. wide and 0,42 m. high. Its inverted bottom is covered with water, the sides projecting 10—12 cm. over the bottom. The camphor vapors enter the box over the surface of the water. To pass them through the water has not proved successful. By means of partitions, 18,5 cm. apart, the condenser is divided into sections. These partitions are each provided with a rectangular opening at the top, one in the right, the next in the left corner, and so forth, so that the camphor vapors must pursue a circuitous path. From the last chamber the vapors can pass out through a bamboo tube loosely plugged with straw. A lateral tube allows the water to flow from the bottom (= cover) of the upper box into the lower receptacle. The upper box inverted with its opening downward is placed into the lower box which is somewhat longer and wider but not so high, so that the water in the latter rises to about one-half of the height of the former on all sides. A lateral exit tube allows the excess of water to flow out. In order to avoid a rapid heating of the

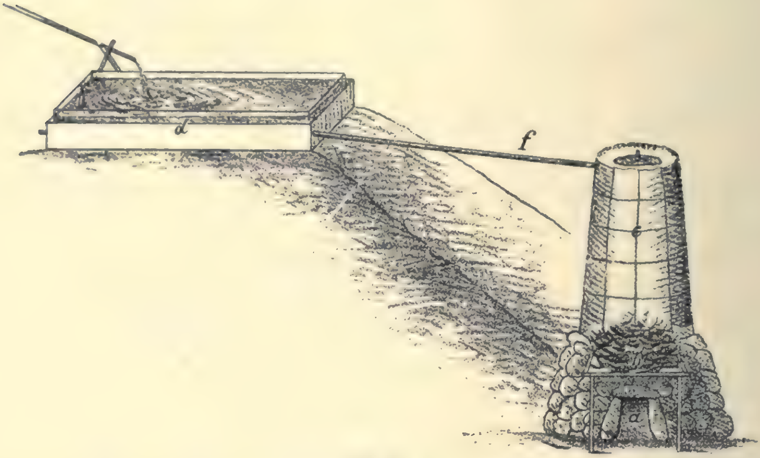

Fig. 39.

water in the condenser, this is protected by a light roof made of boards.

Frequently a third small box, 0,80 m. long, 0,54 m. broad and 0,25 m. high is placed on top of the upper one. This box is also open on the lower side, standing in water 10 cm. deep. The sides likewise project over the top so that a layer of water 5 cm. high remains on it. The vapors from the last chamber (fig. 40, *h*) of the large condenser pass through a tube (fig. 40, *k*) into this smaller box where more camphor is condensed. This upper condenser is provided with a small exit tube for the vapors.

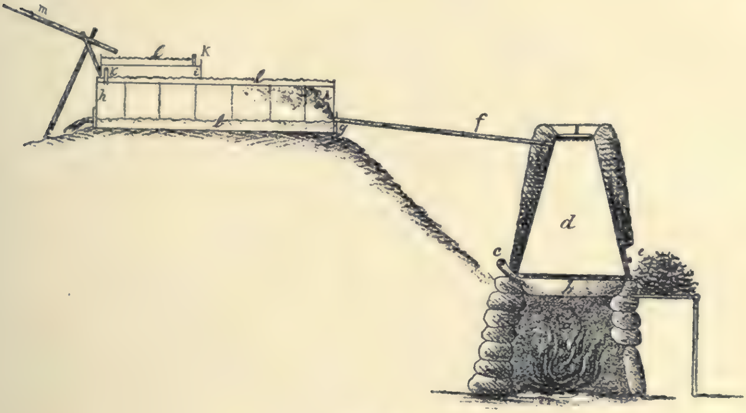

Fig. 40.

The following utensils are used in connection with this apparatus: a wooden shovel of the shape of a spoon-oar for shovelling the distilled chips into the fire place; also an iron poker. In order to protect the stove and tub, a roof of straw and reed is constructed, also a screen of straw matting to the windward (valley) to protect against draught and rain.

The production of camphor is conducted as follows. After the pan has been filled with water, the chips are introduced through the upper opening into the tub, and all cracks and crevices carefully luted, so that the vapors cannot escape. Only a moderate fire is maintained. In the course of the distillation the pan is frequently refilled with water through the tube *c* (fig. 40). The vapors pass through the perforation into the tub (fig. 40, *d*) and convey the camphor vapors from the heated chips through the bamboo tube (fig. 40*f*) into the condenser where they are deposited. In the early part of the distillation, camphor oil only is found in the condenser, later, also solid camphor. Most of the camphor condenses behind the 3rd, 4th and 5th partition of the seven-part condenser. The tub holds 112,5 kg. of chips, a quantity that can be distilled in 24 hours. The exhausted chips are removed from the lateral opening (fig. 40*e*). Every week the condenser is opened; and the camphor and the camphor oil contained therein, removed.

On the surface of the water in the condenser there collects a granular crystalline mass resembling a mixture of snow and ice, which at least in the first chambers is mixed with camphor oil and is colored yellow. On the walls of the condensing chambers not standing under water and on the cover of the box pure, white crystalline camphor is deposited. The yellowish or brownish-black camphor oil floats on the surface, where it mixes with the granular camphor.

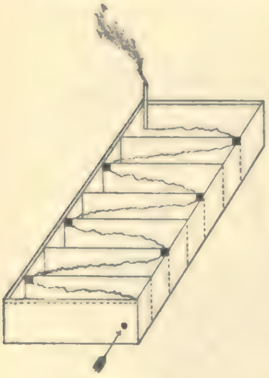
Fig. 41.

This type of distilling apparatus appears to have given satisfaction under the conditions under which it is used. At all events it is much better than the old Chinese equipment which was formerly universally in use in Formosa and which, since the Japanese occupation of the island, is disappearing more and more, being displaced by Japanese apparatus. The accompanying description of the Chinese plant, also the illustration (fig. 42) are taken from the book by Davidson[1]) already referred to.

A rough shed is constructed to cover the plant, which, if of the usual capacity of ten stills, measures about 2,1 × 3 m. Such an equipment is termed "stove." The ground is beaten down, so as to afford a firm foundation. Four planks are now formed into a bottomless box-like frame 18 inches high. This frame is filled with earth which is stamped down hard and allowed to dry and form what might be called the foundation

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[1]) Comp. footnote 1 on p. 448.

of the stove. Ten round holes (A fig. 42), less than a foot apart, are now cut out on each side of this base, each shaped so as to support a circular iron pan (B) 38 cm. in diameter which is intended to hold water. There is no chimney. The smoke is expected to find its way out through the opening through which the wood used as fuel is introduced. After the pan has been covered with a perforated board, a cylinder (C), or rather a truncated cone made of staves and known as a "still" is fastened to this base by means of a mud paste. This still is 0,5 m. high, its lower diameter is 0,3 m., the upper diameter 0,17 m. Two large planks are now placed lengthwise of the structure reaching as high as the retorts. The place thus enclosed is packed full of earth and pounded down hard, thus preventing the retorts from being cooled. Above the retorts are placed inverted earthenware pots (D), 0,43 m. high and 0,35 m. in diameter, in which the camphor collects. This completes the outfit.

Fig. 42.

Chinese still, such as was formerly used in Formosa.

As a rule a man and his family attend to such a still. Both morning and at noon he goes into the forest with basket and axe for the purpose of getting camphor chips from a special tree, which is generally not further than 1,5 km. from the still. After three hours he returns with about 36 kg. of chips 7 to 10 cm. long. Before putting them into the still they are comminuted still farther. This is usually done with a wooden club serrated on the side used. A single charge consists of 5,5 to 6 kg. of chips.

After the pans have been filled with water, the fires are lit, and are allowed to burn slowly during the entire night. The next morning the chips are taken out, the lower half thrown away and the upper half, together with a sufficient quantity of new chips, put into each retort, the partly exhausted chips being placed at the bottom. Twice daily the charge is changed. The water vapors which pass slowly through the chips carry with them the camphor vapors which condense in the earthenware pots. After 10 days the pots are taken off and the camphor, which has sublimed to a snow-white mass, is removed. The amount of camphor that has accumulated in each pot varies between 2,5 and 4 kg.

As becomes apparent from the above account, the process is one of sublimation with water vapor rather than one of distillation proper, for according to this method no camphor *oil* whatever is obtained. Nevertheless a certain amount of oil is admixed with the crude camphor. In the "tubes", a sort of cask, in which the crude camphor is packed for shipment across the ocean, the crude oil settles to the bottom and imparts to the lower layer of camphor a dirty, pasty appearance.

From the interior both camphor and camphor oil, the latter from the newer Japanese distillation equipments, are carried by coolies in bags, boxes and tin cans to one of the six camphor offices¹). Those of Formosa are located in Taipeh, Teckcham (Shinchiku), Maoli (Bioritsu), Taichu, Linkipo, and Lotong (Rato).

The production of camphor in Formosa is associated with great danger and considerable difficulties. The savage natives

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¹) Report of Schimmel & Co., October 1900, 10.

of the interior are still in possession of the camphor forests and regard the camphor workers as their mortal enemies. Wherever possible they attack the workmen, decapitate them and carry home the heads as trophies. The unhealthy climate and the impenetrability of the forests are the best aids of these head hunters in their battles against the Japanese. As a result, the progress of the latter into the interior is but slow[1]).

Composition. Camphor oil is an exceedingly complicated mixture of hydrocarbons and of oxygenated constituents which belong to very different chemical types. The aldehydes are represented by acetaldehyde, the ketones by camphor and menthenone, the alcohols by terpinenol, terpineol, borneol and citronellol, the phenols and phenol ethers by eugenol, carvacrol and safrol, the oxides by cineol, the terpenes by pinene, camphene, fenchene, phellandrene, dipentene and limonene, the sesquiterpenes by bisabolene and cadinene, the acids by caprylic acid.

Arranged according to their boiling points, the constituents are as follows: —

1. *Acetaldehyde.* This substance, which is probably never entirely absent in volatile oils, always becomes noticeable whenever large amounts of oil are rectified. In part it is lost with the first aqueous distillate, but is also found dissolved in the first terpene fraction.

2. d-*α-Pinene* was found in the fraction boiling below 160° (nitrosochloride; m. p. of nitrosopinene 130°[2]); of nitrol benzylamine 124°[3])).

Yoshida[4]) obtained from the oil a strongly lævogyrate fraction $[\alpha]_j - 71,1°$, with the properties of *l*-*α*-pinene (chlorhydrate; nitrosochloride; nitrosopinene). Inasmuch as the lowest fractions of the oil are always dextrogyrate, the lævorotation observed

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[1]) A detailed account of the stirring history of the camphor industry in Formosa would lead too far. Suffice it here to refer to the interesting account given by Adolf Fischer in his book *Streifzüge durch Formosa*, Berlin 1900, also to the even more comprehensive work of Davidson. Both supply numerous details about camphor and camphor production.

[2]) Schimmel's Bericht April **1889**, 8.

[3]) Report of Schimmel & Co., October **1903**, 16.

[4]) Journ. chem. Soc. **47** (1885), 779; Berl. Berichte **18** (1885), 550, abstracts.

by Yoshida is noteworthy and gives rise to the suspicion that his oil was not a normal distillate.

3. *Camphene.* The occurrence of this terpene was first pointed out by J. Bertram and H. Walbaum[1]). However, they did not at first succeed in establishing its identity beyond question. This was accomplished later by the preparation of *iso*borneol (m. p. 210°; m. p. of camphene 50°; of camphor 176°; of camphoroxime 118°)[2]).

4. d-*Fenchene* (*iso*fenchyl alcohol oxidized to *iso*fenchone; m. p. of semicarbazone 220 to 222°)[3]).

5. β-*Pinene* (nopinic acid; nopinone, m. p. of semicarbazone 187 to 189°)[3]).

6. *Phellandrene*[4]) is present in such small quantities that its identification as nitrite, m. p. 102°, offered difficulties.

7. *Cineol* constitutes 5 to 6 p.c. of camphor oil. It was at first isolated and identified by means of the hydrobromide[5]), later by means of the iodol compound[6]).

8. *Dipentene* was found by Wallach[7]) (m. p. of tetrabromide 123°; of nitrolpiperidine 150 to 152°)[8]). An impure dipentene dihydrochloride, melting at 42° instead of 49°, had already been obtained by A. Lallemand[9]) by passing hydrogen chloride into the fraction boiling at 180°.

9. d-*Limonene* (m. p. of β-limonene nitrolpiperidine 110 to 111°)[10]).

10. *Borneol* (m. p. 203°; acid phthalate; m. p. of camphor 176°; of semicarbazone 236°; of oxime 118 to 119°)[11]).

11. *Camphor,* technically the most important constituent of the oil, separates in large quantity as soon as, in the course of the distillation, the thermometer has risen to 200°.

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[1]) Journ. f. prakt. Chem. II. **49** (1894), 19.

[2]) Report of Schimmel & Co. October **1903**, 17.

[3]) Observation made in the laboratory of Schimmel & Co.

[4]) Schimmel's Bericht April **1889**, 8.

[5]) *Ibidem* Oktober **1888**, 8.

[6]) Report of Schimmel & Co. Oktober **1903**, 17.

[7]) Liebig's Annalen **227** (1885), 296.

[8]) Report of Schimmel & Co. April **1908**, 25.

[9]) Liebig's Annalen **114** (1860), 196.

[10]) Report of Schimmel & Co. April **1908**, 25.

[11]) *Ibidem* April **1904**, 17.

12. *Terpinenol-1* (m. p. of terpinene dihydrochloride 50 to 52°; of glycerol 113 to 115°; Δ^1-menthenone-3, m.p. of semicarbazone 224 to 225°)[1]).

13. *α-Terpineol* (m.p. 35°; of phenyl urethane 112°; of nitrol piperidine 158 to 159°)[2]).

14. *Citronellol* (b.p. 225 to 227°; acid phthalate; oxidation to citronellal; m.p. of naphthocinchoninic acid 225°)[1]).

15. *Safrol.* Next to camphor this is the most important constituent of camphor oil. It was found in 1885 by J. Bertram in the laboratory of Schimmel & Co. and since then has been produced by this firm on a large scale[3]).

16. *Δ^1-Menthenone-3* (m.p. of semicarbazone 224 to 226°; of oxaminooxime 166°)[1]). The same substance has been found by Schimmel & Co.[4]) in Japanese peppermint oil.

17. *Carvacrol.* When the oil is shaken with a solution of sodium hydroxide, there is obtained, in addition to the acids referred to below, a mixture of several phenols, one of which is carvacrol (m. p. of phenylurethane 136°). In addition, there is present a second phenol with a somewhat higher boiling point, the phenylurethane of which melts between 85 and 95°[5]).

18. *Cuminic alcohol.* When the higher boiling fractions of camphor oil are heated with phthalic acid anhydride and the resulting compound is saponified, an alcohol is obtained (b.p. 240 to 248°; d_{15° 0,9634; n_{D20° 1,49038) which has the odor of cuminic alcohol. That the substance in question is in reality cuminic alcohol was demonstrated by its oxidation to cuminic aldehyde by means of chromic acid and glacial acetic acid. The aldehyde thus obtained yielded a semicarbazone melting at 210 to 212°. Upon oxidation with silver oxide cuminic acid melting at 111 to 113° resulted[1]).

19. *Eugenol* is the oldest of the known phenols in camphor oil. It was discovered in 1886[6]).

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[1]) Observation made in the laboratory of Schimmel & Co.

[2]) Schimmel's Bericht April 1888, 9; April 1889, 8; Report of Schimmel & Co. October 1903, 15.

[3]) Schimmel's Bericht September 1885, 7.

[4]) Report of Schimmel & Co. October 1910, 97.

[5]) *Ibidem* October 1902, 21.

[6]) Schimmel's Bericht April 1886, 5.

20. *Bisabolene.* The trichlorhydrate of this sesquiterpene, which melted at 79 to 80°, is obtained by saturating fraction 97 to 116° (5 to 6 mm.) with hydrogen chloride after it has been deprived of its phenols[1]).

21. *Cadinene.* By passing hydrogen chloride into fraction 260 to 270° a good yield of cadinene dichlorhydrate, melting at 117°, has been obtained[2]).

22. *Caprylic acid.* During an examination of the phenols found in camphor oil, small amounts of acids of the fatty series were isolated. Among these caprylic acid (congealing point $+15°$; b.p. 113 to 114° under 4 mm. pressure; analysis of calcium and silver salts)[3]) was identified.

23. *The acid* $C_9H_{16}O_2$ can be separated from caprylic acid by means of its calcium salt. It boils at 114 to 115° (4 mm.), is liquid at ordinary temperature and apparently belongs to the olefinic acid series[3]).

24. *Blue oil.* The last fraction that comes over between 280 and 300° (142 to 155° at 6 mm.; sp.gr. 0,95 to 0,96; $\alpha_D + 32°$) consists in the main of a substance alcoholic in character[4]). When heated with acetic acid anhydride the resulting product has a fairly high ester value. When heated with concentrated formic acid, the alcohol loses water and yields a hydrocarbon ($d_{15°}$ about 0,918; α_D about $-22°$; $n_{D20°}$ about 1,512) which boils principally between 265 and 268°. It adds hydrogen chloride, however, without yielding a solid derivative[4]).

A few words should be said about the so-called camphorogenol, which boils between 212 and 213° and to which the formula $C_{10}H_{18}O_2$ has been assigned. According to Yoshida[5]), it polymerizes when heated for a prolonged time, at the same time separating camphor. When acted on by dilute nitric acid, acetic acid anhydride or benzoic acid, it is said to yield camphor, and when heated with sodium and alcohol to be converted into borneol.

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[1]) Report of Schimmel & Co. October 1909, 31.

[2]) Schimmel's Bericht April 1889, 9.

[3]) Report of Schimmel & Co. October 1902, 22.

[4]) *Ibidem* October 1902, 18.

[5]) Footnote 4 on p. 461.

As a matter of fact, no substance with these properties occurs in camphor oil. "Camphorogenol" is nothing more than a fraction consisting principally of camphor and terpineol and behaving toward reagents as "camphorogenol" is reported to behave[1]). When boiled, a portion of the terpineol decomposes into terpenes and water and the camphor, which is less soluble in the terpenes, crystallizes out in part. If the terpineol is removed by oxidation with nitric acid the camphor, which is not readily attacked, remains behind. Sodium reduces the camphor, already present, to borneol.

Properties. Normal camphor oil, *i.e.* an oil with all of its constituents such as is produced upon the distillation of camphor wood, constitutes a soft mass, or is a liquid more or less permeated with camphor. As a rule, however, the designation camphor oil is applied to the oil that results after the removal of the camphor by filtration and pressure. Such a product was placed upon the market about the middle of the eighties. It contained considerable quantities of camphor in solution, which could be separated by fractionation and cooling. At the present time these operations are carried on in Japan, for the oil now exported is almost free from camphor.

Camphor oil is classed in three kinds which differ materially from each other in their composition. Their valuation is based on specific gravity.

1. *Crude camphor oil*[2]). This is the oil that remains after the removal of the crystallized camphor. It is a light yellow to brownish-yellow liquid. Sp. gr. 0,95 to 0,995. It is fractionated in Japan and resolved into white oil, red oil and camphor.

2. *White camphor oil.* It consists of the lowest boiling portions and is composed almost entirely of terpenes and small quantities of cineol. d_{15° 0,87 to 0,91.

3. *Red* or *black camphor oil.* It is the portion of the oil which boils higher than camphor and contains safrol, phenols and sesquiterpenes. d_{15° mostly between 1,000 and 1,035.

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[1]) Schimmel's Bericht April 1888, 9.

[2]) Nakazo Sugiyama, Journ. pharm. Soc. of Japan 1902, No. 242; Report of Schimmel & Co. October 1902, 17.

The normal oil as well as the several fractions are dextrogyrate. All fractions have the odor of camphor, but in the so-called black oil it is greatly obscured by that of safrol.

In Europe and North America the oils 2 and 3 are further fractionated, safrol being obtained as principal product. The resulting by-products enter commerce as *light* (low boiling), *heavy* (high boiling) and *blue* (highest boiling fraction) *camphor oil.*

The properties of these oils vary according to the nature of the raw material and the method of production.

The *light camphor oil* is used as a substitute for turpentine oil in the manufacture of varnishes, also in printing establishments for cleaning types, electroplates and cylinders. Its specific gravity varies between 0,86 and 0,900. The boiling point varies between 175 and 200° and above. The flash point fluctuates between 45 and 60°, being somewhat higher than that of turpentine oil.

Heavy camphor oil is also used in the varnish industry; for perfuming cheap soaps, more particularly soft soap, shoe polish, and hoof ointment, also for the purpose of hiding the odor of mineral oils, wagon-grease and lubricating oils. d_{15° about 0,95; boiling temperature about 270 to 300°.

Blue camphor oil serves similar purposes as the preceding one. d_{15° about 0,95 to 0,96; boiling temperature about 300°.

As to the properties of *camphor leaf oil* mentioned on p. 451, an oil distilled by Schimmel & Co.[1]), from dry leaves was completely permeated by camphor at ordinary temperature. It boiled between 170 and 270°. Two oils distilled in India from fresh leaves by D. Hooper[2]) showed the following properties: 1. d_{15° 0,9322; $\alpha_D + 4° 32'$; camphor content 10 to 15 p.c. 2. d 0,9314; $\alpha_D + 27°$; camphor content 75 p.c. Two oils distilled in Amani, likewise from fresh leaves, were examined by Schimmel & Co.[3]). They had the following properties: 1. d_{15° 0,9236; $\alpha_D + 39° 20'$. The oil corresponded to the filtrate

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[1]) Report of Schimmel & Co. October 1892, 11.

[2]) Pharmaceutical Journ. 56 (1896), 21.

[3]) Report of Schimmel & Co. October 1906, 20; October 1910, 28.

from the camphor which separates spontaneously from the original oil. It contained no safrol. Camphor content, as determined by distillation (see below) 75 p. c. 2. d_{15° 0,9203; $\alpha_D + 39^\circ 42'$.

An oil distilled from *camphor roots*[1]) was solid at ordinary temperature because of the separated camphor. When completely liquified (at 45°) d_{45° 0,957.

Determination of Camphor in Camphor Oil. No method is known whereby an exact determination of the amount of camphor in a volatile oil can be made[2]). Hence one is dependent on technical methods which are modifications of the process by which camphor is obtained on a large scale. They are based on the direct isolation of camphor by fractional distillation. The results may vary more or less, according to the greater or lesser perfection of the fractionation apparatus. Nevertheless the method described by H. Löhr[3]) may be looked upon as sufficiently accurate for technical purposes.

At least 300 g. of the oil to be examined are used. If the oil is rich in camphor it is first placed in a freezing mixture and the crystallized camphor separated and treated as directed below. The oil is then distilled and the distillate collected in three fractions, *viz.* up to 195°, 195 to 220° and above 220°. The first and third fractions contain no camphor. The second is thoroughly cooled in a freezing mixture for an hour, when the separated camphor is filtered off with the aid of a suction pump. In order to remove the adhering oil more completely, the camphor is packed in a straining cloth which is placed between filter paper under a press for half an hour. The cake is then placed between fresh filter paper and pressed for another quarter of an hour. Finally the camphor is separated and weighed. The oil which results after the camphor has been frozen out and filtered off, is again subjected to fractional distillation, fraction 205 to 220° is again separated and subjected to the same treat-

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[1]) Report of Schimmel & Co. October 1892, 11. — See also p. 450.

[2]) The spectroscopic method proposed by Hartley (Journ. chem. Soc. 93 [1908], 961; Report of Schimmel & Co. October 1908, 39) possesses theoretical interest only at present.

[3]) Chem. Ztg. 25 (1901), 292.

ment as before. However, pressure is applied but once and then only for twenty minutes. For the complete isolation of the camphor, five distillations are necessary. Each time fraction 205 to 220° is collected separately and treated for camphor as described above.

Production and Commerce. Up to the middle of the nineties of the past century, Japan was almost the only country that supplied the world's market with camphor and camphor oil. These articles were supplied principally by the Riukiu Islands between Formosa and Japan, also the islands Kiushiu, Tsushima and Shikoku. On the main island Honshiu (Hondo) the districts Totomi, Suruga, Idzu and Kii[1]) are principally concerned. When, after the Japanese-Chinese war, the Chinese island of Formosa (Taiwan) became a Japanese possession, it was one of the first endeavors of the new government to provide a systematic exploration of the rich camphor forests. In order to cover the great expenses caused by this action and in view also of the increasing demand for the product, the Government declared the production of camphor a state monopoly. This took effect in Japan proper in 1899, in Formosa in 1903. For the superintendence of the production a series of so-called camphor offices were established: for Japan proper in Nagasaki, Kobe, Kagoshima, Kumamoto, Fukuoka; for Formosa in Taipeh, Shiuchiku, Bioritsu, Taichu and Bato. The producers are compelled to deliver their entire output to the camphor offices at a fixed price. These in turn sell the crude camphor to refineries either at home or abroad. They also dispose of the oil after first having extracted the camphor. This oil is sold either crude or fractionated. Up to 1909 the English firm of Samuel, Samuel & Co. was entrusted with the sale of the products of the monoply; after that, the Japanese firm Mitsui & Co. Up to the middle of the first decade of the present century the market price of camphor had been driven up to three times its normal value by the management of the monopoly. This was the cause of the opening up of a series of new sources. First of all, the chemical industry took up the synthesis of camphor. This had been accomplished in a technically satisfactory manner

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[1]) Comp. the accompanying map.


125°
130°
120°
CHINA
40°
Tamsui
Keelung
25°
Shinchiku
TAIWAN
(FORMOSA)
Tropic of Cancer
Kagi
Tainan
Takao
120°
CHINA
Sea
Japa
CORE A
35°
Oki
Shima
H
O
Tsu-
Shima
Corea
Str.
Shimonoseki
Fukuoka
Kanazawa
Goto-
Shima
Nagato
Iwami
Izumo
Hoki
Inaba
Suwo
Aki
Bingo
Bitschiu
Mima
saka
Taji
ma
Tango
Wakasa
Kaga
Echizen
Chiku
Hizen
Buzen
Bizen
Harima
Tamba
Nagasaki
Chikugo
Kumamoto
Bungo
Higo
Hiuga
Ivo
Sanuki
Tokushima
Kobe
Awaji
Osaka
Bizen
Izumi
Kawachi
Yamashiro
Omi
Iga
Mino
Owari
Awa
Tosa
Wakayama
Jamato
Ise
Nagoya
Mikawa
Kagoshima
Satsuma
Osumi
Kii
Shima
SCHIKOKU
KIUSCHIU
30°
Tanega-
Shima
Jaku-Sh.
Pacif
135°

Production of Camphor 🟥
and Peppermint 🟨
in Japan (1912).

Scale 1 : 10000000

and, with the high prices demanded, promised to be successful commercially. After that, other natural sources were looked for, particularly in China, where the southern provinces Fokien, Tshekiang, Kwangtung, Kwangsi, Kiangsi, Szetshwan, Hupeh and Hunan contributed fairly considerable quantities of camphor to the market. With the lowering of the world's market price, however, these sources again disappeared.

Owing to the importance of both articles to the several branches of industry, the statistical material covering the production and export of camphor and camphor oil is considerable. However, there are contradictions between the official data supplied by the Japanese, who evidently have no desire to show their hand, and the reports of various European representatives (consuls and experts). In the following tables there will be found the principal data concerning production and export of both articles from the several districts of production.

PRODUCTION OF CAMPHOR.

Japan proper (excl. of Formosa)		From oil (in Kobe).	
1900	2190175 lbs.[1]	—	
1901	2669272 „	1635257 lbs.[1]	
1902	3396908 „	1513795 „	
1903	2948585 „	1613851 „	
1904	900000 „	1979137 „	
1905	1226607 „		
1906	687300 kg.[2]		
1907	733537 „	9156 Piculs[3]	7000 Piculs[4]
1908	951454 „	12009 „	8000 „
1909	1354455 Kin with a value of 798489 Yen[5]	11504 „	8000 „
1910			10000 „
1911			11000 „

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[1] Zeitschr. f. angew. Chem. **19** (1906), 261; Report of Schimmel & Co. April **1906**, 13.

[2] Nachrichten f. Handel u. Industrie **1910**, No. 28; Report of Schimmel & Co. April **1910**, 22.

[3] Deutsches Hand. Arch. February **1911**, 137; Report of Schimmel & Co. April **1911**, 32.

[4] Nachrichten f. Handel u. Industrie **1912**, No. 73, 6; Report of Schimmel & Co. October **1912**, 26.

[5] Financial and Economic Year Book of Japan, **9** (1909); Report of Schimmel & Co. April **1912**, 33. — 1 Picul = 100 Kin = 60,4 kg.

PRODUCTION OF CAMPHOR. (Continuation).

Formosa.

1896	—		1904	3540953 Kin[1]	4519923 lbs.[2]
1897	1534596 Kin[1]		1905	2865117 „	4800000 „
1898	2064406 „		1906	3252408 „	4040838 „ [3]
1899	1819227 „		1907	3914598 „[4]	5388918 „
1900	3479179 „	4511184 lbs.[2]	1908	3834970 „	
1901	3667887 „	4725348 „	1909	3537712 „	
1902	3148742 „	3676060 „	1910	4864704 „	
1903	3595814 „	4071628 „			

			«All 3 grades» (A, BB, B).
1907	2847251 kg.[5]	35000 Piculs[6]	46675 Piculs[7]
1908	3603027 „	35000 „	47948 „
1909		35000 „	60349 „
1910		53000 „	
1911		45000 „	

China.

1904	2219 Piculs[8]	
1905	5363 „	
1906	—	
1907	27198 „	valued at 2168047 Haikwan Taels[9]
1908	15246 „	„ „ 1005297 „ „

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[1] Financial and Economic Year Book of Japan, **6** (1906); Report of Schimmel & Co. April **1907**, 17; Financial and Economic Year Book of Japan, **10** (1910).

[2] Zeitschr. f. angew. Chem. **19** (1906), 261; Report of Schimmel & Co. April **1906**, 13.

[3] Board of Trade Journal 4. VI. 1908; Report of Schimmel & Co. October **1908**, 31.

[4] Diplomatic and Consular Reports No. 4768, August 1911; Report of Schimmel & Co. April **1912**, 34.

[5] Nachrichten f. Handel u. Industrie **1910**, No. 28; Report of Schimmel & Co. April **1910**, 22.

[6] Nachrichten f. Handel u. Industrie **1912**, No. 73, 6; Report of Schimmel & Co. October **1912**, 26.

[7] Deutsches Hand. Arch. February **1911**, 137; Report of Schimmel & Co. April **1911**, 32.

[8] Oriental Physician and Druggist, Yokohama 1 (1907), No. 16; Report of Schimmel & Co. October **1907**, 25. — Presumably the figures for 1904/1905 refer to exports.

[9] Nachrichten f. Handel u. Industrie **1910**, No. 75, p. 3; Report of Schimmel & Co. October **1910**, 26. — 1 Haikwan Tael = (1907) 3,33 ℳ, (1908) 2,74 ℳ, (1909) 2,66 ℳ, (1910) 2,76 ℳ, (1911) 2,75 ℳ.


Camphor Districts
in
FORMOSA
by James W. Davidson
The Island of Formosa.
London and New York 1903.
Tamsui (Hobe)
Zuiho
Kelung
Taihoku (Taipeh)
Shinten (Sintiam)
Sankakuyu
Taikokan
Taihoku
Shinchiku
Gilan
So-o
Koro (Autang)
Giran
Taiko
Gosei (Goche)
Shinzio
Rokko (Lokiang)
Taichu
Taichu
Shoka (Changwha)
Karenko
Shushu
Unrin
Shukoran
Kagi
Hoteishi (Patechna)
Mt Morrison
Mato
Anping
Tainan
Banshoryo
Pinan
Tainan
Takow
Hozan
Toko (Tangkang)
Borio
Koshun
Scale 1:3000000
0 2 4 6 8 10 20 30 40 50
Miles
▨ Camphor Forests

Fig. 43.

PRODUCTION OF CAMPHOR OIL.

Japan proper.

1907	9000 Piculs[1])	1910	16000 Piculs[1])
1908	10000 „	1911	18000 „
1909	11000 „		

Formosa.

1896	—	1904	2805809 Kin[2])	
1897	683603 Kin[2])	1905	2373788 „	
1898	1120979 „	1906	2986023 „	
1899	1369887 „	1907	4180894 „	41000 Piculs[1])
1900	2632108 „	1908	4446823 „	44000 „
1901	2587186 „	1909		38000 „
1902	2388135 „	1910		58000 „
1903	2678794 „	1911		56000 „

Japan (total).

1894	68360 To[3])	valued at	23015 Yen[4])		
1895	82687 „	„ „	40923 „		
1896	89417 „	„ „	93483 „		
1897	175166 „	„ „	181535 „		
1898	103686 „	„ „	82450 „		
1899	20492 „	„ „	51363 „		
1900	9797 „	„ „	79612 „		
1901	42695 „	„ „	195853 „		
1902	26875 „	„ „	158052 „		
1903	14496 „	„ „	129826 „		
1904	714370 „	„ „	202191 „	34346 Piculs[5])	3434689 Kin[6])
1905	652549 „	„ „	189729 „	34175 „	3417531 „
1906	843895 „	„ „	264836 „	34833 „	3484387 „
1907	958106 „	„ „	315885 „		

Concerning the production of camphor oil in China no statistics are available.

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[1]) Nachrichten f. Handel u. Industrie **1912**, No. 73, p. 6; Report of Schimmel & Co. October **1912**, 26.

[2]) Financial and Economic Year Book of Japan, **6** and **9** (1906 and 1909); Report of Schimmel & Co. April **1907**, 17.

[3]) 1 To = 18,04 Liters.

[4]) Financial and Economic Year Book of Japan, **6** to **9** (1906 to 1909); Report of Schimmel & Co. April **1907**, 17; October **1908**, 29; October **1910**, 24. The figures for 1894 to 1897 apply to export only since those for production are wanting.

[5]) Berichte über Handel u. Industrie **10** (1907), 605; Report of Schimmel & Co. October **1907**, 20.

[6]) Deutsche Japan-Post, Yokohama **5** (1907), 8; Report of Schimmel & Co. April **1907**, 22.

EXPORT OF CAMPHOR.

Japan proper.

1868	468154 Kin	valued at	77097 Yen[1]		
1873	650969 „	„ „	88721 „	(Lowest price, 13 Yen per 100 Kin)	
1878	1567598 „	„ „	238166 „		
1883	5008413 „	„ „	869127 „		
1888	6478094 „	„ „	1130596 „		
1893	3064005 „	„ „	1308611 „ [2]		
1894		„ „	1023956 „		
1895		„ „	1526832 „		
1896		„ „	1119196 „		
1897		„ „	1318292 „		
1898	2608241 „	„ „	1174574 „		
1899		„ „	1754496 „		
1900		„ „	3070701 „ [3]		
1901	4165757 „	„ „	3904974 „		
1902	3953211 „	„ „	3404833 „		
1903	3985360 „	„ „	3537844 „		
1904	3140800 „	„ „	3168197 „		31418 Piculs[3]
1905	2284794 „	„ „	2566233 „		22847 „
1906	2656581 „	„ „	3632785 „		26565 „
1907	3057657 „	„ „	5026858 „		30577 „ [4]
1908	1807565 „	„ „	2063410 „		18075 „
1909	4050700 „	„ „	3469368 „		40507 „
1910			2964369 „ [5]		32751 „
1911					34410 „

Formosa. Export to Japan and foreign countries.

1899	valued at 1935001 Yen[6]	1903	valued at 3537844 Yen[6]
1902	„ „ 3718549 „	1904	„ „ 3057293 „

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[1] Toyo Keisai; Chemist and Druggist **73** (1908), 560; Report of Schimmel & Co. October **1908**, 32.

[2] Financial and Economic Year Book of Japan, **8** (1908); Report of Schimmel & Co. October **1908**, 30.

[3] Deutsche Japan-Post, Yokohama, **5** (1907), 8; Report of Schimmel & Co. April **1907**, 22. — Berichte über Handel u. Industrie **10** (1907), 605; Report of Schimmel & Co. October **1907**, 22. — Nachrichten f. Handel u. Industrie **1909**, No. 46, p. 3; Report of Schimmel & Co. October **1909**, 30. — Financial and Economic Year Book of Japan, **9** (1909); Report of Schimmel & Co. October **1910**, 25. — Deutsches Hand. Arch., February **1911**; Report of Schimmel & Co. April **1911**, 32.

[4] Nachrichten f. Handel u. Industrie **1912**, No. 73, p. 6; Report of Schimmel & Co. October **1912**, 26.

[5] Financial and Economic Year Book of Japan **11** (1911); Report of Schimmel & Co. April **1912**, 34.

[6] Financial and Economic Year Book of Japan **6** (1906); Report of Schimmel & Co. April **1907**, 17. — Deutsches Hand. Arch. Jan. **1907**, Part II, 35; Report of Schimmel & Co. April **1907**, 17. — Nachrichten f. Handel u. Industrie **1909**, No. 46, p. 3; Report of Schimmel & Co. October **1909**, 30.

EXPORT OF CAMPHOR. (Continuation.)

1905	2923117	Kin	valued	at	2683523	Yen
1906	2789394	„	„	„	2822871	„
1907	3090950	„	„	„	3567449	„
1908	2073550	„	„	„	2218706	„
1909	4366783	lbs.	„	„	302600	£[1]
1910	6486272	„	„	„	404112	„
1911	5613718	„	„	„	354165	„[2]

Export to Japan.

1907	8261	Piculs[3]
1908	4025	„
1909	—	„
1910	263	„
1911	45	„

To foreign countries.

1904	24034	Piculs	valued at 2199320 Yen[4]
1905	22430	„	„ „ 2052933 „
1906	21774	„	„ „ 2222729 „
1907	22648	„[6];	4121566 lbs.[7] = 2619143 Yen[5]
1908	16710	„ ;	— = 1710493 „
1909	50030	„	valued at 4377818 Yen
1910	48384	„	„ „ 4932750 „
1911	42058	„ ;	5607766 lbs. valued at 353536 £[2]

Exports of crude camphor from Formosa[8].

1906	4060881	Kin	valued	at	4086004	Yen
1907	5349250	„	„	„	6247915	„
1908	3061136	„	„	„	3321034	„
1909	8107550	„	„	„	7115234	„

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[1] Diplomatic and Consular Reports No. 4768 and 4769, August **1911**; Report of Schimmel & Co. October **1911**, 25.

[2] Diplomatic and Consular Reports No. 4996, September **1912**. — Of the exports of 1911 by far the largest part, *viz.*, 2374666 lbs., was shipped to Germany.

[3] Footnote 4, p. 473.

[4] Berichte über Handel u. Industrie **10** (1907), 605; Report of Schimmel & Co. October **1907**, 22.

[5] Diplomatic and Consular Reports No. 4768, August **1911**; Report of Schimmel & Co. October **1912**, 34.

[6] Nachrichten f. Handel u. Industrie **1912**, No. 73, 6; Report of Schimmel & Co. October **1912**, 26.

[7] Board of Trade Journal 4. VI. **1908**; Report of Schimmel & Co. October **1908**, 31.

[8] Financial and Economic Year Book of Japan, **9** (1909); Report of Schimmel & Co. October **1910**, 25.

EXPORT OF CAMPHOR. (Continuation.)

Export of refined camphor from Formosa[1]).

1907	1405671	Kin valued at	1292877	Yen
1909	1532470	„ „ „	1460151	„

Japan (total).

1900	6469220 lbs.[2])		1903	8965568 lbs.
1901	6717319 „		1904	7372343 „
1902	9328399 „			

China.

Exports from all ports.

1903	2185	Piculs valued at	118263	Haikwan Taels[3])	
1904	2219	„ „ „	116708	„ „	
1905	5363	„ „ „	363868	„ „	
1906	14828	„ „ „	1310791	„ „	
1907	25789	„ „ „	2077475	„ „	[4])
1908	13072	„ „ „	850135	„ „	
1909	9759	„ „ „	680827	„ „	
1910	5597	„ „ „	391100	„ „	
1911	3361	„ „ „	31832	£[5])	(Amount: 4001 cwts.)

Export from the several ports.

Foochow.

Province Fo-Kien, which produces most camphor.

1905	4805	cwts. valued at	43039	£[6])
1906	13588	„ „ „	185852	„
1907	23231	„ „ „	271433	„ [7])
1908	9644	„ „ „	69302	„
1909	4686	„		
1910	1161	„		

Foochow and Amoy.

1907	19711	Piculs[8])	
1908	8257	„	
1909	3945	„	
1910	1005	„	
1911	576	„	of this amount 559 Piculs were shipped via Foochow

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[1]) Footnote 8, p. 474.

[2]) Zeitschr. f. angew. Chem. **19** (1906), 261; Report of Schimmel & Co. April **1906**, 13.

[3]) Bericht Journ. No. 3938 des Vereins z. W. d. I. d. chem. Ind. (Copy IV. 12326; Shanghai, 19. X. 1909). — 1 Haikwan Tael = (1907) 3,33 ℳ, (1908) 2,74 ℳ, (1909) 2,66 ℳ, (1910) 2,76 ℳ, (1911) 2,75 ℳ.

[4]) Nachrichten f. Handel u. Industrie **1910**, No. 75, p. 3 and **1912** No. 58, p. 5; Report of Schimmel & Co. October **1910**, 26; October **1912**, 28.

[5]) Diplomatic and Consular Reports No. 4979, **1912**.

[6]) *Ibidem* No. 3913, August **1907**; Report of Schimmel & Co. October **1907**, 44.

[7]) Diplomatic and Consular Reports No. 4379, November **1909**; Report of Schimmel & Co. April **1910**, 27.

[8]) Journ. d'Agriculture tropicale **11** (1911), 319; Report of Schimmel & Co. April **1912**, 35. — Nachrichten f. Handel u. Industrie **1912**, No. 58, p. 5 and No. 63, p. 3.

EXPORT OF CAMPHOR. (Continuation.)

Hankow.

1906	372	Piculs	valued	at	18600	Haikwan	Taels[1]
1907	1300	„	„	„	78300	„	„
1908	213	„	„	„	11408	„	„

Shanghai.

1907	4647	Piculs[2]
1908	4064	„
1909	4889	„
1910	4410	„

EXPORT OF CAMPHOR OIL.

Japan (proper).

1907	18706	Piculs[3]				
1908	12599	„	valued	at	212947	Yen[4]
1909	12727	„	„	„	230319	„
1910	16869	„	„	„	31600	£[5]
1911	17417	„				

Formosa (to Japan).

1907	41950	Piculs[3]						
1908	45193	„						
1909	36394	„ ;	4932573	lbs.	valued	at	164454	£[6]
1910	58766	„ ;	7835519	„	„	„	206449	„
1911	52008	„ ;	6934445	„	„	„	235585	„

Value of Exports:

1899	1075558 Yen[7]
1902	921536 „
1904	1235684 „
1905	2579782 Kin valued at 1156454 Yen.

Japan (total).

1901	1561970	Kin	valued	at	239933	Yen[8]
1902	630985	„	„	„	92488	„
1903	1400921	„	„	„	181919	„
1904	1189921	„	„	„	189124	„

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[1] Chem. Industrie **32** (1909), 521; Report of Schimmel & Co. April **1910**, 27.

[2] Footnote 8, p. 475.

[3] Nachrichten f. Handel u. Industrie **1912**, No. 73, p. 6; Report of Schimmel & Co. October **1912**, 26.

[4] Deutsches Hand. Arch., February **1911**; Report of Schimmel & Co. April **1911**, 32.

[5] Diplomatic and Consular Reports No. 4768, August **1911**; Report of Schimmel & Co. April **1912**, 34.

[6] Diplomatic and Consular Reports No. 4996, September **1912**.

[7] Deutsches Hand. Arch., January **1907**, II, 35; Report of Schimmel & Co. April **1907**, 18.

[8] Deutsche Japan-Post, Yokohama **5** (1907), 8; Report of Schimmel & Co. April **1907**, 21.

EXPORT OF CAMPHOR OIL. (Continuation.)

1905	1264184	Kin	valued	at	216122	Yen[1])	
1906	769279	„	„	„	132502	„	The export of white oil was prohibited!
1907	—				—		
1908	12599	Piculs	„	„	212947	„[2])	
1909	12727	„	„	„	230319	„	

China. Exports via Foochow.

1903	624	cwts.	valued at	993	£[3])	1906	3796	cwts.	valued at	8344	£
1904	744	„	„ „	1380	„	1907	10345	„	„ „	20805	„[4])
1905	349	„	„ „	600	„	1908	99	„	„ „	119	„

Exports via Kiukiang.

1908	2705	cwts.	valued	at	11722	£[5])
1909	2924	„	„	„	9034	„
1910	3555	„	„	„	8243	„

286. Oil of the Leaves of Cinnamomum Camphora × C. glanduliferum.

The botanical examination of a camphor tree growing in the Villa Flora in Cannes revealed it to be a hybrid between *Cinnamomum Camphora,* Nees et Eberm. and *C. glanduliferum,* Meissn.

At ordinary temperature the oil[6]) distilled from the leaves was a viscid mass permeated with camphor, from which 60 p.c. of camphor were obtained upon cooling and application of pressure. The remaining oil had the following properties: d_{15° 1,0465; $\alpha_D + 34^\circ 24'$; A.V. 1; E.V. 23,3; E.V. after acetylation 46,2; soluble in 0,8 vol. of 80 p.c. alcohol; not soluble to a clear solution with 10 vol. of 70 p.c. alcohol.

Safrol was not contained in the oil.

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[1]) Berichte über Handel u. Industrie **10** (1907), 605; Report of Schimmel & Co. October **1907**, 20.

[2]) Deutsches Hand. Arch., February **1911**, 137; Report of Schimmel & Co. April **1911**, 32.

[3]) Diplomatic and Consular Reports No. 3913, August **1907**; Report of Schimmel & Co. April **1908**, 22.

[4]) Diplomatic and Consular Reports No. 4379, November **1909**; Report of Schimmel & Co. April **1910**, 27.

[5]) Diplomatic and Consular Reports No. 4723, p. 11.

[6]) Report of Schimmel & Co. April **1913**.

287. Oil of Persea gratissima.

Persea gratissima, Gærtn., a tree indigenous to tropical America, is now cultivated everywhere in the tropics for its edible fruit known as *Avocato* or *Agnacate.* It does well as far north even as Northern Italy and Southern France. Bark and leaves contain a volatile oil having a tarragon-like odor.

OIL OF THE BARK.

Under the designation "anise bark", Schimmel & Co. received in 1891 from Madagascar a bark[1]), the exterior of which resembled massoy bark, but its odor was very different. It was only later[2]) that its derivation from *Persea gratissima* was established.

The oil obtained from this bark with a yield of 3,5 p.c. was described in the first edition of this book as anise bark oil. It has an anise-like odor, but no sweet taste. d_{15° 0,969; $\alpha_D - 0^\circ 46'$. In addition to small amounts of *anethol, methylchavicol* was found as its principal constituent, the first known natural occurrence of this substance, which had been previously prepared artificially by Eykman.

OIL OF THE LEAVES.

The leaf oil has been distilled twice: once from leaves from the botanical garden in Genoa[3]), and again from leaves from Cannes[4]). The oil, which is faintly yellowish-green and which resembles tarragon oil very closely, both as to odor and taste, had the following constants: 1. d_{15° 0,9607; $\alpha_D + 1^\circ 50'$; $n_{D18,2^\circ}$ 1,5164; 2. d_{15° 0,956; $\alpha_D + 2^\circ 22'$; n_{D20° 1,51389; E.V. 3,8; E.V. after acetylation 18,9; soluble in 6 vol. of 80 p.c. alcohol with slight turbidity due to the separation of paraffin; soluble to a clear solution in about $^1/_2$ vol. or more of 90 p.c. alcohol.

The characteristic principal constituent of the oil is *methylchavicol,* the presence of which was established by its con-

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[1]) Report of Schimmel & Co. April 1892, 53.

[2]) *Ibidem* October 1910, 19.

[3]) *Ibidem* October 1894, 69.

[4]) *Ibidem* October 1906, 59.

version into anethol and oxidation to homoanisic acid (m.p. 84 to 85°)[1]. The first fractions contain d-*α-pinene* (m.p. of nitrol benzylamine 123°)[2]. From the residue it was possible to separate *paraffin,* m.p. 53 to 54°, in silky needles by treating it with 80 p.c. alcohol.

288. Oil of Persea pubescens.

"Swamp red bay" or simply "swamp bay" are the names commonly applied to *Persea pubescens,* (Purch.) Sarg (*P. carolinensis,* Nees), family *Lauraceæ,* which is indigenous to the middle belt of North America. According to F. Rabak[3] the leaves yield 0,2 p.c. of oil with the following properties: d_{25° 0,9272; $\alpha_D + 22,4^\circ$; n_{D25° 1,4695; A.V. 2,8; E.V. 14,5; E.V. after acetylation 64; soluble in $^1/_3$ vol. of 80 p.c. alcohol, the solution, however, becomes turbid upon the addition of 5 vol. or more of the solvent. Of free acids *butyric acid* only was found. In the form of esters, Rabak found *butyric, valeric* and a little *œnanthic* acids. The following substances were also identified: 21 p.c. d-*camphor* (m.p. of semicarbazone 237 to 239°; of oxime 117 to 118°), 19,8 p.c. of *cineol* (m.p. of hydrobromide 55 to 57°) and possibly small amounts of *borneol* and *formaldehyde.*

289. Cayenne Linaloe Oil.

Cayenne-Linaloeöl. — Essence de Bois de Rose femelle. — Essence d'Azélia.

Origin. The linaloe wood of French Guiana, or Cayenne linaloe wood is known as *Likari kanali* by the natives and as *Bois de rose mâle* by the French colonists. It is also known as *bois de rose, sarsaffras, bois de rose femelle, bois jaune, bois de citron de Cayenne, cèdre jaune,* or *copahu.* No doubt, these names are applied to aromatic woods of different botanical origin.

The strongly fragrant wood, which upon distillation yields the Cayenne linaloe oil, is hard and heavy, and cleaves readily.

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[1] Report of Schimmel & Co. October 1894, 69; October 1906, 59.

[2] *Ibidem* October 1906, 59.

[3] U. S. Dep. of Agriculture, Bureau of Plant Industry, Bull. No. 235 (1912), p. 29.

The fresh surface is yellow, the older surfaces are reddish. From Cayenne it is exported in the shape of cord wood from which the bark has not been removed. The size of the pieces admits the inference of large trees.

The plant from which the Cayenne linaloe wood is obtained has not been definitely ascertained. According to J. Möller[1]) it may be assumed with a fair degree of probability that *Ocotea caudata,* Mez. (*Licaria guianensis,* Aubl.), a tree belonging to the family *Lauraceæ,* is the source.

E. M. Holmes[2]) collected the statements of former authors, some of which are rather contradictory. He is of the opinion that the *bois de rose femelle* is derived from *Protium (Icica) altissimum,* March (family *Burseraceæ*), and not, as stated by Möller, from *Ocotea caudata.* The wood of *Ocotea caudata* (*Licaria guianensis* of Aublet, *Plantes de Guiane Française,* p. 313) is known in Cayenne as *Bois de rose mâle.* The natives designate the young trees as *Licari kanali,* but regard the older specimens as a different plant which they call *sarsaffras.* From the account of Holmes, however, it does not appear which of the two woods yields the oil of commerce.

At the present time the large forests between the Maroni and Oyapock Rivers, in French Guiana, yield the bulk of the wood. It is cut by negroes and carried on the back to the nearest river whence it is shipped to the coast. Originally all the wood was shipped to Europe. Later, several factories were erected which distilled nothing but Cayenne linaloe oil. Nevertheless, large shipments of wood occasionally reach Europe. Frequently the best period for cutting, when the wood is richest in oil, is disregarded. Again, the wood is exposed for an unnecessarily long time to the alternating influence of sun and rain, thus causing a decrease in the oil content[3]). As a result the oil yield fluctuates considerably, varying between 0,6 and 1,6 p.c.[4]). The average yield is about 1 p.c.[5]).

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[1]) Pharm. Post **29** (1896), Nos. 46 to 48. — Jahrbuch des Kgl. bot. Gartens zu Berlin **1889**, 378.

[2]) Perfum. and Essent. Oil Record **1** (1910), 32.

[3]) P. Jeancard, Parfumerie moderne **5** (1911), 53.

[4]) E. Theulier, Rev. gén. de Chim. **3** (1900), 262.

[5]) Roure-Bertrand Fils, Perfum. and Essent. Oil Record **1** (1910), 33.

Properties. The oil is a liquid with the pleasant odor of linalool d_{15° 0,870 to 0,880; α_D — 10 to — 19°; n_{D20° 1,461 to 1,463; A.V. up to 1,3; E.V. up to 6,3. The alcohol content, computed as $C_{10}H_{18}O$ and determined by acetylating for 7 hrs. in xylene solution (1 to 5), was 90 to 97 p.c. The oil is soluble in 1,5 to 2 vol. or more of 70 p.c. alcohol, and in about 4 vol. or more of 60 p.c. alcohol.

Composition. Cayenne linaloe oil contains more than 80 p.c. of l-*linalool.* This alcohol was at first found by H. Morin[1]) who called it licareol. P. Barbier[2]) at first regarded linalool and licareol as two distinct alcohols, but later became convinced of their identity[3]). According to Theulier[4]), Cayenne linaloe oil differs from the Mexican by the absence of methyl heptenone, terpineol and geraniol. However, Schimmel & Co.[5]) found in the saponified oil about 5 p.c. of *terpineol* and about 1 p.c. *geraniol* (m. p. of diphenylurethane 80 to 81,5°). According to Roure-Bertrand Fils[6]) *methylheptenone* as well as *nerol* (about 1,2 p.c.) are present.

Of less importance are *cineol* (m. p. of iodol derivative 110 to 111°)[7]) and *dipentene* (m.p. of tetrabromide 124 to 125°, of dihydrochloride 47 to 48°)[7]) which occur in the lower fractions. The aqueous distillate contains *furfurol* (b. p. 159 to 161°; m. p. of phenylhydrazone 96 to 98°, of semicarbazone 196°)[7]), and an aldehyde, presumably iso*valeric aldehyde*[7]), which boils between 90 and 95° and produces irritation and coughing.

The lower fractions appear to contain also an *aliphatic terpene.* Its isolation by fractionation was not possible. When acted upon by glacial acetic acid + sulphuric acid, about 10 p. c. of ester was obtained. The alcohol obtained upon saponification boiled at 210 to 215°; d_{15° 0,915. It resinified readily and its odor reminded one of linalool and terpineol. Inasmuch as the

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[1]) Compt. rend. **92** (1881), 998 and **94** (1882), 733. — Ann. de Chim. et Phys. V. **25** (1882), 427.

[2]) Comp. rend. **114** (1892), 674 and **116** (1893), 883.

[3]) *Ibidem* **121** (1895), 168.

[4]) Rev. gén. de Chim. **3** (1900), 262.

[5]) Report of Schimmel & Co. April **1909**, 68.

[6]) Berichte von Roure-Bertrand Fils October **1909**, 45.

[7]) Report of Schimmel & Co. April **1912**, 90.

fraction used for the hydration, *viz.*, 168 to 170°, yielded no reactions for sabinene, camphene, fenchene or pinene, it may be assumed that the alcohol owes its origin to an aliphatic terpene[1]).

Upon treating the linalool fraction with acetic acid anhydride, Barbier[2]) obtained products that had the odor of dimethylheptenyl acetate and hence assumed the presence of dimethylheptenol in the oil. Schimmel & Co.[3]), however, were of opinion that Barbier's alcohol was methylheptenol and that it should probably be regarded as a decomposition product of linalool. Later they were able to demonstrate[4]) clearly that small amounts of methylheptenol were contained in the lower fractions. The fraction examined had d_{15° 0,8655 and $\alpha_D - 11° 40'$. The alcohol, isolated by means of the acid phthalate, yielded upon oxidation methylheptenone, which was characterized by its semicarbazone melting at 137 to 138°.

290. Oil of Ocotea usambarensis.

OIL OF THE BARK.

Ocotea usambarensis, Engl. is a tree that is also known as the Ibean camphor tree. From the bark there was distilled a volatile oil at the Imperial Biological-Agricultural Institute in Amani, German East Africa, which oil was examined by R. Schmidt and K. Weilinger[5]).

The bark of the tree, which belongs to the *Lauraceæ* and which occurs in large numbers in the primeval forests, yielded 0,15 p. c. of a volatile oil of the following properties: b. p. 50 to 160° (10 mm.); d_{20° 0,913; $\alpha_{D20^\circ} - 11° 12'$; n_D 1,476; A.V. 1,2; E.V. 12,5; content of free alcohol $C_{10}H_{18}O$ 4,5 p. c.; free from nitrogen and sulphur. Upon shaking out the oil with potassium hydroxide solution, 0,3 p. c. of a phenol not further characterized was obtained. With bisulphite solution 1 p. c. of *myristic aldehyde* was obtained. This was characterized by its semicarbazone

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[1]) Report of Schimmel & Co. April **1912**, 90.

[2]) Compt. rend. **126** (1898), 1423.

[3]) Report of Schimmel & Co. October **1898**, 60.

[4]) *Ibidem* October **1911**, 60.

[5]) Berl. Berichte **39** (1906), 652.

(m. p. 100 to 101°) and by its oxidation to myristic acid. Upon shaking the oil with hydrazine benzene sulphonic acid a small amount of a ketone was obtained, the semicarbazone of which melted at 197°. In addition, the oil contained 40 p.c. *cineol* (iodol compound), 40 p.c. l-*terpineol* (b. p. 100 to 110° at 12 mm. pressure; d_{20° 0,922; $\alpha_D - 37° 6'$; n_D 1,484) which was characterized by its conversion into dipentene dihydrochloride (m. p. 46°), and 10 p.c. *sesquiterpene* $C_{15}H_{24}$ (b. p. 136 to 142° at 12 mm.; d_{20° 0,915; $\alpha_D + 7° 46'$; n_D 1,505) the dihydrochloride of which (m. p. 116 to 117°) is not identical with cadinene dihydrochloride.

OIL OF THE WOOD.

In the Imperial Institute[1]), London, a number of samples of the wood have been examined: the sap-wood which had a faint odor of eucalyptus oil; branches and twigs, which, when freshly broken, revealed the same odor, but rather stronger; branches and twigs, stated to be shoots from the stump of a tree which had been cut down some years previously. Upon steam distillation each of the three samples yielded a volatile oil with the following properties respectively: —

	Oil from		
	Sap-wood	Branches and twigs	Branches and twigs from stump
Yield	0,4 p.c.	0,52 p.c.	0,14 %
d_{15°	0,9641	0,9681	0,9327
α_D	$-7° 30'$	$-7° 30'$	$-0° 28'$
S. V.	30,1	30,1	13,3
Solubility in 80 p.c. alcohol	In 1,1 vol.	In 1,1 vol.	Insoluble even in 10 vol.

The two first mentioned oils were light yellow in color and their odor reminded one of that of eucalyptus oil. They contained but little *cineol* and the presence of camphor could not be detected. The oil from the shoots was more limpid than the other two, which it resembled both as to odor and color. Judging from the odor, it contained a higher cineol percentage, but the small amount of oil precluded an analysis.

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[1]) Bull. Imp. Inst. 9 (1911), 340.

291. Ocotea Oil or Laurel Oil from Guiana.

An oil obtained from Demerara, British Guiana, and designated "laurel oil" was examined by Stenhouse[1]). According to Christison the oil was obtained from a tree of the genus *Ocotea* by making incisions near the root, thus opening up the oil containers under the bark. The exuding oil constitutes a yellowish liquid which has a pleasant odor reminding one of turpentine. It boiled at 149,5 to 162,5° and the specific gravity was 0,864 at 13,3°. Upon setting aside a mixture of oil, alcohol and dilute nitric acid, Stenhouse obtained crystals, which after recrystallization separated as rhombic prisms melting at 150°.

The oil appears to consist of *pinene* and the crystals obtained by the action of nitric acid may have been terpin hydrate. With this assumption, however, the melting point of 150°[2]) does not agree, since terpin hydrate melts as low as from 116 to 117°.

292. Venezuela Camphorwood Oil.

Through Professor H. H. Rusby[3]) of the New York College of Pharmacy, Fritzsche Brothers of New York City were supplied with some wood, the botanical origin of which had not been determined, but which probably belonged to a species of *Nectandra* or *Ocotea* (family *Lauraceæ*). The wood of the heavy logs, which had been collected during a botanical expedition on the lower Orinoco, was rather soft and split readily. The cleavage surface has a satiny appearance and is frequently traversed by dark longitudinal and radial lines. The wood has a faint odor reminding one somewhat of borneol.

Upon distillation of the comminuted wood, 1,15 p. c. of a light yellow oil were obtained. It had the remarkably high specific gravity of 1,155 and an angle of rotation $\alpha_D + 2° 40'$[4]),

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[1]) Philos. Magaz. and Journ. of Science **20** (1842), 273 and **25** (1844), 200. — Liebig's Annalen **44** (1842), 309 and **50** (1844), 155. Compare also Hancock, Bull. des sciences math. phys. et chim., Febr. 1825, p. 125; Trommsdorff's Neues Journ. der Pharm. **11**, I. (1825), 171.

[2]) In Gmelin, *Organ. Chem.* ed. IV, vol. 7, p. 282 the melting point of the substance as found by Stenhouse is recorded as 125°.

[3]) Comp. Rusby, Botany of Venezuela, Pharmaceutical Journ. 57 (1896), 292.

[4]) Report of Schimmel & Co. April 1897, 45.

its faint odor recalling that of *Asarum canadense.* At ordinary temperature it congealed to a crystalline mass. Drained and recrystallized, beautiful colorless prisms melting at 28,5° were obtained. In concentrated sulphuric acid this substance dissolved with a blood-red color. Boiled with alcoholic potash it was changed to a substance which crystallized from alcohol in beautiful plates melting at from 55 to 56°. Judging from this behavior it becomes apparent that this substance, which constitutes 90 p.c. of the oil, consists of *apiol.* A more careful comparison of its properties with those of the ordinary parsley apiol revealed the identity of the two substances in every particular.

293. Mountain Laurel Oil.

Origin. All parts of the mountain laurel of California, *Umbellularia californica,* Nutt. (*Oreodaphne californica,* Nees, *Tetranthera californica,* Hook. et Arn., also known as California bay tree)[1], contain volatile oil. This is particularly true of the leaves which upon distillation yield from 2,4[2] to 5,17 p.c.[3] of oil.

Properties. The oil is light yellow in color. Its odor is pungently aromatic, reminding one of nutmeg and cardamom. If breathed in deeply it attacks the mucous membranes and causes tears to flow. Its taste is warm and camphor-like. d_{15° 0,936 to 0,948; α_D — 22 to — 24°; A.V. 4,7; E.V. 5,5; E.V. after acetylation 50,8 (but one determination in each case); soluble in 1,5 to 2,2 vol. of 70 p.c. alcohol.

Composition. Older investigations have been carried out by J. P. Heaney[4] and by Stillman[5]. Our present knowledge of the oil, however, we owe to F. B. Power and F. H. Lees[6]. According to these investigators the oil contains traces of *formic* and *higher fatty acids* in the free state, small amounts of *eugenol* (m.p. of

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[1] W. Busse, *Über die Blätter des kalifornischen Lorbeers.* Berichte d. deutsch. pharm. Ges. **6** (1896), 56.

[2] J. M. Stillmann, Berl. Berichte **13** (1880), 630.

[3] Report of Schimmel & Co. November **1908**, 126.

[4] Americ. Journ. Pharm. **47** (1875), 105. — Pharmaceutical Journ. III. **5** (1875), 791.

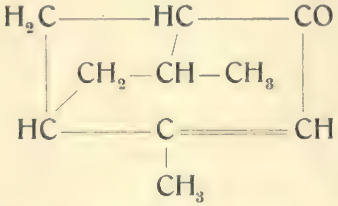
[5] Berl. Berichte **13** (1880), 630.

[6] Journ. chem. Soc. **85** (1904), 629.

benzoyl eugenol 69 to 70°), l-*α-pinene* (m. p. of nitrol piperidine 119 to 120°; of nitrol benzylamine 124 to 125°), *cineol*[1] (m. p. of iodol compound 115°), very little *safrol* (m. p. of piperonal 35°), *methyleugenol* (m. p. of bromeugenol methyl ether dibromide 78 to 79°; of veratric acid 177°). The principal constituent, however, is *umbellulone* which is present to the extent of from 40 to 60 p.c.

Umbellulone is a ketone $C_{10}H_{14}O$ which, in the pure condition when regenerated from its semicarbazide-semicarbazone, has the following properties: b. p. 219 to 220° (749 mm.)[2], 92,5 to 93° (10 mm.)[3]; d_{20° 0,950[3]; α_D —36°30′[3]; n_D 1,48325[3]. It yields a semicarbazide-semicarbazone (m. p. above 200°) and a normal monosemicarbazone which melts between 240 to 243°, according to the mode of heating. Umbellulone yields a solid dibromide which melts at 119°. Upon oxidation it yields umbellulonic acid, $C_9H_{14}O_3$, m. p. 102°, an unsaturated keto acid. Upon distillation this is converted in part into an unsaturated lactone $C_9H_{12}O_2$, b. p. 218 to 221°.

Based upon the results of Power and Lees[2], Lees[4], as well as F. Tutin[5], in connection with the preparation of numerous derivatives, the action of bromine on umbellulone and its oxidation with permanganate, Tutin proposed the following formula for this ketone:—



Semmler[3] reduced umbellulone with sodium to dihydroumbellulol $C_{10}H_{18}O$ which, upon oxidation with chromic acid, yielded β-dihydroumbellulone $C_{10}H_{16}O$. Upon oxidation with permanganate, the benzylidene compound of this ketone yielded

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[1] Report of Schimmel & Co. October **1893**, Table in supplement, p. 26.

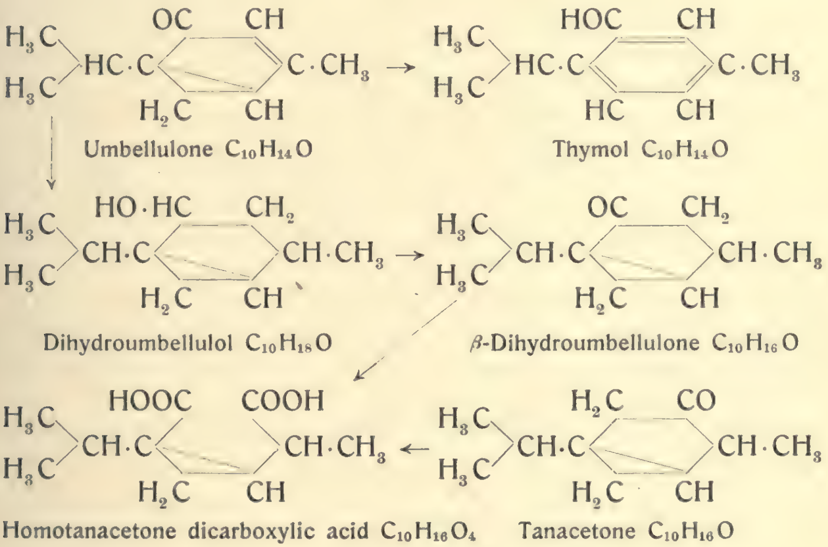
[2] Journ. chem. Soc. **85** (1904), 629.

[3] F. W. Semmler, Berl. Berichte **40** (1907), 5017 and **41** (1908), 3988.

[4] Journ. chem. Soc. **85** (1904), 644.

[5] *Ibidem* **89** (1906), 1104; **91** (1907), 271, 275; **93** (1908), 252.

homotanacetone dicarboxylic acid. From this Semmler concluded that in dihydroumbellulone the same arrangement of carbon atoms prevails as in tanacetone. However, whereas in tanacetone the keto group is in carvone position, in dihydroumbellulone it is in menthone position. A further proof for the grouping assumed by Semmler is found in the quantitative change of umbellulone to thymol when the ketone is heated in a sealed tube to 280° for 18 hours. These changes are illustrated by the following structural formulas.



294. Pichurim bean Oil.

The volatile oil of the cotyledons of *Nectandra Puchury-major,* Nees, and of *Nectandra Puchury-minor,* Nees, the pichurim beans of the drug market, was first prepared by Robes[1]) in 1799 and again by Bonastre[2]) in 1825.

The oil was investigated in 1853 by A. Müller[3]). Inasmuch as the beans contain starch he added sulphuric acid during the distillation in order to prevent the formation of paste. In this

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[1]) Berl. Jahrb. d. Pharm. 5 (1800), 60.

[2]) *Ibidem* 37 (1825), 160. — Repert. f. d. Pharm. I. 21 (1825), 201.

[3]) Journ. f. prakt. Chem. 58 (1853), 463.

manner he obtained 0,7 p.c. of a volatile oil greenish-yellow in color and of the peculiar pichurim odor.

From the oil, which distilled between 180 and 270°, Müller obtained, upon repeated fractionation, a hydrocarbon which had a well-nigh constant boiling point at 150° (pinene?). Fraction 167 to 170° had the odor of orange and appears also to have been a terpene. Between 255 and 256° an oil with a deep indigo blue color passed over. From a fraction with a still higher boiling point crystals of „pichurim fatty acid" *(lauric acid)* separated.

Inasmuch as the pichurim beans have a decided odor of *safrol,* this substance is very probably a constituent of the Pichurim bean oil.

295. Caparrapi Oil.

According to F. J. Tapia[1]), the oil of *Nectandra Caparrapi,* family *Lauraceæ,* has long been known in Columbia as caparrapi oil. The tree which yields this oil is popularly known as *canelo,* probably because of the cinnamon-like odor of the bark. The production of the oil corresponds in a measure to that of turpentine. At the foot of the trunk, a broad and deep incision is made from which the oil, which is used as a substitute for copaiba balsam, exudes.

According to whether or not heat is applied to remove the water, the oil enters the market more or less colored. The oil contains a *monobasic acid* $C_{15}H_{26}O_3$ which melts at 84,5°. Only from the light colored oils can this acid be obtained in crystalline form. The oil freed from acid consists principally of a sesquiterpene alcohol $C_{15}H_{26}O$, the *caparrapiol,* which when dehydrated yields $C_{15}H_{24}$, caparrapene. Alcohol as well as hydrocarbon are readily polymerized, especially under the influence of heat so that about $^3/_4$ of the oil remains behind in a resinified condition when distilled with steam.

296. Clove Bark Oil.

The bark of the Brazilian *Dicypellium caryophyllatum,* Nees (*Persea caryophyllata,* Mart.) formerly found a place in the apothecary shops as *Cortex caryophyllatus.* It is also

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[1]) Bull. Soc. chim. III. 19 (1898), 638.

known as *Cassia caryophyllata,* Ger. *Nelkenrinde, Nelkenzimt*[1]), *Nelkencassie* and *Nelkenholz.*

Upon distillation of the powdered bark, J. B. Trommsdorff[2]) obtained 4 p. c. of a light yellow oil which sank in water and had the odor of cloves.

With caustic potassa, soda and ammonia the oil yielded crystalline compounds from which it was separated unchanged upon addition of sulphuric acid. This behavior as well as its odor and density render it very probable that clove bark oil contains the same phenol as clove oil, *viz., eugenol.*

297. Massoy Bark Oil.

Origin. The massoy barks of commerce originate from several plants. The genuine massoy bark is derived from *Massoia aromatica,* Beccari, (*Sassafras Gœsianum,* T. et B.). It is a native of New Guinea. *Cinnamomum xanthoneuron,* Blume, is likewise mentioned as the mother plant. It also is a native of New Guinea. Recently[3]) this plant has been pronounced identical with *M. aromatica* although this is not in accordance with the Index Kewensis. Massoy bark is also obtained from *Cinnamomum Burmanni,* Blume (*C. Kiamis,* Nees). Finally certain massoy barks of commerce, which are said to come from Dutch East India, agree with the bark of *Cinnamomum Culilawan,* Blume.

The botanical origin of the bark from German New Guinea, from which Schimmel & Co., in 1888, distilled the first commercial massoy bark oil, is unknown. Upon comparing it with the genuine massoy bark from *Massoia aromatica,* Beccari, E. M. Holmes[4]) arrived at the conclusion that the two were not identical. Moreover, he pronounced the bark of Schimmel & Co. very similar to the *Cortex Culilabani Papuanus* of the Hanbury collection, the botanical origin of which is likewise unknown.

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[1]) The oil from the leaves of the Ceylon cinnamom shrub (see p. 423) was for a time designated as *Nelkenzimtöl.*

[2]) Trommsdorff's Neues Journ. d. Pharm. **23**, I. (1831), 7.

[3]) J. Wiesner, *Die Rohstoffe des Pflanzenreichs.* 2nd ed. Leipzig 1900, vol. I, 778.

[4]) Pharmaceutical Journ. III. **19** (1888), 465 and 761.

Of a contrary view is N. Wender[1] who expresses himself in the following manner: "In its anatomical structure the massoy bark (namely that of Schimmel & Co.) is unquestionably one of the *Lauraceæ* and in other respects agrees best with the bark of *Sassafras Gœsianum* or *Massoia aromatica.*"

According to the anatomical data of Pfister[2] it is regarded as impossible that this bark belongs to *Massoia aromatica.*

Properties. Upon distillation the massoy bark of German New Guinea yields 6 to 8 p.c. of an oil with a pleasant odor reminding one of cloves and nutmeg. d_{15° 1,04 to 1,065.

Composition. According to Schimmel & Co.[3] the oil consists principally of *eugenol* (70 to 75 p.c.) and *safrol.* In addition to these E. F. R. Woy[4] isolated a fraction boiling at about 172°, in which he thought to have discovered a new terpene, the *„massoyene".* However, O. Wallach[5] demonstrated that the so-called massoyene consisted of a mixture of at least three terpenes, *viz., α-pinene* (m. p. of pinene nitrol benzylamine 123°; of nitrosopinene 133°), *limonene* (m. p. of limonene nitrolbenzylamine 93°) and *dipentene* (m. p. of tetrabromide 123°).

298. Sassafras Oil.

Oleum Sassafras. — Sassafrasöl. — Essence de Sassafras.

Origin and History. The sassafras tree, *Sassafras officinale,* Nees., family *Lauraceæ,* is widely distributed over the American continent from Canada to Florida and Alabama, and westward as far as Kansas[6] and northern Mexico. In the southern states it often attains a height of 15 m. and the trunk a thickness of $^1/_3$ m.

Contrary to earlier statements, the older bark and the wood are odorless. When crushed, the green parts of the tree are slightly aromatic, but do not smell of safrol. The wood of younger stems contains oil cells which disappear later. The

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[1] Zeitschr. d. allg. österr. Apoth. Ver. **29** (1891), 2.

[2] Forsch.-Ber. üb. Lebensmittel u. i. Bezieh. z. Hyg. **1** (1894), 13.

[3] Schimmel's Bericht October **1888**, 42.

[4] Arch. der Pharm. **228** (1890), 22 and 687.

[5] Liebig's Annalen **258** (1890), 340. — Arch. der Pharm. **229** (1891), 116.

[6] R. J. Brown, Medicinal Flora of Kansas. — Proceed. Americ. Pharm. Ass. **29** (1881), 446.

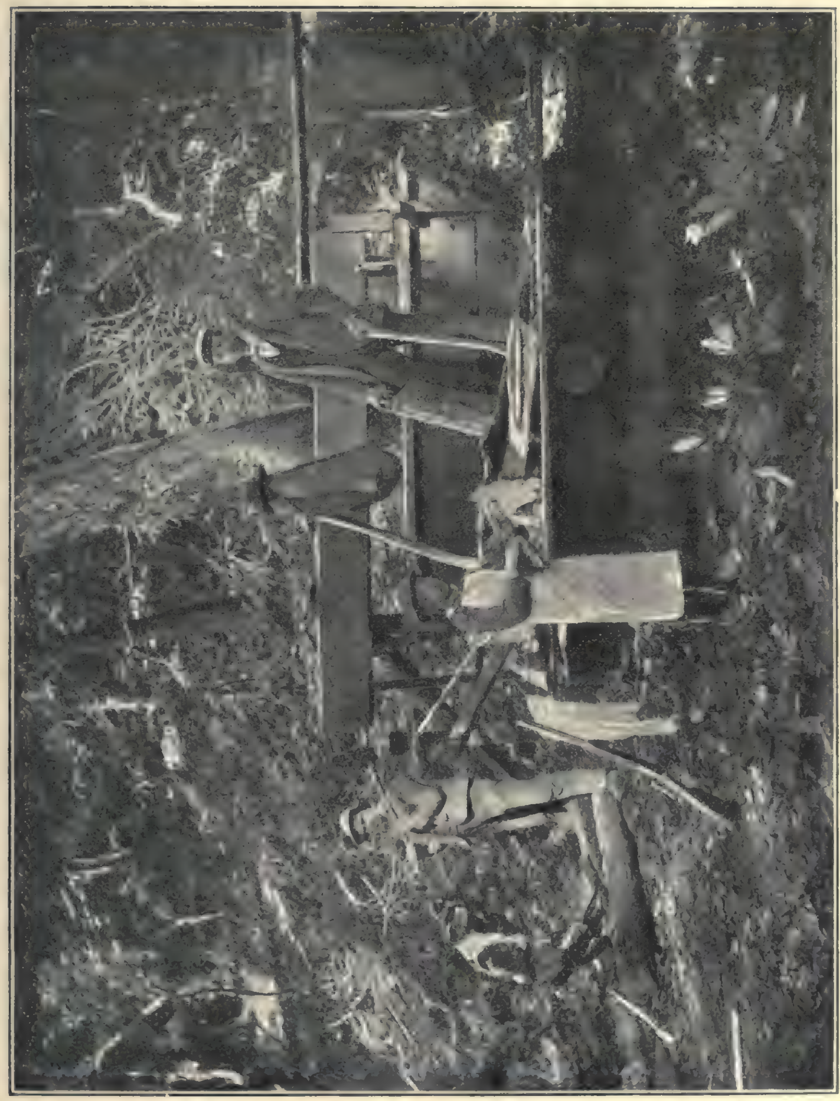

Fig. 43.

One of the smaller sassafras stills in Virginia.

wood of the roots is richer in oil cells, more particularly the root bark.

The distillation of sassafras oil began early in the past century. Like that of wintergreen oil and sweet birch oil, it has been carried out in the most rudimentary fashion up to the present time[1]). The still consisted of a barrel of heavy oak staves, the bottom of which was many times perforated. The barrel was tightly fitted into a conical iron vessel. The lid of the barrel was so arranged that it could be removed for filling the barrel with sassafras bark and put back steam-tight. An iron pipe, twice bent at right angles, was placed in a hole bored in the lid. The long arm turned downward passed through a barrel which served as condenser and which was supplied with cold water. The iron vessel was filled with water almost up to the perforated bottom of the barrel. The water was kept boiling, and was replaced as evaporation required until the bark was completely exhausted.

This method of distillation was very slow but was carried out by the farmers themselves. Moreover, the cost of production consisted merely of the price of the cheap utensils and the labor.

In recent years the distillation has been conducted more rationally. The unpeeled roots are delivered in logs about a meter in length. With the aid of a saw mill, mostly driven by water power, they are cut into thin slices. Through a hopper they are transferred directly to the still constructed of 3 inch pine planks. This still, 4 to 5 ft. high and 12 ft. square, is held together by iron bands. One of the side walls is provided with two tight fitting doors: one above for filling, the other below for discharging. The steam generated in a boiler is conducted by means of a pipe into the bottom of the still and then passes through the root wood resting on a false bottom. The vapors saturated with oil are condensed by means of a worm cooler and the distillate is collected in a large copper flask with a capacity up to 20 gal. About two inches from the bottom the receiver is provided with a stop cock through which the oil is drawn off from time to time. After the wood has been exhausted the

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[1]) W. Procter jr., Proceed. Americ. pharm. Ass. 14 (1866), 211 to 222. — Americ. Druggist 1887, 45. — New Remedies (New York) 1883, 224. — Oil, Paint and Drug Reporter, Sept. 14. 1891. — Pharmaceutical Journ. III. 22 (1891), 491.

Fig. 44.
Sassafras saw mill and still in Lexington (Virginia).

still is emptied, the wood is dried by exposure to the sun and utilized as fuel under the boiler.

A still of this description has a capacity of about 20000 lbs. and the distillation of this quantity lasts about 48 to 50 hrs.

The root bark yields 6 to 9 p.c., the root wood somewhat less than 1 p.c. of oil.

Up to the middle of the past century the distillation of sassafras oil was conducted principally in the states of Pennsylvania, Maryland and Virginia, Baltimore and Richmond being the principal commercial centres for this oil. At the beginning of the civil war, in 1860, as much as 50000 lbs. of sassafras oil are said to have entered the market from Baltimore alone[1]). After the sixties much oil was also distilled in New Jersey, New York, Ohio, Indiana, Tennessee and Kentucky[2]), as well as in the New England states, until the lack of trees in many parts of these states rendered the enterprise unprofitable.

Properties. Sassafras oil is a yellowish or reddish-yellow liquid with an odor of safrol and an aromatic taste. d_{15° 1,070 to 1,080; $\alpha_D + 2$ to $+ 4^\circ$; n_{D20° about 1,530; A. V. 0; E. V. 1 to 2; soluble in all proportions of 95 p.c. alcohol and in 1 to 2 vol. of 90 p.c. alcohol. An oil distilled by Schimmel & Co.[3]) (yield 3,25 p.c.) had the following properties: d_{15° 1,075; $\alpha_D + 2^\circ 14'$; n_{D20° 1,52885; A. V. 0; E. V. 1,9; soluble in 1,8 vol. or more of 90 p.c. alcohol. 100 cc. of oil were distilled from an ordinary fractionating flask and the distillate collected in fractions of 10 cc. each: —

		d_{15°	α_D
1.	208 to 216°	1,0066	$+ 5^\circ 40'$
2.	216 „ 221°	1,0546	$+ 4^\circ 36'$
3.	221 „ 225°	1,0764	$+ 3^\circ 55'$
4.	225 „ 225°	1,0830	$+ 2^\circ 57'$
5.	225 „ 226°	1,0877	$+ 2^\circ 5'$
6.	226 „ 227°	1,0916	$+ 1^\circ 30'$
7.	227 „ 228°	1,0930	$+ 0^\circ 45'$
8.	228 „ 229°	1,0942	$+ 0^\circ 12'$
9.	229 „ 234°	1,0905	$- 0^\circ 19'$
10.	Residue	1,0770	

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[1]) Alpheus P. Sharp, Americ. Journ. Pharm. **35** (1863), 13. — W. Procter, *ibidem* **33** (1861), 1 and **38** (1866), 484.

[2]) F. Rabak, Americ. Perfumer **5** (1910), 220.

[3]) Report of Schimmel & Co. April **1906**, 61.

Fig. 45.
Grubbing of sassafras roots.

Composition. The odor and the most important properties of the sassafras oil are due to its principal constituent, *safrol*, $C_{10}H_{10}O_2$. This substance was observed by Binder[1] in 1821, it having separated out in a crystalline condition from the oil. Later investigators[2] restricted their experiments to the action of chlorine, bromine, &c. on the oil and the safrol contained therein. Thus, while Faltin[3] neutralized with lime and distilled with steam an oil that had been saturated with chlorine, he discovered a second constituent, *viz.*, the ordinary *camphor*[4].

The name safrol was introduced by E. Grimaux and J. Ruotte[5] who also ascertained the composition of the substance as $C_{10}H_{10}O_2$. In addition, they isolated a fraction $C_{10}H_{16}$ boiling between 155 and 157° and named the hydrocarbon *safrene*. They also observed a phenol which had the odor of cloves and which yielded a green color with ferric chloride. Its identity with *eugenol* was later established by Pomeranz[6].

A better insight into the composition of the oil, however, was first obtained by Power and Kleber[7] who examined an oil distilled by themselves.

The air-dried root bark yielded 7,4 p.c. of oil; d_{15° 1,075 and $\alpha_D + 3^\circ 16'$. After most of the safrol had been removed by freezing, the eugenol (m. p. of benzoyl eugenol 69°) was shaken out with lye. The oil, freed from both safrol and eugenol, wasthen fractionated. Fraction 155 to 160° revealed itself as *α-pinene* (m. p. of nitrol benzylamine base 123°). Fraction 160 to 175° contained *phellandrene* as was shown by its nitrite. Hence the so-called safrene of Grimaux and Ruotte is nothing more nor less than pinene.

From the next higher fraction camphor (m.p. of camphoroxime 115°) separated which proved to be the common dextro-

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[1] Buchner's Repertorium f. d. Pharm. **11** (1821), 346.

[2] Bonastre, Journ. de Pharm. et Chim. II. **14** (1828), 645; Trommsdorff's Neues Journal der Pharm. **19**, I. (1829), 210. — Saint-Èvre, Annal. de Chim. et Phys. III. **12** (1844), 107. — Compt. rend. **18** (1844), 705; Liebig's Annalen **52** (1844), 396.

[3] Liebig's Annalen **87** (1853), 376.

[4] The statement made by G. R. Pancoast and W. A. Pearson (Americ. Journ. Pharm. **80** (1908), 219), *viz.*, that sassafras oil contains no camphor is evidently based on an insufficient knowledge of the literature upon this subject.

[5] Compt. rend. **68** (1869), 928.

[6] Monatsh. f. Chem. **11** (1890), 101; Chem. Zentralbl. **1890**, II. 62.

[7] Pharm. Review **14** (1896), 101.

gyrate modification. Its quantitative determination — reduction to borneol and acetylation of this alcohol — showed that the oil contains 6,8 p.c. of camphor. Fraction 260 to 270° presumably contains a sesquiterpene.

According to this investigation, oil of sassafras consists of 80 p.c. safrol, 10 p.c. pinene and phellandrene, 6,8 p.c. *d*-camphor, 0,5 p.c. eugenol, high boiling portions, sesquiterpene and residue about 3 p.c. = 100,3 p.c.

Adulteration. In America sassafras oil is very often adulterated with camphor oil. Indeed it may be said that a strictly pure oil is rarely met with in commerce. Inasmuch as camphor oil contains all the constituents of sassafras oil, its detection is exceedingly difficult. It can be proved only when the physical constants, more particularly the boiling temperature, deviate greatly. Fractions of camphor oil, the specific gravity of which correspond to that of sassafras oil, are sold as "artificial sassafras oil".

299. Sassafras Leaf Oil.

So far as is known, the oil of sassafras leaves has been distilled but once. From fresh leaves Power and Kleber[1]) obtained 0,028 p.c. of an oil with an exceedingly pleasant odor reminding of lemons: d_{15° 0,872 and $\alpha_D + 6°25'$.

The lowest boiling fraction consists of a mixture of *α-pinene* (nitrol benzylamine) and *myrcene.* This representative of the olefinic terpenes, which have been found in a number of volatile oils, *e.g.* bay oil, oil of hops, origanum oil and oil of rosemary, was hydrated by means of Bertram's method. The resulting alcohol had the odor and boiling point of linalool. The alcohol was further identified by its oxidation product, citral, and the condensation product of the latter with naphthylamine and pyrouvic acid. The third terpene found in sassafras leaf oil is *phellandrene* (nitrite). In addition the presence of a *paraffin* (m.p. 58°) and of a *sesquiterpene* was established.

Of oxygenated constituents sassafras leaf oil contains *citral* (citryl-β-naphthocinchoninic acid), as well as the two isomeric alcohols *linalool* and *geraniol,* both of which occur free and as *acetate* and *valerate.*

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[1]) Pharm. Review 14 (1896), 103 ff.

300. Trawas Leaf Oil.

The leaves of *Litsea odorifera,* Valeton, one of the *Lauraceæ* of Java, are known there as *trawas* leaves and are sold as a popular remedy. According to van Romburgh[1]) they yield a volatile oil of the following properties: d_{15° 0,836 to 0,846; α_D — 0° 10′ to — 7° (in a 200 mm. tube). The bulk of the oil distils at 233° (120 to 125° under 10 mm. pressure). With semicarbazide it forms a semicarbazone melting at 116°, from which a ketone was regenerated. This ketone van Romburgh treated with potassium permanganate and thus obtained another ketone (m.p. 12°; b.p. 234°; d_{17° 0,829; m.p. of semicarbazone 124°) which proved to be *methyl nonylketone.* From the oxidation liquid, an acid $C_{10}H_{18}O_3$, m.p. 49°, *viz.,* 2-ketodecylic acid, was isolated. Upon oxidation with chromic acid and sulphuric acid, it yielded suberic acid, whereas upon oxidation with sodium hypobromite it yielded azelaic acid and carbon tetrabromide. Hence the unsaturated ketone contained in the oil must be *nonylene-1-methyl ketone.* Inasmuch as the semicarbazone mixture obtained from the original oil could not be resolved into its components by recrystallization, the regenerated ketone mixture was brominated with a methyl alcoholic solution of bromine. When thus treated it was almost exclusively the unsaturated ketone which reacted. After the saturated ketone had passed over, the dibromide distilled at 204° (15 mm.). From this the bromine was removed by means of zinc dust and alcohol, whereby a ketone with the following properties resulted: m.p. — 7°; b.p. 235°; $d_{11,5^\circ}$ 0,848; mol. refr. 52,47; computed for $C_{10}H_{20}O/\overline{\overline{1}}$ 52,51.

In like manner the alcohols of the trawas oil were separated. They proved to be l-*methyl*-n-*nonylcarbinol* (α_D — 5° 40′) and *undecene-1-ol-10* (b. p. 233°; d_{10° 0,835). The methylnonylcarbinol was characterized by oxidation to methyl-*n*-nonylketone. The undecenol yielded, upon oxidation with chromic acid and sulphuric acid, a ketone the semicarbazone of which melted at 113°. Upon oxidation with potassium permanganate it yielded 2-ketodecylic acid.

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[1]) Koninkl. Akad. Wetensch. Amsterdam, Meeting of Oct. 28, 1911, p. 325; Report of Schimmel & Co. April 1912, 121.

Four oils labeled as *Trawas olie*[1]), when examined in the laboratory of Schimmel & Co., revealed the following properties: d_{15° 0,9084 to 0,9222; $\alpha_D - 18^\circ 7'$ to $-20^\circ 54'$; n_{D20° 1,46377 to 1,46506; soluble in 1 vol. or more of 80 p.c. alcohol, the diluted solution showing faint opalescence. One of the principal constituents is *cineol*[2]), the presence of which could be recognized by its odor. In other respects the odor reminded one of that of cardamoms.

301. Tetranthera Oil.

Origin. *Tetranthera polyantha* var. *citrata,* Nees (family *Lauraceæ*) is a shrub which grows in the Himalayas and in the Indian archipelago, more particularly in Java where it is known as *Ki-Lemolo.* Its fruits, leaves and bark possess a strongly aromatic odor, due to volatile oil.

OIL OF THE FRUITS.

The fruits are sometimes designated as citronella fruits and, in India, are regarded as a panacea. Upon distillation they yield 3,9 to 5,5 p.c. of an oil with a strong odor resembling that of verbena oil. Hence it is also called Java verbena oil. d_{15° 0,885 to 0,896; $\alpha_D + 6$ to $+ 13^\circ$; aldehyde content determined with bisulphite 73 to 86 p.c., with sulphite 64 to 75 p.c. The oil contains *citral*[3]) but no citronellal[4]). In addition it contains 19 p.c. of alcohol, presumably *geraniol,* and 2 p.c. of ester[4]).

OIL OF THE BARK.

Yield 0,13[5]) to 0,81 p.c.[6]); d_{15° 0,866 to 0,906[7]); $\alpha_D + 10$ to $+ 21^\circ$; E.V. after acetylation 230 to 252. Judging from the melting

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[1]) According to de Clerq (*Nieuw plantkundig woordenboek voor Nederlandsch-Indië,* Amsterdam 1909, p. 310) the word *Trawas* is also used to designate a fern, *viz.,* the *Polypodium quercifolium,* L. and possibly also the dried leaves of *Tetranthera brawas,* Bl.

[2]) Report of Schimmel & Co. April **1912**, 121.

[3]) Schimmel's Bericht October **1888**, 44. The specific gravity, *viz.,* 0,980, recorded in this report presumably is due to a misprint and should read 0,890. In two distillates obtained later 0,894 and 0,896 were found.

[4]) Compt. rend. **146** (1908), 349. — Bull. Soc. chim. IV. **3** (1908), 383. — Berichte von Roure-Bertrand Fils October **1907**, 20.

[5]) Jaarboek dep. Landb. in Ned.-Indië, Batavia **1907**, 67.

[6]) Report of Schimmel & Co. April **1905**, 87.

[7]) *Ibidem* April **1909**, 87.

point of the naphthocinchoninic acid, which lay between 220 and 225°, Schimmel & Co.[1]) concluded that the aldehydes of the oil consist of a mixture of *citral* and *citronellal*. E. Charabot and G. Laloue[2]) confirm this supposition. In one oil they found 8 p.c. citral, 10 p.c. citronellal, 56,5 p.c. alcohols $C_{10}H_{18}O$ (geraniol?) and 2,4 p.c. esters.

OIL OF THE LEAVES.

Yield 5,4 p.c.[1]); $d_{15°}$0,899 to 0,904; α_D —12 to —16°. It contains *cineol* (m. p. of iodol compound 111°)[1]). One oil, tested according to the phosphoric acid method, yielded 21,2 p.c.[2]); another oil yielded 35 p.c. regenerated from the solid resorcinol compound[3]). *Citral* was likewise present (m.p. of naphthocinchoninic acid 198 to 200°)[1]) but not citronellal. Twice[2])[1]) 6 p.c. of aldehyde were found (sulphite method), once[4]) 22 p.c. In one oil the acetylation method revealed the presence of 21,2 p.c. alcohol $C_{10}H_{18}O$ (geraniol?).

302. Oil of Cryptocaria moschata.

Cryptocaria moschata, Nees et Mart. is a Brazilian tree, 10 to 15 m. high. It is known popularly as *Nos moscato do Brasil* or Brazilian nutmeg. The ripe fruits are somewhat smaller than nutmegs and have a strongly aromatic odor resembling that of a mixture of laurel, sassafras, cajuput and nutmeg.

Ten kilos of fruits deprived of their fleshy pericarp and comminuted, yielded upon distillation with water 37 g. of volatile oil[5]). This was limpid, yellowish-brown in color, of penetrating aromatic odor and burning, spicy taste. $d_{15°}$ 0,917. In 90 p.c. alcohol it is soluble in all proportions.

303. Oil of Cryptocaria pretiosa.

Cryptocaria pretiosa, Mart. (*Mespilodaphne pretiosa,* Nees et Mart.; *Ocotea pretiosa,* Benth. et Hook.[5]); Ger. *Mispellorbeer;*

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[1]) Report of Schimmel & Co. April **1905**, 87.

[2]) Footnote 4, p. 499.

[3]) Report of Schimmel & Co. April **1909**, 87.

[4]) Jaarboek dep. Landb. in Ned.-Indië, Batavia **1907**, 67.

[5]) Th. Peckolt, Pharm. Review **14** (1896), 248.

family *Lauraceæ)* is a tree 5 to 15 m. high and a native of northern Brazil. It is known locally as *Pao pretiosa, Casca pretiosa, Canelila,* the famous cinnamon of the Orinoco, and as *Pereirora.* The drug consisting of twigs, bark and wood is known as *Priprioca*[1]). All parts of the plant are rich in volatile oil.

OIL OF THE BARK.

The bark consists of canaliculate pieces which are one meter in length, 6 to 8 cm. wide and 1 cm. in thickness. Odor and taste are pleasantly aromatic and cinnamon-like.

Upon distillation the bark yielded 0,83[2]) to 1,16 p. c. of oil with a strong, cinnamon-like odor and a specific gravity of 1,118[3]) to 1,120[2]). Although the odor would seem to indicate cinnamic aldehyde, this substance does not appear to be present in the oil. When shaken with sodium acid sulphite, no crystalline product separated[3]). The behavior of the oil towards potassium hydroxide solution indicates the presence of a *lactone*[2]).

From a drug labelled new coto bark[4]), C. Hartwich[5]) obtained 1,2 p.c. of oil: d 1,108, $\alpha_D - 2°40'$. On account of its cinnamon-like odor, the oil was shaken with bisulphite but did not react. However, 90 p.c. of the oil were dissolved by potassium hydroxide solution.

OIL OF THE TWIGS AND LEAVES.

The oil obtained from the twigs and leaves has a pleasant odor reminding one of linaloe oil. $d_{15°}$ 0,8912; $\alpha_D + 7°20'$; $n_{D20°}$ 1,469; A.V. 1,4; S.V. 13,3; S.V. after acetylation 165,2; soluble in 1¼ vol. of 70 p. c. alcohol and in every proportion in 80 p. c. alcohol. The oil appears to consist principally of linalool[6]).

OIL OF THE WOOD[6]).

Upon distillation the oil separated into a heavier and a lighter portion. The combined oil had the following proper-

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[1]) Bericht von Roure-Bertrand Fils October **1910**, 3. The report of the botanical anatomical investigation by E. G. and A. Camus recorded in this report is supplemented by four plates. — G. Laloue, Bull. Soc. chim. IV. **11** (1912), 602.

[2]) Report of Schimmel & Co. April **1913**, 76.

[3]) *Ibidem* April **1893**, 71.

[4]) Comp. also p. 415.

[5]) Arch. der Pharm. **237** (1899), 430.

[6]) Bericht von Roure-Bertrand Fils October **1910**, 19.

ties: d_{15° 0,9808; $\alpha_D + 7° 12'$; n_{D20° 1,519; A.V. 2,1; S.V. 128,1; S.V. after acetylation 219,8. The oil contains large amounts of esters, presumably of *geraniol* and *linalool.* The acids obtained upon saponification consisted in part of *benzoic acid* (m. p. 119 to 120°[1])).

304. Kuro-Moji Oil.

Oleum Kuromoji. — Kuromojiöl. — Essence de Kuro-moji.

Origin. *Lindera sericea,* Bl. (family *Lauraceæ*) is a shrub that occurs in all of the mountainous regions of Japan[2]). All parts contain volatile oil, small amounts being contained even in the wood, which is used universally for the manufacture of toothpicks.

LEAF OIL.

The oil was introduced into European commerce by Schimmel & Co. in 1889. It is obtained from the leaves and young shoots. The distillation is conducted on a small scale by farmers who restrict their operations to the shrubs growing on their own land.

Properties. Kuro-moji leaf oil is dark yellow in color and possesses a delicately aromatic and balsamic odor. d 0,890 to 0,905; $\alpha_D - 0° 4'$.

Composition. According to W. Kwasnik[3]) the oil contains two terpenes and two oxygenated constituents, *viz.,* d-*limonene* (m. p. of tetrabromide 104°), *dipentene* (m. p. of tetrabromide 124°), *terpineol* (m. p. of terpinyl phenyl urethane 109,5°) and l-*carvone* which occurs but very rarely in volatile oils (m. p. of hydrogen sulphide compound 214°).

KURO-MOJI OIL DISTILLED FROM SOME OTHER PART OF THE PLANT THAN THE LEAVES.

An oil that was likewise designated kuro-moji oil, but which differed from it in its properties and hence must be regarded

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[1]) Bericht von Roure-Bertrand Fils October 1910, 20.

[2]) As early as 1712 the shrub was described in Kämpfer's *Amœnitates exoticæ* as *Kuro nohji.* An illustration of the branch may be found in the Chemist and Druggist **47** (1895), 502.

[3]) Arch. der Pharm. **230** (1892), 265.

as being obtained from some other part of the plant, was twice reported upon by Schimmel & Co.[1]).

Properties. A pale yellow oil with a delicate aroma of coriander: d_{15° 0,8947 and 0,8942; $\alpha_D - 14^\circ 29'$ and $-22^\circ 26'$; E.V. 29,87 and 27,3.

Composition. This oil differs greatly in composition from the leaf oil. In addition to lævogyrate terpenes it contains *cineol* (iodol compound), i-*linalool* (m. p. of phenyl urethane 62 to 63°; oxidation to citral; m. p. of citryl-β-naphthocinchoninic acid 196 to 197°) and *geraniol* (m. p. of diphenyl urethane 81,8°) which is present principally as acetate.

305. Spicewood Oil.

Benzoin odoriferum, Nees *(Laurus Benzoin,* L., *Lindera Benzoin,* Meissn., Ger. *Benzoelorbeerstrauch)* is known in North America as spicewood, spicebush, and feverbush. It contains volatile oil in all of its parts, more particularly in the bark and the berries[2]). Locally the bark is used as a domestic remedy.

OIL FROM THE BARK AND TWIGS.

Under the name of spicewood oil it was brought into the market by Fritzsche Brothers of New York in 1885. Its odor recalls that of wintergreen, its specific gravity is 0,923, and it boils between 170 and 300°. It consists of hydrocarbons and about 9 to 10 p.c. of *methyl salicylate.* By treatment with caustic soda solution, 16 g. of salicylic acid were isolated from 200 g. oil.

OIL OF THE BERRIES.

The berries contain 4 to 5 p. c. of an oil with an aromatic, spicy and camphor-like odor. It boils between 160 and 270° and has a specific gravity of 0,850 to 0,855.

OIL OF THE LEAVES.

The leaves yield about 0,3 p. c. of oil. The odor of the oil is very pleasant and lavender-like. Specific gravity 0,888.

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[1]) Report of Schimmel & Co. April 1904, 95 and April 1907, 61.

[2]) Schimmel's Bericht October 1885, 27 and Report of Schimmel & Co. October 1890, 62.

306. Oil of Laurel Leaves.

Oleum Lauri foliorum. — Lorbeerblätteröl. — Essence de Laurier.

Origin. The laurel oil of commerce is distilled from the leaves of the laurel, *Laurus nobilis,* L. According to the quality of the leaves the yield varies between 1 and 3 p. c.

Properties. Laurel leaf oil is a light yellow liquid, the odor of which at first reminds one of cajuput oil, but later is rather sweetish. d_{15° 0,915 to 0,932; α_D — 15 to — 18°; n_{D20° 1,467 to 1,477; A.V. up to 3,0; E.V. 28 to 50; E.V. after acetylation 58 to 78 (2 determinations); soluble in 1 to 3 vol. of 80 p.c. alcohol; some oils, particularly French ones, are also soluble in from 3 to 10 vol. of 70 p.c. alcohol. In addition to the oils distilled in France and Germany, other kinds are in the market. In this connection mention should be made of oils of very good quality distilled along the coast and in the islands of the Mediterranean and in Palestine. In the accompanying table the properties of various oils have been compiled[1]: —

	d_{15°	α_D	n_{D20°	A. V.	E. V.	E. V. after acetyl.	soluble
German and French . .	0,915 to 0,932	—15° to —18°	1,467 to 1,477	up to 3,0	28 to 50	58,3 to 77,7	in 1 to 3 vol. of 80 p.c. alc., some (part. French) sol. in 3 to 10 vol. of 70 p.c. alc.
Fiume . . .	0,9281	—13° 52′	1,47156	1,0	31,9	—	in 2,5 vol. and more of 70 p.c. alc.
Corfu	0,9177 to 0,9211	—16° 40′ to —21° 40′	1,46862 to 1,47107	up to 1,5	29,8 to 43,8	36,2 to 83,5	in 1 to 2 vol. of 80 p.c. alc., mostly in 3 to 6 vol. of 70 p.c. alc.
Cyprus . . .	0,934 to 0,944	— 4° 40′ to — 5° 40′	1,466 to 1,474	up to 1,8	22 to 25	62 to 96	in 2 to 3 vol. or more of 70 p.c. alc.
Palestine . .	0,916 to 0,924	—14° to —21°	1,465 to 1,469	up to 2,2	21 to 49	43,2 to 81,4	in 1 to 2 vol. of 80 p.c. alc., some in 4 to 7 vol. of 70 p.c. alc.
Asia Minor	0,9268	—15° 50′	1,46575	0,8	34,8	60,1	in 1 vol. or more of 80 p.c. alc.
Dalmatia . .	0,9268	—14° 36′	1,46813	0,5	29,9	68,6	in 2,5 vol. or more of 70 p.c. alc.[2].
Syria	0,9161	—14° 20′	—	—	—	—	in 1 vol. or more of 80 p.c. alc.[3].

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[1] Report of Schimmel & Co. April 1909, 60.

[2] *Ibidem* October 1911, 56.

[3] Berichte von Roure-Bertrand Fils April 1911, 26.

Composition. As was first pointed out by Wallach[1]), the lowest fraction contains *α-pinene* (m.p. of nitrol piperidine 118°), more particularly the lævogyrate modification thereof[2]), presumably also *phellandrene*[2]). Of oxygenated constituents the following have been identified: *cineol*[1]), l-*linalool* (m. p. of phenylurethane 65°; oxidation to citral)[3]), *geraniol* (m.p. of diphenylurethane 83°; oxidation to citral, m.p. of citryl-β-naphthocinchoninic acid 197°)[4]), *eugenol* (m.p. of benzoyleugenol 70°)[5]) and *methyleugenol* (m. p. of veratric acid 178°)[3]). The highest boiling portions appear to contain sesquiterpenes and sesquiterpene alcohols[4]) that have not been further investigated.

The acid reaction of the oil is due to acetic, *iso*butyric and *iso*valeric acids[4]). The esters are composed on the one hand of the alcohols linalool and geraniol, also of the phenol eugenol, on the other hand of a mixture of acids in which Thoms and Molle have identified the following acids: *acetic acid, valeric acid, capronic acid* and an acid $C_{10}H_{14}O_2$ which melts at 146 to 147°.

As to the quantitative composition of the oil, Thoms and Molle found it as follows: free eugenol about 1,7 p.c., esterified eugenol about 0,4 p.c., cineol 50 p.c. The acid $C_{10}H_{14}O_2$ constitutes 0,07 p.c. of the oil. The higher fatty acids were present in the ratio of 40 p.c. of valeric acid to 60 p.c. of capronic acid.

307. Laurel Oil from the Berries.

Origin. The oil obtained by pressure from the fruits of the laurel tree consists of a mixture of fatty oil with about 2,5 p.c. of volatile oil[6]). It finds application in the drug stores under the designation *Oleum Lauri expressum.* The volatile oil appears to be of no practical value, hence it has been prepared only occasionally for scientific purposes. The yield, computed from the berries, amounts to about 1 p.c.

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[1]) Liebig's Annalen **252** (1889), 96.

[2]) H. Hænsel, Chem. Zentralbl. **1908**, I. 1837.

[3]) Report of Schimmel & Co. April **1906**, 43.

[4]) H. Thoms and B. Molle, Arch. der Pharm. **242** (1904), 161; Arbeiten aus dem pharmazeut. Institut Berlin **1** (1903), 95.

[5]) Report of Schimmel & Co. April **1899**, 29.

[6]) H. Matthes and H. Sander, Arch. der Pharm. **246** (1908), 165.

Properties. The oil of the berries is somewhat more viscid and its odor is a little less delicate than that of the leaves. Because of its lauric acid content it occasionally congeals at temperatures above 0°. $d_{15°}$ 0,915 to 0,935. The angle of rotation, determined for a single oil was — 14° 10′. The same oil was insoluble in 80 p.c. alcohol, but dissolved in ½ vol. or more of 90 p.c. alcohol.

Composition[1]. The lowest fractions of the fruit oil contain the same constituents[2] as does the leaf oil, *viz.,* but very little *α-pinene* (m. p. of nitrol benzylamine 122 to 123°) and much *cineol* (cineol hydrobromide). The supposed *laurene*[3] has revealed itself as a mixture of these two substances. The portion of the oil which boils at about 250° (d 0,925; α_D — 7,2°) is of the composition $C_{15}H_{24}$, hence a *sesquiterpene*[4].

Another constituent of the fruit oil, the amount of which varies with the length of the distillation, is *lauric acid.* It can be withdrawn from the oil by means of caustic alkali; when pure, it melts at 43°[5]. In addition to these substances, the laurel berry oil contains *ketones* and *alcohols* which form solid compounds with sodium. Regenerated with water, they constitute a viscid oil which under 20 mm. pressure distills over between 71 and 184°.

The statements made by Gladstone[6] that eugenol is contained in the oil of the laurel berries was not confirmed by Blas and Müller. Although Gladstone designates his oil as a bay oil from the berries of *Laurus nobilis,* it is not impossible that his oil was, in all probability, a bay oil which consisted largely of eugenol.[7]

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[1] The earliest investigations were conducted by Bonastre (Journ. de Pharm. **10** [1824], 36 and **11** [1825], 3; Repert. f. d. Pharm. I. **17** [1824], 190) and by Brandes (Arch. der Pharm. **72** [1840], 160).

[2] Wallach, Liebig's Annalen **252** (1889), 97. — J. W. Brühl and F. Müller, Berl. Berichte **25** (1892), 547.

[3] Brühl, Berl. Berichte **21** (1888), 157.

[4] C. Blas, Liebig's Annalen **134** (1865), 1.

[5] Brühl and Müller, *loc. cit.*

[6] Journ. chem. Soc. II. **2** (1864), 1; Jahresb. f. Chem. **1863**, 545.

[7] As becomes apparent from a paper by Ashton (Chemist and Druggist, July 2, 1892) it is evident that in England the terms bay oil and laurel oil are frequently confounded.

308. Guiana Sandalwood Oil.

From a lot of sandalwood from Guiana, about the botanical origin of which nothing could be ascertained, P. Jeancard and C. Satie[1]) distilled several oils the constants of which fluctuated between the following limits: d_{15° 0,9630 to 1,0122; $\alpha + 0^\circ 30'$ to -6°; S. V. 13 to 65; E. V. after acetylation 65 to 117; soluble in 1,5 to 12 vol. of 75 p.c. alcohol and in 0,8 to 1,1 vol. of 80 p.c. alcohol. The oils contained from 59 to 80 p.c. of a fraction that boiled between 155 and 160° (20 mm.) (d_{26° 1,024 to 1,037; $\alpha - 4^\circ 20'$ to -6°; soluble in 1,8 vol. of 70 p.c. alcohol).

The properties of the oil depends very largely on the nature of the material from which it is prepared. For this reason oils were distilled from the branches (I), the trunk wood (II) and from pieces of the bark (III), the constants of which are herewith tabulated.

	I	II	III
d_{15°	0,9665	0,9806	0,9968
α	$-6^\circ 16'$	0	$+0^\circ 30'$
Solubility in 85 p.c. alcohol .	0,4	0,4	0,3
„ „ 80 „ „ .	1	1	0,9
„ „ 75 „ „ .	1,7	10,8	20
S. V.	44,1	46,9	13,3
E. V. after acetylation . . .	92,4	96,6	65,8
Percentage of fraction 155 to 160° (20 mm.)	44 %	51,4 %	49,8 %
Percentage of fraction 160 to 165° (20 mm.)	9,4 %	12,6 %	24 %

Fraction 155 to 160° (20 mm.) contained a constituent which boiled between 155 and 159° (20 mm.) (d_{23° 1,0378; $\alpha_D - 6^\circ$; soluble in 1,6 vol. of 70 p.c. alcohol, in 2,7 vol. of 65 p.c. alcohol and in 6,5 vol. of 60 p.c. alcohol) which Jeancard and Satie have named *maroniol* and which probably is a tertiary alcohol. The alcohol cannot be acetylated according to the ordinary method. When heated with acetic acid anhydride for an hour, a saponification value of 147 was found, after three hours one of 168, and after five hours one of 189.

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[1]) Perfum. and Essent. Oil Record 2 (1911), 79.

In 1910, Schimmel & Co.[1]) also distilled Guiana sandalwood. According to Dr. Giessler, Custodian at the Botanical Institute of the University of Leipzig, the wood belongs to the family *Lauraceæ* and is probably derived from one of three species of *Acrodiclidium* or *Ocotea.* The constants of the oils were:

	I	II	III
Yield	3,28 %	2,48 %	4,14 %
d_{15°	1,0036	0,9570	0,9990
α_D	$-4^\circ 26'$	$-0^\circ 46'$	$-0^\circ 44'$
A. V.	1,9	3,7	0,9
E. V.	10,6	68,8	2,4
E. V. after acetylation .	72,9	113,3	54,1
Solubility in 80 p.c. alcohol	1 vol. or more	2 vol. or more	1 vol. or more

309. Shiu Oil.

Origin. Under the designation shiu oil (Ger. *Schiuöl*), the Japanese have offered, as a substitute for linaloe oil, an oil rich in linalool, which is distilled in Formosa and said to be derived from a variety of the camphor tree. Apparently this is the same oil which was examined in 1903 by K. Keimazu[2]). According to this investigator it seems doubtless that the oil-yielding plant in question belongs to the *Lauraceæ.* The oil is distilled by the natives in central Formosa and is placed upon the market partly mixed with camphor oil. They call it *Schú-Yu, i. e.* bad-smelling oil. Inasmuch, however, as this name does not apply, Shimoyama has named it *Oleum apopinense* or apopino oil after the place of production, *viz.,* Aupin.

Under the title "Shiu oil" there appeared in 1912 an illustrated brochure by K. Nagay. As it is written in Japanese and has not been translated, nothing can be stated about its contents.

Properties. The oil referred to above as having been examined by Keimazu had the following constants: d_{15° 0,9279; $\alpha_D + 17^\circ 6'$ to $+ 17^\circ 19'$. Very different in their properties

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[1]) Report of Schimmel & Co. October 1911, 82.

[2]) Journ. of the Pharm. Soc. of Japan No. 253, March 1913; No. 258, August 1903. An abstract of the paper submitted by T. Kumagai may be found in the Report of Schimmel & Co. October 1903, 10 and April 1904, 10.

were 8 samples of shiu oil received in Europe from Japan in recent years: d_{15° 0,870 to 0,8952; $\alpha_D - 0^\circ 51'$ to $-15^\circ 30'$; A. V. up to 0,6; E. V. 0,5 to 28; $C_{10}H_{18}O$ content 65,5 to 90 p.c. determined by acetylation of the oil after dilution with 4 vol. of xylene; soluble in 1,8 to 10 vol. of 70 p.c. alcohol.

The cause for these deviations may be explained in two ways. Either the oil examined by Keimazu was adulterated with camphor oil and the substances found, *viz.,* camphor, eugenol, safrol and cineol, were in part due to this adulterant, or the samples examined later were no normal oils but fractions greatly enriched in linalool[1]).

Composition. Keimazu identified the following constituents: 1. *Formaldehyde* (Rimini-Vitali's reaction). 2. d-*α-Pinene* (m.p. of nitrol piperide 118 to 119°). 3. *Cineol* (m.p. of hydrobromide 53 to 54°; of cineoliodol 120°). 4. *Dipentene* (m.p. of tetrabromide 124 to 125°). 5. Apopinol. Keimazu obtained a fraction which upon oxidation yielded citral (elementary analysis; m. p. of naphthocinchoninic acid 200 to 202°). Inasmuch as the odor of the acetate of the alcohol differed from that of linalool, he supposed that he had a new alcohol which he named apopinol. There can be no doubt, however, that he had impure *linalool.* 6. d-*Camphor* (m. p. 176°; m. p. of oxime 117 to 118°). 7. *Eugenol* (m.p. of benzoate 69°). 8. *Safrol* (b.p. 230 to 232°; m.p. $+8$ to $+10^\circ$; oxidation to homopiperonylic acid, m. p. 127 to 128°; *iso*safrol, oxidation to piperonal, m. p. 37°).

Family: PAPAVERACEÆ.

310. Oil of Celandine.

Upon steam-distillation of the dry herb of *Chelidonium majus,* L. (family *Papaveraceæ*), H. Hænsel[2]) obtained 0,013 p.c. of a brown oil with a pleasant odor which congealed in the cold and which was soluble in 45 parts of 90 p. c. alcohol. d_{40° 0,9374.

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[1]) Comp. also Perfum. and Essent. Oil Record **3** (1912), 111, 124, 239.

[2]) Apotheker Ztg. **23** (1908), 279. — Chem. Zentralbl. **1908**, II. 1837.

Family: CRUCIFERÆ.

The volatile oils obtained from the crucifers are not contained as such in the parts of plants that yield them, but in the form of glucosides. They result from a process of fermentation, the hydrolysis of the glucosides being brought about by enzymes which are present in the same organs. The products of this hydrolysis are glucose and mustard oils, the latter being esters of *iso*thiocyanic acid (See mustard oil, p. 522). According to L. Guignard[1]) the cruciferous glucosides are located in the parenchymatous tissues, more particularly those of the bark and the embryo of the seeds. The enzyme, mostly *myrosin,* is deposited in special "myrosin cells" that are distributed throughout all the tissues, including those of the pericarp. Whether the enzyme of all crucifers is the same has not yet been determined. This much, however, has been established, that the enzymes of this family are able to hydrolyze the glucosides contained therein.

According to T. Bokorny[2]) the action of the enzyme is restricted to certain limits of temperature. Water of 75° kills the myrosin in fifteen minutes, a fact to be borne in mind when distilling the volatile oils. Moreover, the enzymes are rendered inactive by the presence of certain substances, such as formaldehyde, 1 p. c sulphuric acid, a 0,1 p. c. solution of corrosive sublimate, or silver nitrate. However, for the purpose of hydrolyzing the glucoside, the destroyed enzyme of the plant in question can be replaced by the water-soluble ferment of comminuted white mustard.

Not all the mustard oil glucosides have been isolated in the pure state. In some instances conclusions have been drawn from the end products of the reaction as to the nature of the glucoside.

Of this group of glucosides, *sinigrin,* the glucoside of black mustard, has been known longest and is most thoroughly investigated. In addition to black mustard it occurs in *Thlaspi arvense,* L., *Cochlearia Armoracia,* L., *Sisymbrium Alliaria,* Scop., and

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[1]) Compt. rend. 111 (1890), 249.

[2]) Chem. Ztg. 24 (1900), 771, 817, 832.

Brassica Rapa, L. *Glucotropæolin* (hydrolyzable to benzyl mustard oil) is found in *Lepidium sativum,* L. and in *Tropæolum majus,* L. belonging to the family *Tropæolaceæ. Glucocochlearin* (yielding *sec.* butyl mustard oil) is contained in *Cochlearia officinalis,* L. and *Cardamine amara,* L. *Gluconasturtiin* (yielding phenylethyl mustard oil) is found in *Nasturtium officinale,* R. Br., in *Barbaræa præcox,* in *Brassica Rapa,* var. *rapifera,* Metzg. and probably also in *Reseda odorata* (family *Resedaceæ*). The glucoside of *Brassica Napus,* L. has been named *gluconapin* (yielding crotonyl mustard oil). Mustard oil-like compounds which are, no doubt, referrable to glucosides, are yielded by *Iberis amara,* L., *Capsella bursa pastoris,* Mönch., *Sisymbrium officinale,* Scop., *Matthiola annua,* R. Br. and other plants[1]).

311. Oil of Garden-Cress.

The oil of common-cress was first prepared by F. Pless[2]) in 1846. He observed that the herb and seeds of *Lepidium ruderale,* L., also the seeds of *Lepidium sativum,* L. and *Lepidium campestre,* R. Br. (family *Cruciferæ*) upon distillation yield sulphur-containing oils which sink in water. He assumed that the oil occurred as such in the herb, but that from the seeds it resulted upon the action of the water. According to whether the herb is comminuted or not, totally different oils are obtained.

A. W. Hofmann[3]) conducted the first scientific examination of the oil. He distilled the non-comminuted herb of *Lepidium sativum,* L. (Ger. *Gartenkresse*) immediately after the flowering period in a wooden still[4]) with water vapor. As the oil remained

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[1]) Comp. the chapter *Die Senföle* in F. Czapek, *Biochemie der Pflanzen,* Jena 1905, vol. II., p. 232. — H. ter Meulen, Recueil trav. chim. des P.-B. **19** (1900), 33 and **24** (1905), 444. — A. Oliva, *Vergleichende anatomische und entwicklungsgeschichtliche Untersuchungen über die Cruciferensamen.* Zeitschr. d. allg. österr. Apoth. Ver. **43** (1905), 1001, 1033, 1073, 1109, 1141, 1169, 1197, 1225, 1253, 1281, 1309, 1343.

[2]) Liebig's Annalen **58** (1846), 39.

[3]) Berl. Berichte **7** (1874), 1293.

[4]) Copper vessels should be avoided for the distillation of this and other sulphur-containing oils, otherwise a partial decomposition with the formation of copper sulphide takes place.

dissolved in the aqueous distillate, it was extracted by shaking with benzene. The yield amounted to 0,115 p. c. The light-yellow crude oil became colorless upon rectification. Three-fourths of the oil boiled at 231,5°, the boiling point of *phenylacetonitrile* or *benzyl cyanide,* $C_6H_5 \cdot CH_2 \cdot CN$. The identity of the oil with this substance was established by converting it into phenylacetic acid melting at 77° and by the analysis of its silver salt. The lower fractions of the oil contain small amounts of a sulphur-containing compound, the composition of which was not determined.

The fact that the herb of the garden-cress produces a pronounced odor of mustard oil, suggests to J. Gadamer[1]) that in all probability the investigation of A. W. Hofmann does not at all refer to the real oil of cress but to a decomposition product thereof, as has been observed in connection with the oil of *Tropæolum majus.* Unless the herb is very carefully comminuted before distillation, the enzyme which it contains cannot reach the glucoside deposited in other cells, but is destroyed by the heat. Hence the hydrolysis of the glucoside into benzyl mustard oil and glucose cannot take place, but the direct action of hot water on the glucoside causes benzylcyanide, found by Hofmann, to be formed[2]).

The seeds of the garden-cress presumably contain the same substance which causes the formation of oil in the herb. If the ground seeds are subjected to the action of water[1]) and some white mustard seed for several hours and then distilled with steam, the distillate separates a slightly yellow-colored oil, the odor of which cannot be distinguished from that of the garden nasturtium *(Tropæolum majus).* When treated with alcoholic

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[1]) Arch. der Pharm. 237 (1899), 508.

[2]) H. ter Meulen (Recueil trav. chim. des P.-B. 19 [1900], 42) is of opinion that the abnormal results obtained by A. W. Hofmann were not due to imperfect comminution, as assumed by Gadamer, but to the large amount of material used for a single distillation. However, the distillation of a larger amount of material need not require more time than that of a small amount, provided the size of the still and the supply of steam be adequate. But if the material is not comminuted, the distillation lasts much longer. Consequently both expressions of opinion are in practical agreement as to results.

ammonia, crystals of benzyl thiourea, melting at 162°, separate. Hence the oil from the seeds of the garden-cress consists in part of *benzyl mustard oil* which owes its formation to a glucoside called *glucotropæolin*[1]), the latter being hydrolyzed by the enzyme myrosin contained in the white mustard oil. On account of its feeble capacity to crystallize the glucotropæolin from the seed of the garden-cress has not been isolated thus far.

Upon distillation, the fresh herb of *Lepidium latifolium,* L.[2]) yields a sulphur-containing oil that sinks in water.

312. Oil of Thlaspi arvense.

According to F. Pless[3]), an oil is obtained if the herb or seeds of *Thlaspi arvense,* L. are covered with cold water, allowed to stand for some time and then distilled. This oil is colorless, possesses a peculiar, penetrating odor and a leek-like taste. It reminds one both of garlic and mustard.

If the oil is saturated with ammonia and distilled with water, thiosinamine (m. p. 72°) remains behind.

With platinic chloride the same double compound is obtained which T. Wertheim[4]) had obtained from garlic oil. Hence Pless regarded this portion of the oil as identical with garlic oil or allyl sulphide.

However, Semmler[5]) has shown that Wertheim's statements are erroneous and that garlic oil does not contain allyl sulphide. Hence the occurrence of allyl sulphide in the oil of *Thlaspi arvense* is rendered very problematical.

The formation of thiosinamine must be regarded as a proof of the presence of *allyl mustard oil.*

313. Oil of Spoonwort.

Oleum Cochleariæ. — Löffelkrautöl. — Essence de Cochléaria.

Origin. Spoonwort, *Cochlearia officinalis,* L., family *Cruciferæ,* flourishes in the wild state in the proximity of the sea

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[1]) Comp. oil of *Tropæolum majus.*

[2]) Steudel, *Dissert. de Acredine nonnull. Vegetabil.* Tübingen 1805.

[3]) Liebig's Annalen 58 (1846), 36.

[4]) *Ibidem* 51 (1844), 298.

[5]) Arch. der Pharm. 230 (1892), 434.

coasts of the northern continents, also in isolated high areas of the Central European Alps. It is also successfully[1]) cultivated as an economic plant.

Production. In order to obtain good yields, it is absolutely necessary to mix the well comminuted herb with water and to allow it to stand over night. This must be done in order to give the enzyme an opportunity to come into contact with the glucoside which is to be hydrolyzed and which is located in different cells[2]). Dry herb as well as fresh herb may be used. In the former case, however, some powdered white mustard should be added, since the enzyme of the herb becomes inactive upon drying. When fresh herb is used such addition is unnecessary, for Schimmel & Co.[3]) have shown that the yield of oil is not increased thereby. The yield from dry herb amounts to 0,175[3]) to 0,305 p.c.[2]) (computed for fresh herb this amounts to 0,0173 and 0,030 p.c. respectively). The yield from fresh, non-flowering herb amounts to 0,03 to 0,04 p.c., from fresh flowering herb up to 0,048 p.c.

From the seeds an oil can also be obtained upon the addition of white mustard[4]). In its composition this oil is identical with the one obtained from the herb.

Properties. Spoonwort oil has a pungent but not unpleasant odor, similar to that of mustard oil. d_{15° 0,933 to 0,950; $\alpha_D + 52$ to $+ 56^\circ$; soluble in 3 to 10 vol. of 80 p.c. alcohol, occasionally with slight opalescence, also in 1 vol. or more of 90 p.c. alcohol. It contains from 87 to 98 p.c. of butyl mustard oil. (For method of analysis see below.)

Upon fractionation of 42,8 g. the following results were obtained: between 150 and 154° 6,3 g., between 154 and 156° 12,2 g., between 156 and 158° 10,0 g., between 158 and 162° 12,0 g., residue 2 g. The specific gravity of these fractions fluctuated between 0,941 and 0,943, the angle of rotation between $+ 51,41^\circ$ and $+ 62,78^\circ$[5]).

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[1]) E. Lücker, Apotheker Ztg. **21** (1906), 1006.

[2]) J. Gadamer, Arch. der Pharm. **237** (1899), 92.

[3]) Report of Schimmel & Co. April **1900**, 16.

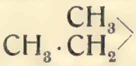
[4]) W. Urban, Arch. der Pharm. **241** (1903), 691.

[5]) Gadamer, *loc. cit.*

Composition. Simon[1]) records the boiling point of the oil as being 156 to 159°. He found that it contains sulphur and that with ammonia it yields a substance similar to thiosinamine.

Geiseler[2]) believed the oil to be free from nitrogen and to contain oxygen, hence regarded it as an hydroxysulphide of allyl.

A. W. Hofmann[3]) ascertained the composition of spoonwort oil. Upon the distillation of the fresh herb, pounded to a pulp and mixed with water, 0,034 p.c. of an oil boiling between 158 and 165° were obtained. Fraction 161 to 163, obtained after several fractionations, yielded upon analysis results that agreed with butyl mustard oil.

Comparison between the natural oil and the synthetic product enabled Hofmann to establish the identity of spoonwort oil with the *iso*thiocyanate of secondary butyl alcohol having the structural formula  ${}^{CH_3}_{CH_3\cdot CH_2}{>}CH\cdot N:C:S$. It is a colorless liquid (d_{12° 0,944; b.p. 159,5°) with the characteristic odor of the oil of spoonwort. When heated with ammonia to 100° it yields an optically active thiourea which melts at 136 to 137°.

As demonstrated by Gadamer[4]), spoonwort oil contains small amounts of several other constituents. Whereas the two lower fractions, *viz.,* up to 156° (see under Properties) consist quantitatively of pure *benzyl mustard oil,* the higher fractions are admixed with a substance which has a lower specific gravity and a higher angle of rotation. Its odor reminds one of that of Curaçao peels, and Gadamer supposes it to be *limonene.*

According to Moreigne[5]), oil of spoonwort contains *raphanol.*

For the preparation of spirit of spoonwort 0,7 g. of the natural oil are dissolved in one litre of dilute alcohol.

For the preparation of this spirit from the dry herb, Gadamer gives the following directions: four parts of dry spoonwort[6]), one part of coarsely comminuted white mustard, forty parts of water,

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[1]) Poggend. Annalen **50** (1840), 377.

[2]) Otto Geiseler, *De Cochlearia officinali ejusque oleo dissertatio.* Berol. 1857.

[3]) Berl. Berichte **2** (1869), 102; **7** (1874), 508.

[4]) *Loc. cit.*

[5]) See Spanish radish oil, p. 529.

[6]) For its preparation from fresh herb comp. E. Lücker, Apotheker Ztg. **21** (1906), 1006.

and fifteen parts of alcohol (90 p.c.). The finely cut herb and the white mustard are covered with water in a glass retort and set aside for 3 hours. The alcohol is then added and 20 parts of spirit are distilled over.

For the analysis, Gadamer[1]) gives the following directions:

To 50 g. of spirit of spoonwort, contained in a measuring flask of 100 cc. capacity, 10 cc. of 1/10-N-silver nitrate solution and 5 cc. of ammonia water are added, the flask is well stoppered and set aside for 24 hours. Enough water is then added to fill the flask to the 100 cc. mark. 50 cc. of the filtrate, to which 4 cc. of nitric acid and a few drops of ferric sulphate have been added, should not require more than 2,5 cc. of 1/10-N-ammonium sulphocyanate solution to produce a red color.

According to these directions, the mustard oil contained in 50 g. of spirit of spoonwort should convert the silver nitrate of at least 5 cc. of the 1/10 normal solution into silver sulphide. According to the equation $C_4H_9NCS + 3NH_3 + 2AgNO_3 = Ag_2S + N{:}C{\cdot}NHC_4H_9(NH_4{\cdot}NO_3)_2$, one molecule of butyl mustard oil (= 115) corresponds to two molecules of silver nitrate (= 340), hence 1 cc. of 1/10-N-silver nitrate (= 0,017 g. $AgNO_3$) is the equivalent of 0,00575 g. butyl mustard oil. Therefore 0,00575 × 5 will yield the butyl mustard oil content of 50 g. of spirit of spoonwort, or 0,00575 × 10, the percentage content. According to this a minimum content of 0,0575 p.c. is required.

According to W. Urban[2]), spirit of spoonwort can also be prepared from the seed.

314. Oil of Horse Radish.

The pungent taste of horse radish, the root of *Cochlearia Armoracia,* L. is due to an oil. According to the investigations of J. Gadamer[3]), this oil in all probability owes its origin to the presence of *sinigrin,* which, when the succulent root is grated, is hydrolyzed, by a ferment that is present, with the formation of a mustard oil. Distilled in glass vessels a yield of 0,05 p.c. is obtained.

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[1]) *Loc. cit.* 107.

[2]) Arch. der Pharm. **241** (1903), 691.

[3]) *Ibidem* **235** (1897), 577.

The crude oil is light yellow in color and has a consistence of cinnamon oil. The rectified oil is colorless, d 1,01. The odor is penetrating, causes tears to flow and cannot be distinguished from that of mustard oil. Like the latter, it causes a burning sensation and produces blisters when applied to the skin.

Oil of horse radish contains sulphur. Basing his conclusions on elementary analysis and on the thiosinamine compound, Hubatka[1]) is of opinion that the oil has the same composition as that of mustard oil. The statements of Hubatka have since been verified by the investigations of G. Sani[2]).

An oil that had been kept with water for years in a well-closed container had disappeared and in its place acicular crystals with a silver lustre had been formed. These had an odor reminding one first of horse radish, later of peppermint and finally of camphor[3]).

315. Oil of Hedge Garlic.

From the *roots* of *Alliaria officinalis,* Andr. *(Sisymbrium Alliaria,* Scop.) (Ger. *Lauchhederich*), T. Wertheim[4]) obtained upon distillation 0,033 p. c. of an oil that could not be distinguished from mustard oil. Like the latter, it yielded a thiosinamine melting at 74°.

Judging from the odor, the *herb* contains the same constituent as garlic oil.

According to F. Pless[5]), the oil from the *seed* consists to the extent of about $^9/_{10}$ of ordinary *mustard oil* and $^1/_{10}$ *garlic oil.*

316. Oil of Eruca sativa.

According to S. Hals and J. F. Gram[6]), the seeds of *Eruca sativa,* Lam., when treated with water and subsequently distilled, yield a volatile oil which contains nitrogen and sulphur and which differs from the mustard oils of the rape seeds.

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[1]) Liebig's Annalen **47** (1843), 153.

[2]) Accad. Linc. **1892**; Report of Schimmel & Co. April **1894**, 36.

[3]) Einhof, Neues Berlinisches Jahrbuch **5** (1807), 365.

[4]) Liebig's Annalen **52** (1844), 52.

[5]) *Ibidem* **58** (1846), 38.

[6]) Landw. Vers. Stat. **70** (1909), 307; Chem. Zentralbl. **1909**, II. 138.

The formation of the oil is attributed to enzyme action, since it is not formed when the enzyme is destroyed with boiling water.

317. Mustard Oil.

Oleum Sinapis. — Senföl. — Essence de Moutarde.

Origin. Black mustard is the designation applied to the seeds of *Brassica nigra,* Koch (*Sinapis nigra,* L.) and *Brassica juncea,* Hooker fil. et Thomson (*Sinapis juncea,* L.), family *Cruciferæ. Brassica nigra* belongs to the European-Asiatic floral area. For the sake of the seed, it is cultivated in most civilized countries, but particularly in Holland, Apulia and the Levant. *Brassica juncea,* however, is cultivated even on a larger scale in Sarepta, in the Russian government Saratow, in East India and in North America[1]). By far the largest amount of seed is used for the preparation of table mustard, a much smaller amount for medicinal purposes and for the distillation of mustard oil.

Commercial seed is frequently a mixture of seeds of different species and is sometimes admixed with the seeds of weeds. Inasmuch as the determination of the parent plant is frequently desirable, reference should here be made to an extensive investigation by C. Hartwich and A. Vuillemin[2]). Not only does the report contain an exhaustive reference to the literature on the subject, but all questions that may come into consideration, such as the anatomical relations of the several seeds, are discussed in detail. Of special value is a table for the determination of the several species based on the microscopic structure of the seed shells.

Production. Mustard oil as such is not contained in the seed, but is formed by a process of fermentation. First the ground seeds[3]) are deprived of their fatty oil as completely as possible

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[1]) Concerning the quantities of mustard seed imported at Hamburg between 1897 and 1909, also concerning their source, a geographical and statistical paper by O. Tunmann supplies interesting information. Apotheker Ztg. **26** (1911), 580.

[2]) Apotheker Ztg. **20** (1905), 162, 175, 188, 199.

[3]) According to the fifth edition of the German Pharmacopœia (comp. also vol. I, p. 605), the mustard oil assay of the seed is conducted in the following manner: To 5 g. of powdered black mustard contained in a flask, 100 cc. of water, having a temperature of from 20 to 25°, are added. The

by hydraulic presses. The crushed oil cakes are mixed with lukewarm water and allowed to ferment for some time. As soon as the fermentation is completed, the oil formed is distilled with

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stoppered flask is set aside for two hours, being shaken repeatedly. 20 cc. of alcohol and 2 cc. of olive oil are then added and the mixture distilled, taking special care to cool the distillate. The 40 to 50 cc. distilling over first are collected in a 100 cc. flask containing 10 cc. of ammonia, and 20 cc. of $^1/_{10}$-N-silver nitrate solution are added. The opening of the flask having been covered with a small funnel, it is heated in a water-bath for an hour. After cooling, the contents of the flask are diluted to 100 cc.; 50 cc. of the clear filtrate, to which 1 cc. of nitric acid and 1 cc. of ferric ammonium sulphate have been added, should require at most 6,5 cc. of $^1/_{10}$-N-ammonium sulphocyanate solution to produce a red color. This corresponds to 0,7 p.c. allyl mustard oil (1 cc. of $^1/_{10}$-N-silver nitrate solution = 0,004956 g. of allyl mustard oil, using ferric ammonium sulphate as indicator).

From the results obtained by D. Raquet (Ann. Chim. analyt. appl. **17** (1912), 174; Chem. Zentralbl. **1912**, II. 457) in an investigation on the analysis of mustard oil in mustard seed, it becomes evident that it is preferable to replace the aqueous maceration by an alcoholic one. According to Raquet, 5 g. of ground mustard seed, 100 cc. of water and 20 cc. of 90 p.c. alcohol are mixed in a flask of 250 cc. capacity, the flask stoppered and heated for an hour from 30 to 35° or set aside at room temperature for 6 hours with frequent shaking. The distillation is conducted from a glycerin bath, the distillate being collected in a 100 cc. measuring flask containing 10 cc. of ammonia (d_{15° 0,925). After about 50 cc. have distilled over, 20 cc. $^1/_{10}$-N-silver nitrate solution are added, the mixture is shaken and the distillation continued until the 100 cc. mark has been reached. The flask is then connected with a reflux condenser and heated to 80 or 85° for an hour. After cooling any loss of water is replaced and the mixture filtered through filter paper free from chlorine. As usual, 50 cc. of the filtrate are titrated with $^1/_{10}$-N-ammonium sulphocyanate solution. If N represents the number of cc. consumed, $10-N$ the number of cc. of $^1/_{10}$-N-silver solution, then $(10-N)\cdot 0{,}198$ is the amount of allyl mustard oil obtained from the 100 g. of powdered mustard seed.

According to this method English mustard yielded 1,386 p.c., Greek 1,198 p.c., that of Merville 1,08 p.c., Sicilian 0,99 p.c., that of Bari 0,99 p.c. and Bombay mustard 0,81 p.c. of allyl mustard oil.

Comp. E. Dieterich, Helfenberger Annalen **1896**, 332. — J. Gadamer, Arch. der Pharm. **235** (1897), 58; **237** (1899), 110, 372. — P. Rœser, Journ. de Pharm. et Chim. VI. **15** (1902), 361. — R. Firbas, Zeitschr. d. allg. österr. Apoth. Ver. **42** (1904), 222; Apotheker Ztg. **19** (1904), 53; Report of Schimmel & Co. April **1906**, 45. — Schlicht, Pharm. Ztg. **48** (1903), 184. — A. Vuillemin, Pharm. Zentralh. **45** (1904), 384. — C. Pleijel, Apotheker Ztg. **22** (1907), 521. — M. Kuntze, Arch. der Pharm. **246** (1908), 58. — H. Pénau, Journ. de Pharm. et Chim. VII. **6** (1912), 160.

steam. The yield amounts to from 0,5 to more than 1 p.c. of the original seed.

At a temperature above 70° fermentation no longer takes place, since the myrosin coagulates and becomes inactive.

It has been claimed that black mustard does not contain sufficient myrosin to hydrolyze all the glucoside sinigrin present. In order to obtain better results, the addition of some white mustard to the fermentation mixture has been recommended. The investigations by H. J. Greenish and D. J. Bartlett[1]) in respect to this have demonstrated that this supposition is wrong. Not only do the seeds contain sufficient myrosin to hydrolyze the sinigrin present, but the amount of this enzyme is so great at times that it suffices to hydrolyze thirteen times the quantity of sinigrin present in the seeds. The addition of white mustard during the fermentation does not improve the yield of oil.

According to Greenish and Bartlett, the addition of sodium fluoride, recommended by Brioux[2]), acts very favorably, 0,4 p.c. of the fluoride being sufficient. The sodium fluoride does not interfere with the action of the myrosin, but kills micro-organisms that destroy the allyl mustard oil.

Another observation, made by Greenish and Bartlett, is also of interest, *viz.,* that black mustard, harvested in 1905, when tested in 1911 revealed a normal myrosin content, thus showing that storage does not appear to injure the myrosin.

In the course of the chemical reaction which takes place in the formation of mustard oil, the glucoside of the mustard seed, sinigrin (potassium myronate), is hydrolyzed by the protein-like enzyme, in the presence of water, with the formation of mustard oil, *d*-glucose and potassium acid sulphate.

$$\underset{\text{Sinigrin}}{C_{10}H_{16}NS_2KO_9} + \underset{\text{Water}}{H_2O} = \underset{\text{Mustard Oil}}{CSNC_3H_5} + \underset{\text{Grape sugar}}{C_6H_{12}O_6} + \underset{\substack{\text{Potassium}\\\text{bisulphate}}}{KHSO_4}$$

In addition other reactions take place which account for two substances that are never entirely absent in mustard oil, *viz.,* allylcyanide (cyanallyl) and carbon disulphide.

According to Gadamer[3]) the mustard oil glucosides are in all probability referable to a hypothetical alkyl iminothiocarbonic acid

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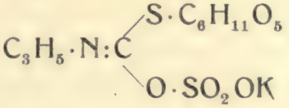
[1]) Pharmaceutical Journ. **88** (1912), 203.

[2]) Annal. Chim. analyt. appl. **17** (1912), 6.

[3]) Arch. der Pharm. **235** (1897), 47. — Berl. Berichte **30** (1897), 2322, 2328.

of the general formula R.N:C(SH)OH. In his opinion sinigrin has the following formula:



$$C_3H_5 \cdot N : C \begin{matrix} \diagup S \cdot C_6H_{11}O_5 \\ \diagdown O \cdot SO_2OK \end{matrix}$$

Hence sinigrin is an allyliminothiolcarbonic acid, in which the hydroxyl hydrogen is replaced by the potassium acid sulphate radical in ester combination, and the sulfhydryl hydrogen by the glucose residue in ether combination.

W. Schneider[1]) is occupied with experiments to produce synthetic compounds of the above general formula and thus to supply experimental proof for this hypothetical conception.

When kept in contact with water for any length of time, or when brought into contact with the copper of stills, mustard oil is converted into allylcyanide with separation of sulphur:

$$\underset{\text{Mustard Oil}}{CSNC_3H_5} + \underset{\text{Copper}}{Cu} = \underset{\text{Allylcyanide}}{CNC_3H_5} + \underset{\text{Copper sulphide}}{CuS}$$

In the case of careless distillation the amount of allylcyanide thus resulting may be so large that the entire oil becomes lighter than water[2]) (Sp.gr. of allyl cyanide 0,835 at 17,5°).

The source of the carbon disulphide found in mustard oil, even in the artificial oil, has not yet been fully ascertained. Experiments[3]) have shown that when mustard oil is boiled with water in a flask connected with a reflux condenser, no carbon disulphide is formed. However, both carbon disulphide and carbon dioxide are formed in appreciable quantities when mustard oil and water are heated in a sealed tube, hence under pressure, for several hours to a temperature of from 100 to 105°. It may be assumed that mustard oil has a greater capacity for reaction in the nascent state and that under these conditions the presence of water causes a reaction to take place in the direction indicated by the following equation.

$$\underset{\text{Mustard Oil}}{2CSNC_3H_5} + \underset{\text{Water}}{2H_2O} = \underset{\text{Allylamine}}{2C_3H_5NH_2} + \underset{\substack{\text{Carbon}\\\text{dioxide}}}{CO_2} + \underset{\substack{\text{Carbon}\\\text{disulphide}}}{CS_2}$$

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[1]) Berl. Berichte **45** (1912), 2961.

[2]) H. Will and W. Körner, Liebig's Annalen **125** (1863), 278.

[3]) Gadamer, Arch. der Pharm. **235** (1897), 53.

Carbon disulphide is also formed by prolonged contact of mustard oil and water. For the detection of carbon disulphide see under "Examination".

The time required to complete the fermentation, so far as pure sinigrin is concerned, is 80 minutes[1]).

As the potassium acid sulphate resulting from hydrolysis has a destructive effect on the mustard oil in course of being formed, a better yield is obtained (if pure sinigrin be employed) by neutralizing the reaction mixture with alkali. However, an excess of alkali should be carefully avoided, as it reduces the yield very considerably. For this purpose calcium carbonate has been found to be a suitable agent.

With mustard meal, however, the results are very different. Not only is calcium carbonate of no use, but it is directly harmful. The cause for this peculiar behavior is unknown. Presumably the sinapine, an alkaloid contained in the mustard seed, is responsible. Being liberated by the calcium carbonate, it possibly reacts with the mustard oil, with the formation of a nonvolatile compound similar to thiosinamine[1]).

Composition. Apart from variable amounts of *carbon disulphide* and *allyl cyanide* present, mustard oil consists almost entirely of *allyl mustard oil* or *allyl*iso*thiocyanate* $CSNC_3H_5$. Possibly traces of the isomeric thiocyanallyl $CNS \cdot C_3H_5$, also of higher boiling (polymeric) substances of unknown composition are present.

C. Pomeranz[2]) assumes that natural mustard oil contains the isomeric propenyl mustard oil $CSN \cdot CH:CH \cdot CH_3$ besides allyl mustard oil $CSN \cdot CH_2 \cdot CH:CH_2$ referred to above. For the synthetic oil this has been proved. Upon oxidation it yields not only much formic acid but acetic acid as well, which can result only from the propenyl mustard oil. However, this reaction has not yet been carried out in connection with natural mustard oil, hence the presence of propenyl mustard oil in the latter has not yet been established.

The chemical reactions of mustard oil are essentially those of allyl*iso*thiocyanate which can be found in every text-book of

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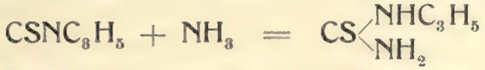
[1]) Gadamer, *loc. cit.*

[2]) Liebig's Annalen **351** (1907), 354.

chemistry. Here only those are recorded that are necessary for an understanding of the tests.

For the quantitative determination of allyl*iso*thiocyanate in mustard oil, its property to form a solid, non-volatile compound with ammonia is utilized. If an excess of ammonia and alcohol be added to mustard oil, the odor of both mustard oil and ammonia disappears, gradually in the cold, more rapidly when heated. At the same time crystals of thiosinamine are formed.



$$\underset{\text{Mustard Oil}}{CSNC_3H_5} + \underset{\text{Ammonia}}{NH_3} = \underset{\text{Thiosinamine}}{CS\begin{matrix}\diagup NHC_3H_5\\ \diagdown NH_2\end{matrix}}$$

Thiosinamine or allylthiourea crystallizes in rhombic prisms which melt at 74°. It has a faintly leek-like odor and taste and is readily soluble in water, alcohol, and ether.

If to a small amount of mustard oil twice its volume of concentrated sulphuric acid is added a violent evolution of carbon oxysulphide[1]) and sulphurous acid[2]) takes place, resulting in the formation of allylamine sulphate which remains in the test tube as a faintly colored liquid, which, under certain conditions, may congeal.

Artificial Mustard Oil is obtained by the interaction of allyl iodide and potassium thiocyanate in alcoholic solution

$$\underset{\text{Allyl iodide}}{C_3H_5I} + \underset{\substack{\text{Potassium}\\ \text{thiocyanate}}}{CNSK} = \underset{\text{Mustard oil}}{CSNC_3H_5} + \underset{\text{Potassium iodide}}{KI}$$

Allylthiocyanide $CNSC_3H_5$ is first formed, but rearranges itself to mustard oil when heated.

Mustard oil is likewise formed when potassium allyl sulphate and potassium thiocyanate are subjected to dry distillation.

$$\underset{\substack{\text{Potassium}\\ \text{allyl sulphate}}}{C_3H_5KSO_4} + \underset{\substack{\text{Potassium}\\ \text{thiocyanate}}}{CNSK} = \underset{\text{Mustard oil}}{CSNC_3H_2} + \underset{\substack{\text{Potassium}\\ \text{sulphate}}}{K_2SO_4}$$

The properties of synthetic mustard oil have been described in vol. I, p. 547.

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[1]) A. W. Hofmann, Berl. Berichte **1** (1868), 182.

[2]) Flückiger, Arch. der Pharm. **196** (1871), 214.

Properties. Mustard oil is a limpid liquid, colorless to yellow, strongly refractive, optically inactive and with a strong odor, causing the flow of tears. Brought in contact with the skin, it produces a burning sensation and even blisters. For reasons mentioned under "Preparation", its specific gravity varies between 1,016 and 1,022 and at times is as high as 1,030. n_{D20°1,52681 to 1,52804. Mustard oil dissolves in from 160 to 300 parts of water, also in from 7 to 10 vol. of 70 p.c. alcohol and in from 2,5 to 3 vol. of 80 p.c. alcohol. With 90 p.c. alcohol, with ether, amyl alcohol, benzene and petroleum ether it forms clear solutions in all proportions. The bulk of the oil boils between 148 and 154° (760 mm.)[1].

Exposed to light, mustard oil gradually assumes a reddish-brown color. At the same time the inner surface of the flask is coated with an orange-yellow deposit consisting of carbon, nitrogen, hydrogen and sulphur.

A mustard oil prepared by Schimmel & Co.[2]) from *Brassica juncea* had quite abnormal properties and differed greatly in composition from ordinary mustard oil. Its constants were: d_{15° 0,9950; $\alpha_D + 0° 12'$; n_{D20° 1,51849.

Whereas ordinary mustard oil contains only small amounts of substances boiling above 155°, the bulk of the oil in question distilled above this temperature. The third fractionation of 750 g. of oil yielded the following results:

from	40	to	150°,	53 g.	or about	7 %,
„	150	„	160°,	200 „	„ „	30 %,
„	160	„	174°,	160 „	„ „	20 %,
„	174	„	178°,	290 „	„ „	40 %.

These results showed clearly that, unlike the normal mustard oil, this oil was evidently not a chemical unit. Furthermore, the indefinite melting point of the thiourea, which solidified but slowly, *viz.*, from 67 to 70°, led to the inference that the product was a mixture of several bodies.

This product contained but 40 p.c. of allyl mustard oil instead of 90 p.c. for the normal oil. In its place 50 p.c. of *crotonyl mustard oil* $CSN \cdot C_4H_7$ were found present. Fraction

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[1]) The boiling point of pure *iso*thiocyanallyl is at 150,7°.

[2]) Report of Schimmel & Co. October 1910, 81.

175 to 176°, which consists principally of crotonyl mustard oil, had the following properties: d_{15° 0,9941; $\alpha_D + 0° 3'$; n_{D20° 1,52398. Upon elementary analysis it yielded results agreeing with the above formula. The thiourea crystallized in long needles which melted at 69 to 70°. The crotonylthiocarbamic acid bornyl ester[1]) melted at from 55 to 56°. The constitution of the crotonyl group was not ascertained, but the oil probably is not the normal crotonyl mustard oil, the thiourea of which melts at 65 to 66°. The mixture of the normal thiourea with that from the natural oil melted between 45 and 50°[2]).

In addition, the oil probably contained a substance that is identical with *allylcyanide* (m.p. of the crotonic acid 70° in place of 72°), as well as traces of *dimethyl sulphide.*

The production of such an abnormal oil from *Brassica juncea* is contrary to all previous experience. No explanation therefor could be found.

Examination. Inasmuch as there exists no means to distinguish between natural and artificial mustard oils, the latter has been made official in the 5th edition of the German Pharmacopœia. The requirements are as follows: d_{15° 1,022 to 1,025; soluble in all proportions of 90 p.c. alcohol; it should contain at least 97 p.c. of allyl mustard oil.

Particulars as to the method of analysis will be found on p. 605 of vol. I.

Determination of Carbon Disulphide in Mustard Oil. For the purpose of detecting larger amounts of carbon disulphide added as adulterant, the latter can be converted into copper xanthogenate[3]) and can thus be determined quantitatively.

For this purpose a current of air is slowly passed through 20 to 25 g. of mustard oil heated on a water bath, the flask being provided with a condenser. The carbon disulphide vapors are carried into a solution of alcoholic potassa and thus converted into potassium xanthogenate. The alkaline solution is then neutralized and $^1/_{10}$-N-copper sulphate solution added until a drop removed from the reaction liquid is colored reddish-

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[1]) Comp. M. Roshdestwensky, Chem. Zentralbl. **1910**, I. 910.

[2]) For a different crotonyl mustard oil see Oil of *Brassica Napus,* p. 527.

[3]) Macagno, Zeitschr. f. anal. Chem. **21** (1882), 133.

brown by potassium ferrocyanide, in other words until a slight excess of copper sulphate is present and all potassium xanthogenate has been converted into cuprous xanthogenate. From the amount of copper solution consumed the amount of carbon disulphide can be computed (1 cc. corresponds to 0,0152 g. of carbon disulphide).

The precipitate of cuprous xanthogenate may be collected on a filter, washed with water, dried and heated in a crucible to a red heat, thereby converting it into cupric oxide. 1 g. of cupric oxide corresponds to 1,918 g. of carbon disulphide.

For the quantitative determination of the traces of carbon disulphide found in every mustard oil, the method of A. W. Hofmann[1]) is resorted to. According to this method the carbon disulphide is converted into a compound with triethyl phosphine, $P(C_2H_5)_3 + CS_2$, and weighed.

318. Mustard Oil from White Mustard Seed.

Corresponding to the sinigrin of the black mustard, the white mustard (*Sinapis alba,* L.; *Brassica alba,* Boiss.) contains the glucoside sinalbin. It was first prepared by Robiquet and Boutron-Charlard[2]) who boiled the seeds, deprived of their fatty oil, with alcohol. The examination of this glucoside, and more particularly the elucidation of the reaction observed in its hydrolysis, and of the products of hydrolysis produced by myrosin, were undertaken by H. Will and A. Laubenheimer[3]), later by J. Gadamer[4]).

The identity of sinalbin mustard oil with p-*hydroxybenzyl* iso*thiocyanate* has been established by H. Salkowski[5]).

Sinalbin mustard oil, $C_6H_4OH^{[1]} \cdot CH_2NCS^{[4]}$ is but sparingly volatile with water vapor[6]), hence cannot be obtained from white mustard seed by distillation. It is an oily liquid with a burning taste. It draws blisters, but much more slowly than allyl mustard

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[1]) Berl. Berichte 13 (1880), 1732.

[2]) Journ. de Pharm. II. 17 (1831), 279.

[3]) Liebig's Annalen 199 (1879), 150.

[4]) Arch. der Pharm. 235 (1897), 83.

[5]) Berl. Berichte 22 (1889), 2143.

[6]) Ground white mustard seed mixed with water has a pungent taste but is nearly odorless.

oil. The pungent odor becomes noticeable only when heated. In the cold the oil has but a faint odor reminding one of anise. It is soluble in dilute alkalies. Sinalbin mustard oil is prepared by hydrolysis of the glucoside, which also yields glucose and sinapin sulphate:

$$\underset{\text{Sinalbin}}{C_{30}H_{42}N_2S_2O_{15}} + \underset{\text{Water}}{H_2O} = \underset{\text{Sinalbin mustard oil}}{C_7H_7ONCS} + \underset{\text{Glucose}}{C_6H_{12}O_6} +$$

$$\underset{\text{Acid sinapin sulphate.}}{C_{16}H_{24}N_2O_5HSO_4}$$

Artificially it is obtained by the action of carbon disulphide on *p*-hydroxybenzylamine, followed by treating the reaction product with mercuric chloride.

319. Oil of Brassica Napus.

Symptoms of poisoning having been observed in feeding colza cakes to animals, B. Sjollema[1]) examined the oil obtained from the seeds of *Brassica Napus,* L. (*B. campestris,* L.). After the bulk of the fatty oil had been expressed, the oil cakes were placed in hot water. When cooled, ground white mustard seed was added. The resulting mustard oil was distilled from a water bath under reduced pressure. Part of the oil floated on the surface of the aqueous distillate, another part was shaken out of the aqueous solution with ether. The yield amounted to as much as 0,8 p.c. Its density was $d_{4^\circ}^{11^\circ}$ 0,9933; α_D inactive; b.p. (not corrected) about 174°. The mustard oil in question is a *crotonyl mustard oil,* the thiourea (white needles) of which melted at 64°. A comparison of the molecular refraction and molecular dispersion of the thioureas of allyl mustard oil and of this crotonyl mustard oil by Eykman pointed to the probable homology of these two compounds, hence the formula

$$CSN \cdot CH_2 \cdot CH_2 \cdot CH : CH_2$$

may be assigned to the crotonyl mustard oil of *Brassica Napus.*

Apparently this crotonyl mustard oil is not identical with the one obtained later by Schimmel & Co.[2]) from the seed of *Brassica juncea,* the thiourea of which melted at 69 to 70°.

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[1]) Recueil trav. chim. des P.-B. **20** (1901), 237; Chem. Zentralbl. **1901**, II. 299.

[2]) Report of Schimmel & Co. October **1910**, 83. See mustard oil, p. 524.

320. Oil of Brassica Rapa var. rapifera.

Upon distilling the shells of *Brassica Rapa* var. *rapifera,* Metzger (Ger. *Wasserrübe, Stoppelrübe*), M. Kuntze[1]) obtained a very small amount of a volatile oil, the odor of which resembled that of *Cardamine amara* (See p. 531). It consisted of *phenyl-*

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[1]) Arch. der Pharm. **245** (1907), 660. In connection with his investigations of the fatty oils of the crucifers, C. Grimme (Pharm. Zentralh. **53** [1912], 733. — Pharm. Ztg. **57** [1912], 520) determined the volatile oil content of a number of species of *Brassica* and *Raphanus* according to the method for assaying black mustard of the fifth edition of the German Pharmacopœia. The percentage of mustard oil is computed with reference to allyl mustard oil. The chemical nature of the individual mustard oils still remains to be ascertained.

No.	Botanical source	Mustard oil in the oil cake %	Mustard oil in the seed %
1	*Brassica oleracea acephala vulgaris*	0,119	0,079
2	„ „ „ *quercifolia*	0,079	0,051
3	„ „ „ *crispa*	0,159	0,103
4	„ „ *gemmifera*	0,198	0,144
5	„ „ *sabanda*	0,178	0,129
6	„ „ *capitata alba*	0,357	0,258
7	„ „ „ *rubra*	0,357	0,259
8	„ „ *gongylides*	0,198	0,142
9	„ „ *botrytis*	0,159	0,104
10	„ „ *asparagoides*	0,178	0,119
11	„ *Rapa oleifera annua*	0,119	0,085
12	„ „ „ *hiemalis*	0,159	0,093
13	„ „ *rapifera*	0,252	0,166
14	„ „ *teltoviensis.*	0,198	0,132
15	„ *Napus oleifera annua*	0,156	0,097
16	„ „ „ *hiemalis*	0,119	0,071
17	„ „ „ *flora alba*	0,099	0,056
18	„ „ *rapifera (Erdkohlrabi) (chou-navet)*	0,099	0,062
19	„ „ „ *(Wruke)*	0,020	0,012
20	*Raphanus sativus albus*	0,263	0,164
21	„ „ *niger*	0,179	0,108
22	„ „ *Radiola*	0,159	0,106
23	„ „ *oleiferus*	0,199	0,133

In an investigation of the crucifer family for other sulphone mustard oils, W. Schneider and W. Lohmann (Berl. Berichte **45** [1912], 2955) established the presence of allyl mustard oil and myrosin in cauliflower seed (*Brassica oleracea* var. *botrytis,* L.). When ground cauliflower seeds were added to black mustard meal, in which the myrosin had previously been destroyed allyl mustard oil was liberated. However, the reaction was but a faint one.

ethyl mustard oil. Its thiourea, obtained by the action of alcoholic ammonia, was inactive and melted at 137°. This mustard oil was obtained as a product of hydrolysis brought about by an enzyme in the presence of water. It could not be obtained from the inner tissues of the plant.

321. Oil of Spanish Radish.

Upon distillation with water, the roots and seeds of *Raphanus sativus,* L. (Ger. *Rettich,* fam. *Cruciferæ*) yield a small amount[1]) of a colorless oil which contains sulphur and is heavier than water. It possesses the taste, but not the odor, of radish[2]).

Bertram and Walbaum[3]) distilled 75 kg. of comminuted Spanish radish with water vapor. They obtained an aqueous distillate of an unpleasant odor. When shaken out with petroleum ether, a few grams of an oil were obtained that did not react with ammonia. Gadamer[4]) repeated the experiment with similar results. The distillate, which had an unpleasant odor of cabbage, contained traces of sulphur but was free from mustard oil. He concluded that the volatile oil of radish does not distil without decomposition with water vapor and he therefore extracted freshly grated Spanish radish with ether. In this manner he obtained a brownish oil that had the characteristic odor and taste of radish. Upon standing for some time, crystals separated which probably consisted of *raphanol* (See below). The oil reacted with ammonia, but no crystalline thiourea could be obtained.

That Spanish radish oil results from the hydrolytic action of an enzyme upon a glucoside was proved by Gadamer in the following manner. A Spanish radish cut into thin slices was dropped into strong alcohol in order to prevent the action of the enzyme on the glucoside. When dried, the slices no longer produced the radish odor with water. This odor, however, was produced when some myrosin was added.

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[1]) For the yield comp. footnote 1 on p. 528, No. 20—21.

[2]) Pless, Liebig's Annalen **58** (1846), 40.

[3]) Journ. f. prakt. Chem. II. **50** (1894), 560.

[4]) Arch. der Pharm. **237** (1899), 520.

Upon the distillation of the root of *Raphanus niger,* H. Moreigne[1]) obtained traces of oil and 0,0025 p.c. of a crystalline substance which melted at 62° and which he named *raphanol,* or, since it possessed the properties of a lactone, *raphanolid.*

Raphanolid contains neither nitrogen nor sulphur. According to elementary analysis and molecular weight determination, the formula $C_{29}H_{58}O_4$ should be assigned to it. When boiled with acetic acid anhydride, it yields an acetyl derivative melting at 122 to 123°.

The liquid portion of radish oil contains sulphur but no nitrogen. It does not combine with ammonia.

Moreigne found raphanolid also in the following plants, *viz.,* in the small garden radish, in white and in the common turnip, in water-cress, in spoonwort and in stock (Ger. *Levkoje.*)

322. Oil of Barbaræa præcox.

According to the investigations of J. Gadamer[2]), the so-called American or perennial winter-cress, *Barbaræa præcox,* R. Br. contains the glucoside *gluconasturtiin,* also found in *Nasturtium officinale,* L. (Ger. *Brunnenkresse*). Upon distillation both plants yield identical oils, consisting principally of *phenyl ethyl mustard oil* (m.p. of thiourea 135 to 136°).

323. Oil of Water-Cress.

A. W. Hofmann[3]) prepared the oil of *Nasturtium officinale,* L. in the following manner: The aqueous distillate (600 kg.) of 600 kg. of herb, which had not been comminuted, was shaken out with petroleum ether. After evaporation of the petroleum ether from a paraffin bath at 140°, 40 g. = 0,066 p.c. of oil not absolutely free from petroleum ether remained. The oil did not have a cress-like odor; d_{18° 1,0014; it began to boil at 120°, but the temperature soon rose to 200° and finally to 280°. After repeated fractionation, the bulk of the oil distilled at 261°. Its behavior

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[1]) Journ. de Pharm. et Chim. VI. 4 (1896), 10. — Bull. Soc. chim. III. 15 (1896), 797.

[2]) Arch. der Pharm. 237 (1899), 518. — Berl. Berichte 32 (1899), 2335.

[3]) Berl. Berichte 7 (1874), 520.

towards alkali revealed its nature as a nitrile. The acid liberated from the alkali melted at 47°, and was phenyl propionic acid as proved by analysis. Hence the principal substance of the oil thus obtained is *phenylpropionic acid nitrile,* $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CN$. In addition to this substance the oil contained hydrocarbons which may have been due to the petroleum ether used in its preparation.

From the higher boiling fractions beautiful dodecahedra separated. On account of the small amount of material these could not be further examined.

Utterly different results were obtained by Gadamer[1]) who distilled the carefully comminuted herb. He obtained an oil which separated at the bottom of the receiver and which had a strong mustard oil odor reminding of that of Spanish radish. Its identity with *phenylethyl mustard oil* was established by means of the thiourea melting at 135 to 136°[2]).

Water-cress contains a glucoside $C_{15}H_{20}KNS_2O_9 + x\,H_2O$ named *gluconasturtiin,* which has not yet been isolated. Enzymes hydrolyze it to glucose and phenyl ethyl mustard oil.

As in the case of the common cress, the deviating results obtained by Hofmann are due to the fact that he distilled uncomminuted herb, whereas Gadamer carefully comminuted his material to a pulp, in a meat grinder. Thus the glucoside and enzyme, which are deposited in different cells of the plant, are enabled to come into contact, producing the ordinary hydrolysis of the glucoside. When the entire herb is distilled, the ferment is destroyed, the glucoside being exposed to the destructive influence of the hot water vapors.

In the water-cress H. Moreigne[3]) found *raphanolid.*

324. Oil of Cardamine amara.

Upon the distillation with water vapors of the comminuted fresh, but not flowering, herb of *Cardamine amara,* L., K. Feist[4]) obtained a brown liquid with a decided odor of water-cress.

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[1]) Arch. der Pharm. **237** (1899), 510. — Berl. Berichte **32** (1899), 2335.

[2]) Comp. Bertram and Walbaum, Journ. f. prakt. Chem. II. **50** (1894), 557.

[3]) See oil of Spanish radish, p. 530.

[4]) Apotheker Ztg. **20** (1905), 832.

When acted upon with ammonia a thiourea was obtained, the melting point (134 to 135°) and its sulphur content (an average of 24,23 p. c.) agree with the thiourea of *secondary butyl mustard oil*. Feist records 0,0357 p. c. as the secondary butyl mustard oil content of the fresh herb.

M. Kuntze[1]) found the melting point of the thiourea obtained from the oil at 136°, and its optical rotation in alcoholic solution $[\alpha]_D + 19,96°$. In addition, an optically inactive thiourea melting at 159° was found. This may have been benzyl thiourea and would seem to indicate a contamination of the raw material with *Lepidium sativum*.

325. Oil of Erysimum Perofskianum.

From the seed of *Erysimum Perofskianum*, Fisch. et Mey. (family *Cruciferæ*) W. Schneider and H. Kaufmann[2]) obtained a sulphone mustard oil, $C_6H_{11}O_2NS_2$, named *erysolin*. It is a homologue of cheirolin, $C_5H_9O_2NS_2$ found in wallflower seeds (Ger. *Goldlack*.)

The yield of the fresh seed, not deprived of its fat, was 0,05 p. c. at best. Recrystallized from ether, erysolin is obtained in beautiful, colorless prisms (m. p. 59 to 60°) which irritate the mucous membrane. With alcoholic ammonia it yields a thiourea melting at 143 to 144°. Saponification with hydrochloric acid yielded the corresponding base. Upon oxidation with nitric acid this yielded δ-aminobutyl methyl sulphone. Hence erysolin is *δ-thiocarbimidobutylmethyl sulphone:* $CH_3 \cdot SO_2 \cdot (CH_2)_4 \cdot NCS$. The correctness of this formula was established by synthesis.

326. Oil of Wallflowers.

Upon extraction of the flowers of *Cheiranthus Cheiri*, L. (Ger. *Goldlack*, family *Cruciferæ*) with low boiling solvents, Kummert-E.[3]) obtained a dark colored extract of salve-like consistence. When treated with strong alcohol, the extract was freed of wax and vegetable fats and subsequently distilled with water-vapor. The yield of oil thus obtained amounted to 0,06 p.c.;

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[1]) Arch. der Pharm. **245** (1907), 657.

[2]) Liebig's Annalen **392** (1912), 1.

[3]) Chem. Ztg. **35** (1911), 667.

it possessed the following properties: b. p. 40 to 150° (3 mm.); d_{15° 1,001; A. V. 0,35; E. V. 20,0; S. V. 20,35. In concentrated condition the oil had a disagreeable odor, in very diluted condition it reproduced the odor of the flowers very faithfully.

When distilled in a vacuum of 3 mm., only a small amount of oil came over below 40°. The odor of these substances, presumably mustard oils[1]), was very disagreeable. With semicarbazide the higher boiling fractions yielded a mixture of semicarbazones that was decomposed with oxalic acid. The product thus obtained had an odor reminding one of hawthorn (Ger. *Weissdorn*) and violet, thus indicating possibly the presence of *anisic aldehyde* and *irone.*

When the oil that had been deprived of aldehydes and ketones was treated with phthalic acid anhydride, *nerol* (m. p. of the diphenyl urethane 50°), *geraniol* (m. p. of the diphenylurethane 82°) and *benzyl alcohol* (m. p. of the acid phthalic ester 106°) were shown to be present. *Linalool* (m. p. of phenylurethane 65°) is also present in the oil. After the removal of traces of phenols (possibly *p*-cresol) and lactones (possibly cumarin-like compounds) Kummert found the following acids in the saponification liquid: *acetic acid, salicylic acid* (m. p. 156°) and *anthranilic acid* (m. p. 145°).

The highest fractions had a decided odor of indol. To the ethereal solution, prepared with three volumes of ether, sulphuric acid was added. The precipitate resulting was decomposed with warm soda solution. Thus Kummert isolated the *methyl ester of anthranilic acid.* The bases freed from ether were then dissolved in petroleum ether. The addition of picric acid to this solution caused the precipitation of a red picrate which, when decomposed with soda solution, yielded *indol* (m. p. 52°), also a small amount of bases that had the odor of pyridine.

327. Oil of Wallflower Seed.

From the seeds of *Cheiranthus Cheiri,* L. (Ger. *Goldlack*), P. Wagner[2]) obtained a sulphur-containing compound which

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[1]) Possibly substances similar to those found in the seeds. See p. 534.

[2]) Chem. Ztg. 32 (1908), 76.

he named *cheirolin.* Somewhat later this compound was examined by W. Schneider[1]) who recognized it as a mustard oil, *viz., γ-thiocarbimidopropyl methyl sulphone,* $CH_3 \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot N:C:S$.

Cheirolin also occurs in the seeds of *Erysimum arkansanum,* Nutt. (*E. asperum,* DC.). For its preparation the seeds of the wallflower are first extracted with ether in order to remove the fat. A 5 p.c. soda solution is added to decompose the glucoside-like cheirolin compound and the solution shaken out with ether. The cheirolin thus extracted by the ether amounts to a yield of from 1,6 to 1,7 p.c. computed with reference to the seeds. The pure product crystallizes from ether in colorless and odorless prisms that melt at 47 to 48°, boil at about 200° (3 mm.) and are optically inactive. When distilled under atmospheric pressure it is decomposed. It produces a decided irritation on the mucous membrane. When saponified it decomposes quantitatively into hydrogen sulphide, carbonic acid and *γ-aminopropylmethyl sulphone* (m. p. 44°; of the hydrochloride 146°; m. p. of the picrate 190 to 192°), which yields a quaternary iodomethylate that melts at 150 to 152°. This is regarded as evidence of the primary character of the nitrogen in the γ-aminopropylmethyl sulphone. When cheirolin is acted upon by mercuric oxide, there results, first upon the action of one-half molecule of this reagent, *di-(γ-methylsulphone propyl) thiourea* (m. p. about 125°), and upon the renewed action of the mercuric oxide *di-(γ-methylsulphone propyl) urea* (m. p. 172°).

Cheirolin is contained in the wallflower seed as glucoside which can be extracted by means of alcohol after the fat has been removed[2]). It is exceedingly soluble in water and possesses no characteristic melting point. Separated from the alcoholic solution, it contains from 6 to 7 p.c. of alcohol (of crystallization?) which it loses in vacuum over sodium at water-bath temperature. This glucoside has not yet been obtained in a pure condition but it is analogous to other mustard oil glucosides. It contains cheirolin, glucose, sulphuric acid and potassium. The sulphur present exists in three forms; as sulphuric acid radicle, as

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[1]) Liebig's Annalen 375 (1910), 207.

[2]) W. Schneider and W. Lohmann, Berl. Berichte 45 (1912), 2954.

mustard oil sulphur and as sulphonic sulphur. Cheirolin can be isolated from the glucoside by hydrolyzing the latter with the enzyme from the white mustard. The wallflower seed itself contains an enzyme that hydrolyzes the sinigrin of black mustard with the formation of mustard oil, hence it is physiologically equivalent, if not identical, with myrosin.

By treating the fatty oil of the seeds obtained by ether extraction with water-vapor, M. Matthes and W. Boltze[1]) obtained 0,0073 p.c. (computed with reference to the seeds) of a colorless volatile oil that had an odor which reminded one of waterfennel: b. p. 120 to 125° (15 mm.); d_{15° 0,9034; $[\alpha]_D$ — 12,73°; n_{D20° 1,6920. Potassium permanganate and bromine are both decolorized immediately by the oil. An elementary analysis yielded 85,68 p.c. of carbon and 11,56 p.c. of hydrogen.

Family: RESEDACEÆ.

328. Oil of Mignonette Flowers.

Upon distillation of fresh mignonette flowers from *Reseda odorata,* L. (family *Resedaceæ*), a yield of but 0,002 p.c. of oil is obtained. Noteworthy is the decided formation of hydrogen sulphide observable during the distillation[2]).

The oil from the flowers is dark in color and solid at ordinary temperature, being of the same consistence as orris oil. Greatly diluted it has the odor of fresh mignonette blossoms[3]).

In order to obtain it in a more suitable form, it is distilled with geraniol (1 kg. geraniol to 500 kg. of fresh blossoms). The product thus obtained enters commerce as *Reseda-Geraniol,* literally mignonette-geraniol[4]).

A product with a better odor is obtained by extraction of the fresh blossoms with a volatile solvent[5]) such as petroleum

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[1]) Arch. der Pharm. **250** (1912), 217.

[2]) Report of Schimmel & Co. October **1891**, 51.

[3]) *Ibidem* October **1893**, 44.

[4]) *Ibidem* October **1894**, 67.

[5]) Comp. vol. I, p. 248.

ether. All of the extracts prepared from fresh flowers[1]) are characterized by a naturalness of the aroma. However, in addition to the volatile oil which alone is the bearer of the perfume, they contain appreciable amounts of odorless substances, some of which are difficultly soluble in alcohol (plant wax, resin, paraffin, &c.). These odorless substances can be removed in part by treatment of the extract with alcohol, more completely by distillation with water-vapor. Because of the small amount of volatile oil present, a relatively large porportion remains dissolved in the aqueous distillate from which it can be shaken out with ether after the addition of salt thereto. The pure volatile oil obtained after the recovery of the ether contains the perfume of the flowers in the most concentrated form.

In this manner 0,003 p. c. of a mignonette flower oil were obtained[2]). It was of a yellow color, possessed an intense mignonette odor, congealed in the cold, did not fluoresce, and revealed the following constants: d_{15° 0,961; $\alpha_{D17^\circ} + 31^\circ 20'$; A. V. 16; E. V. 85.

With alcoholic potassa the odor of ammonia bases was produced. The presence of aldehydes was likewise observed.

329. Oil of Mignonette Root.

Upon distillation of fresh mignonette root with water-vapor 0,014 to 0,035 p. c. of oil were obtained.

The oil of mignonette root is light brown in color and has an odor very much like that of Spanish radish: d_{15° 1,010 to 1,084; $\alpha_D + 1^\circ 30'$. At 255° it begins to boil with a decided evolution of gas. Even in vacuum it does not distil without decomposition.

A small amount of this oil was first distilled from fresh roots by A. Vollrath[3]) in 1871, who recognized its character as that of a mustard oil. However, his supposition that it is identical with allyl mustard oil proved erroneous. As shown by J. Bertram and H. Walbaum[4]), the mustard oil of mignonette root oil is *phenylethyl mustard oil* $C_6H_5CH_2 \cdot CH_2NCS$.

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[1]) Yield 1,3 to 1,5 p. c. Comp. vol. I, p. 251.

[2]) H. von Soden, Journ. f. prakt. Chem. II. **69** (1904), 264.

[3]) Arch. der Pharm. **198** (1871), 156.

[4]) Journ. f. prakt. Chem. II. **50** (1894), 555.

Phenylethyl mustard oil smells quite like mignonette root oil. When heated with ammonia beautiful crystals of the thio-urea that melt at 137° are obtained, $NH_2 \cdot CS \cdot NHC_2H_4C_6H_5$. When the thio-urea is treated with silver nitrate and baryta water, silver sulphide and phenylethyl urea, crystallizing in long slender needles that melt at 111 to 112°, are formed. If the phenylethyl mustard oil be heated with concentrated hydrochloric acid in sealed tubes, laminar crystals of phenylethylamine chlorhydrate melting at 217° are formed. With ethyl oxalate the phenylethylamine combines to form diphenylethyloxamide which melts at 186°.

All of these derivatives of phenylethyl mustard oil were prepared by Bertram and Walbaum from the natural oil obtained from mignonette root and from the phenylethyl mustard oil prepared artificially from phenylethylamine and carbon disulphide[1]). The corresponding products from both sources were identical throughout.

Family: SAXIFRAGACEÆ.

330. Black Currant Oil.

From the *buds* of the black currant *(Ribes nigrum,* L., Ger. *Schwarze Johannisbeere,* family *Saxifragaceæ)* Schimmel & Co.[2]) obtained a volatile oil with a yield of 0,75 p. c. It had the following properties: $d_{15°}$ 0,8741; $\alpha_D + 2° 30'$; $n_{D20°}$ 1,48585; A.V. 0; E.V. 5,6; soluble in 6,5 vol. or more of 90 p.c. alcohol. This solution is slightly turbid, but the turbidity disappears upon greater dilution (1:10). The oil was pale green as to color and, judging by its odor, contained cymene.

From the *leaves* Huchard[3]) obtained a volatile oil which upon hydrolysis yielded *quinic acid* and a very *active oxidase.* Constants and other properties of the oil are not enumerated but mention is made of its diuretic properties.

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[1]) A. Neubert, Berl. Berichte **19** (1886), 1824.

[2]) Report of Schimmel & Co. April **1907**, 106.

[3]) Journal des Praticiens; through The Practitioner **1909**, 428. According to Pharmaceutical Journ. **82** (1909), 528.

Family: PITTOSPORACEÆ.

331. Oil of Pittosporum undulatum.

According to F. B. Power and F. Tutin[1]), the crushed fruits of *Pittosporum undulatum,* Vent. (family *Pittosporaceæ*), which is indigenous to south-eastern Australia, yields 0,44 p. c. of oil which upon prolonged standing undergoes apparent changes: d_{15° 0,8615; $\alpha_D + 74^\circ 4'$. Upon fractional distillation 4 p. c. of d-*α-pinene* (nitrosochloride; m. p. of nitrolbenzylamine 123°) passed over below 165°. Between 173 and 180°, 75 p. c. of *limonene* (m. p. of tetrabromide 104°) passed over, and between 200 and 225° a substance, presumably an *alcohol,* which upon oxidation yielded a ketone $C_9H_{14}O$ that had the odor of cumarin. Finally, between 263 and 274° an optically inactive *sesquiterpene* $C_{15}H_{24}$ (d_{15° 0,910; n_{D20° 1,5030) passed over. Not a single crystalline derivative was obtainable, neither could it be identified with any of the known sesquiterpenes. Its molecular refraction indicated the presence of two rings and two double bonds. In addition, the presence of traces of *palmitic* and *salicylic acids* was ascertained, also of a *phenol* that had the odor of eugenol. Traces of *esters of valeric, formic* and other acids were also found present. The oil was insoluble in 10 vol. of 70 p. c. alcohol.

332. Oil of Pittosporum resiniferum.

Because of their petroleum-like odor, the fruits of *Pittosporum resiniferum,* Hemsl., a tree that is widely distributed throughout the Philippines, are known as petroleum nuts. Even the green, fresh fruits burn with a bright flame if touched with a burning match. An investigation of the petroleum nuts by R. F. Bacon[2]) revealed the presence of *heptane* and of a *dihydroterpene.* Subjected to pressure, 1 kg. of fresh nuts yielded 52 g. of oil and the residue, when ground and expressed a second time, 16 g. of additional oil with the following properties: d 0,883; n_{D30° 1,4577; other optical constants could not be determined. The oil was quite sticky and, when exposed in a thin layer, resinified rapidly.

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[1]) Journ. chem. Soc. 89 (1906), 1083.

[2]) Philippine Journ. of Sc. 4 (1909), A, 115.

Ignited in an open dish it burned with a sooty flame. Up to 165° it distilled without decomposition. Above that temperature decomposition set in and a resinous oil passed over.

The lowest fraction boiled between 97 and 101°. Shaken with concentrated sulphuric acid and distilled over sodium, the oil had the following constants: $d_{4°}^{30°}$ 0,6752; $\alpha_D + 0°$; $n_{D30°}$ 1,3840. Bromination of this fraction, which had the odor of diphenyl methane and which doubtless is *heptane*, yielded *n*-heptyl bromide. It boiled between 178 and 181° (93° under 70 mm. pressure) and, when heated with fused sodium acetate and acetic acid, yielded *n*-heptyl acetate, b. p. 192°.

The terpene fraction 150 to 160° after having been distilled three times over sodium, finally boiled between 158 and 160°: $d_{4°}^{30°}$ 0,8252; $\alpha_{D30°}$ (+?) 29,6°; $n_{D30°}$ 1,4587. The liquid hydrochloride had the following properties: b. p. 114 to 116° under 34 mm. pressure; $d_{4°}^{30°}$ 0,9343; $\alpha_{D30°} + 9°$; $n_{D30°}$ 1,4655. When acted upon with magnesium and subsequently with water, a hydrocarbon with the following properties was obtained: b. p. 168 to 170°; $d_{4°}^{30°}$ 0,8050; $\alpha_{D30°} + 1,1°$; $n_{D30°}$ 1,4460. From these data the conclusion was drawn that the hydrocarbon in question was hexahydro-*p*-cymene. Hence the hydrocarbon in the original oil was a *dihydroterpene*. As is the case with limonene and phellandrene, the chloride when treated with magnesium and benzaldehyde yielded a hydrocarbon with two additional hydrogen atoms. Benzoin also was formed.

333. Oil of Pittosporum pentandrum.

The small, ground fruits of *Pittosporum pentandrum* (Blanco), Merrill, which grows principally in the lowlands of the Philippines, yielded upon distillation[1]) an oil (210 cc. from 16 kg.) which boiled between 153 and 160°. Washed with solution of caustic alkali and distilled over sodium, it had the following properties: b. p. 155 to 160° (principally 157 to 160°); $d_{4°}^{30°}$ 0,8274; $\alpha_{D30°}$ (+?) 40,4°; $n_{D30°}$ 1,4620. Hence it may be assumed that the oil consisted principally of the *dihydroterpene* found in the petroleum nuts as described above. Heptane, however, was not present.

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[1]) Bacon, *loc. cit.* 118.

Family: HAMAMELIDACEÆ.

334. Oil of Storax.

Oleum Styracis. — Storaxöl. — Essence de Styrax.

Origin. The oriental storax, *Liquidambar orientale,* Mill. (Ger. *Styraxbaum,* family *Hamamelidaceæ*), which resembles the plane and which attains a height of 30 m., is indigenous to the southern part of Asia Minor. In its cortical tissues the tree secretes a fragrant balsam which congeals to a resin-like mass when exposed to the air. It is obtained by boiling the bark with water and subsequent expression. This product constitutes the *styrax liquidus* of commerce. This is a tough, dirty gray or greenish-gray, resinous mass of a peculiar aromatic odor and a sharp, spicy taste.

Upon distillation with water, storax yields 0,5 p.c. of a volatile oil; when high tension steam is used, 1 p.c. and more.

Properties. Storax oil is a bright yellow to dark brown liquid with a pleasant odor. According to the style of distillation employed it varies greatly in character. If the hydrocarbons predominate, the oil is lighter than water. The presence of a larger percentage of alcohols and cinnamic acid esters causes it to sink in water. Hence the specific gravity fluctuates between 0,89 and 1,06; $\alpha_D - 38°$ to $+ 0° 30'$; $n_{D20°}$ 1,53950 to 1,56528; A. V. 0,5 to 33; E. V. 0,5 to 130; soluble in 1 vol. of 70 p.c. alcohol, the addition of from 2 to 5 vol. generally causing opalescence; soluble in all proportions of 80 p.c. alcohol, but in this case also the dilute solution mostly shows opalescence. Oils with a higher ester-number are less readily soluble.

Composition. The peculiar odor of storax oil which reminds one somewhat of paraffin oil is due to its *styrene*[1]) content.

Styrene or phenylethylene $C_6H_5 \cdot CH:CH_2$ boils at 146°, is optically inactive and can be identified by its dibromide $C_6H_5 \cdot CHBr \cdot CH_2Br$ which melts at 74°. (Comp. vol. I, p. 281).

According to van 't Hoff[2]), the optical rotation of oil of storax is due to the presence of a substance $C_{10}H_{16}O$ or $C_{10}H_{18}O$ called *styrocamphene*.

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[1]) E. Simon, Liebigs Annalen **31** (1839), 265.

[2]) Berl. Berichte **9** (1876), 5.

Upon distillation of the storax, a part of the more or less volatile *cinnamic acid esters, viz.,* of *ethyl*[1]), *benzyl*[2]), *phenylpropyl,* and of *cinnamyl* alcohols (styracin), also their alcoholic components, principally phenylpropyl alcohol and cinnamyl alcohol, further *vanillin*[3]) pass over in part into the oil.

An investigation of storax by A. Tschirch and L. van Itallie[4]) verified the statements made by von Miller and by K. Dieterich.

From an oil of storax bark H. von Soden and W. Rojahn[5]) isolated *naphthalene* (m. p. 79°).

Adulteration. Two oils that had been greatly adulterated have been examined by Schimmel & Co.[6]) They possessed the following properties:

1. d_{15° 1,0986; $\alpha_D - 1°55'$; n_{D20° 1,56149; A.V. 0,5; E.V. 239,9; soluble in 2 vol. of 80 p.c. alcohol forming an opalescent solution.

2. d_{15° 0,8731; $\alpha_D + 19°20'$; n_{D20° 1,47763; A.V. 0,1; E.V. 5,0; soluble in 5 to 6 vol. of 90 p.c. alcohol to a turbid solution.

The first oil was suspicious because of its high specific gravity and the high ester value at once indicated adulteration. A more careful examination revealed the fact that the oil was nothing more nor less than benzyl benzoate perfumed with styrene. When fractionated under 4 mm. pressure it yielded 5 p.c. of a first fraction that distilled over between 35 and 40°, whereas 90 p.c. of the oil came over between 156 and 157°. The latter showed the constants of benzyl benzoate; d_{15° 1,1246; n_{D20° 1,57000; congealing point + 18,1°; E. V. 262,3.

The second oil had a very low specific gravity; the index of refraction was too low and the dextro-rotation correspondingly too high. The suspicion that this oil also was adulterated was confirmed by its boiling temperatures. Upon fractionation about 45 p.c. passed over between 156 and 160° (757 mm.). This fraction consisted of α-pinene (d_{15° 0,8668; $\alpha_D + 21°33'$; n_{D20° 1,47225; m.p. of pinene nitrolbenzylamine 121,5°). Inasmuch as this hydrocarbon has heretofore not been found in storax

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[1]) W. von Miller, Liebig's Annalen **188** (1877), 184.

[2]) A. Laubenheimer, *ibidem* **164** (1872), 289.

[3]) K. Dieterich, Pharm. Zentralh. **37** (1896), 425.

[4]) Arch. der Pharm. **239** (1901), 506.

[5]) Pharm. Ztg. **47** (1902), 779.

[6]) Report of Schimmel & Co. April **1910**, 101.

oil and since larger amounts thereof cannot be contained in genuine oil it follows without doubt that the oil in question was grossly adulterated with turpentine oil.

335. Oil of American Storax.

Origin. *Liquidambar styracifluum,* L., a tree belonging to the family *Hamamelidaceæ,* grows in the southern United States, in Mexico and Central America. The resinous balsam which is of honey-like consistence secretes from the sap-wood under the bark when incisions are made into the trunk and the branches. However, inasmuch as the balsam secretes freely only in hot climates, the drug enters commerce generally from Central America[1]). Upon distillation of this balsam Bonastre[2]) obtained 7 p.c. of oil.

Properties and Composition. According to W. von Miller[3]) the oil obtained from American storax is dextrogyrate ($\alpha_D + 16° 33'$). It contains *styrene* (m. p. of dibromide 73°) and an oxygenated substance which has the odor of turpentine, is optically active and has not been characterized.

In addition to vanillin and *cinnamyl cinnamate* (styracin), American storax contains the *cinnamic ester of phenylpropyl alcohol,* but neither the ethyl nor benzyl esters of cinnamic acid[4]).

The *leaves* of the American storax tree have a peculiar, turpentine-like odor. Their distillation[5]) yielded 0,085 p.c. of oil. It is greenish yellow and limpid; $d_{15°}$ 0,872; $\alpha_D - 38° 45'$; S. V. 5,9; E. V. after acetylation 25,2. The odor of the oil resembles that of *Abies alba.* Apparently it contains borneol and bornyl acetate in addition to the terpenes.

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[1]) Kalm, *Reise nach dem nördlichen Nordamerika in den Jahren* 1748 *bis* 1749. Göttingen 1754. Vol. 1, p. 294 and 566; Vol. 3, p. 131. — Schöpf, *Materia medica Americana.* Erlangæ 1787. Vol. 1, p. 170. — Schöpf, *Reise durch einige der mittleren und südlichen Vereinigten Staaten.* 1783 *bis* 1784. Erlangen 1787. Vol. 1, p. 415. — C. Mohr, Pharm. Rundsch. (New York) **13** (1895), 57.

[2]) Journ. de Pharm. II. **17** (1831), 338; Trommsdorff's Neues Journ. d. Pharm. **24**, II. (1832), 236.

[3]) Arch. der Pharm. **220** (1882), 648.

[4]) Comp. also A. Tschirch and L. van Itallie, *ibidem* **239** (1901), 532.

[5]) Report of Schimmel & Co. April **1898**, 53.

336. Rasamala Wood Oil.

Upon the distillation of *rasamala*[1]), a wood obtained from the Dutch East Indies, Schimmel & Co.[2]) obtained 0,17 p. c. of volatile oil.

At ordinary temperature rasamala wood oil forms a light brown, crystalline mass which melts between 30 and 40°. Its odor reminds one of that of cinnamon and rhubarb.

The principal constituent is a crystalline substance that melts at 54 to 55°. Presumably it is a ketone, since with hydroxylamine it forms a compound that melts at 106 to 107°. The second constituent of the oil is liquid.

According to a communication by Professor Dr. van Romburgh, the name *rasamala* is applied not only to the genuine but rare rasamala tree, *Altingia excelsa,* Nor. (*Liquidambar Altingia,* Bl.), family *Hamamelidaceæ,* but also to several Indian drugs. Among these are the liquid storax from *Liquidambar orientale (Getah Rasamala)* and other balsams with a similar odor, also the fragrant wood of *Canarium microcarpum,* Willd. *(Kaju Rasamala).*

Whether the wood distilled by Schimmel & Co. was derived from one of the above-named species, and if so from which remains uncertain. Possibly it was from the so-called aloe wood (Ger. *Aloeholz*) or eagle wood from *Aquilaria Agallocha,* Roxb., which is sold in Indian markets as *kaju lakka* and the characteristic rhubarb-like odor of which[3]) corresponds with that of the wood distilled by Schimmel & Co.

337. Honduras Balsam Oil.

According to A. Tschirch[4]), Honduras balsam, which occasionally is met with in the market, is derived from a species of *Liquidambar.* The properties of such a balsam were as follows[5]):

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[1]) A. Tschirch and L. van Itallie who have examined *Rassamala-resin* have found the volatile constituents to consist of a mixture of aldehydes, presumably *benzaldehyde* and *cinnamic aldehyde.* Arch. der Pharm. **239** (1901), 541.

[2]) Report of Schimmel & Co. April **1892**, 56.

[3]) *Ibidem.* — According to a detailed investigation made by J. Möller (Pharm. Post **1898**), aloe wood is odorless and develops a peculiar aroma only upon being burnt.

[4]) *Die Harze und die Harzbehälter,* 2nd ed., vol. I, p. 322. Leipzig 1906.

[5]) Observation made in the Laboratory of Schimmel & Co.

d_{15° 1,0932; $\alpha_D + 6^\circ 22'$; n_{D20° 1,59407; E. V. (hot) 151,0; S. V. (cold) 163,7.

Under the heading of white Peru balsam, the Honduras balsam has been described and examined by H. Thoms and A. Biltz [1]), also by A. Hellström [2]). Further investigations into its composition have been made by M. Burchhardt [3]) and by A. Tschirch and J. O. Werdmüller [4]).

Upon distillation of the sample of balsam mentioned above, Schimmel & Co.[5]) obtained 15 to 20 p. c. of volatile oil. However, the quantity was too small to determine its constants.

According to the investigators mentioned above, the Honduras balsam contained the following volatile constituents: *cinnamic* acid, free and as ester, *cinnamic alcohol, phenylpropyl alcohol,* hydrocarbons C_8H_8, C_5H_{10}, C_9H_{12} and a *sesquiterpene* boiling at 261 to 262°. All of these substances may be expected to occur in the oil.

338. Oil of Hamamelis virginiana.

When the twigs of witch-hazel, *Hamamelis virginiana,* L. are subjected to distillation on a large scale, the distillate separates small quantities of a green, fatty substance with a decided odor which, for a long time, has been regarded as the therapeutically important constituent.

The soft, greasy "oil" with its strong odor has been examined by W. L. Scoville [6]). It was distilled with water-vapor and the aqueous distillate was cohobated until the distillate had become clear. The yellowish oil, which had distilled over very slowly, possessed a very strong odor reminding one distinctly of *Aqua hamamelidis* without, however, being identical with it. This may be due to the fact that the original oil contains a substance that is more readily soluble in water than in the oil itself as is the case with oil of rose.

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[1]) Zeitschr. d. allg. österr. Apoth. Ver. **42** (1904), 943.

[2]) Arch. der Pharm. **243** (1905), 218.

[3]) Schweiz. Wochenschr. f. Chem. u. Pharm. **43** (1905), 238; Chem. Zentralbl. **1905**, I. 1705.

[4]) Arch. der Pharm. **248** (1910), 420.

[5]) Footnote 5, p. 543.

[6]) Paper read before the 59th Annual Meeting of the American Pharmaceutical Association, New York, September 1907, according to Americ. Perfumer **2** (1907), 119.

From different raw materials two samples of oil with the following properties were obtained: $d_{25°}$ 0,8984 and 0,8985; $\alpha_D + 4,6$ and $+ 5,05°$; $n_{D20°}$ 1,4830 and 1,4892; S. V. 3,80; S. V. after acetylation 30,3.

The bulk of the oil boiled between 250 and 263° and consisted of a terpene (sesquiterpene?). It also contained about 7 p.c. of an alcohol and a smaller percentage of ester. The wax remaining after the distillation of the oil constituted about 72 p.c. of the original material and revealed a granular fraction like bees-wax.

Family: ROSACEÆ.

339. Spiræa Oil.

OIL FROM THE FLOWERS.

Upon distillation of the flowers of *Spiræa Ulmaria,* L. (family *Rosaceæ*), Pagenstecher[1]) in 1835 obtained a heavy oil that sank in water and which he gave to Löwig[2]) for examination. Dumas[3]), to whom the oil was shown, recognized the similarity of the oil with salicylic aldehyde (salicyl-hydrogen) recently obtained by Piria from salicin. Ettling[4]) confirmed the surmise expressed by Dumas by showing that spiræa oil consists of two or three volatile substances, one of which is *salicylic aldehyde.*

Upon distillation of the flowers, Ettling obtained 0,2 p.c. of oil. According to W. Wicke[5]), the yield from cultivated double varieties is greater than that from the wild plants. Spiræa oil is heavier than water and at —18 to —20° congeals completely.

From the investigations of A. Schneegans and J. G. Gerock[6]), it becomes apparent that in addition to salicylic aldehyde (formerly designated spiroyl-hydrogen, spiræic acid, salicyl

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[1]) Repert. f. d. Pharm. **49** (1835), 337; Pharm. Centralbl. **1835**, 137.

[2]) Löwig, Poggend. Ann. **36** (1835), 383. — Löwig and Weidmann, Pharm. Centralbl. **1839**, 129.

[3]) Liebig's Annalen **29** (1839), 306.

[4]) *Ibidem* **29** (1839), 309; **35** (1840), 241.

[5]) *Ibidem* **83** (1852), 175.

[6]) Journ. der Pharm. f. Elsaß-Lothr. **19** (1892), 3 and 55; Jahresb. f. Pharm. **1892**, 164.

hydrogen, spiroylic or spiric acid) the oil contains *methyl salicylate,* also traces of *heliotropin* (piperonal) and *vanillin.* Furthermore, Ettling found a small amount of a camphor-like substance that crystallized in white, pearly laminæ (paraffin?), and an indifferent oil of the composition C_5H_8, *i. e.* that of a terpene or sesquiterpene.

As demonstrated by Schneegans and Gerock, the flowers themselves contain no salicylic aldehyde as such. This is produced by the action of a ferment on an unknown substance during the process of distillation. This substance is not salicin, as was assumed by Buchner[1]). In addition to *methyl salicylate* the flowers contain free *salicylic acid.*

OIL OF THE ROOTS.

The statement made by W. Wicke, that the roots of *Spiræa Ulmaria,* L. contain salicylic aldehyde, is incorrect. According to R. Nietzki[2]), the oil obtained by the distillation of the roots consists principally of *methyl salicylate* and of traces of another substance, presumably a hydrocarbon.

According to M. W. Beijerinck[3]), the roots, rhizomes and lower portions of the herb of *Spiræa Ulmaria, Sp. Filipendula* and *Sp. palmata* contain the glucoside *gaultherin.* Acted upon by the enzyme *gaultherase,* which is likewise present, it yields methyl salicylate. The older roots and rhizomes of *Spiræa Kamtschatica* also contain a second glucoside, the *spiræin,* which, when hydrolyzed by gaultherase, yields salicylic aldehyde.

OIL OF THE HERB.

In the distillate obtained from the herb, W. Wicke proved the presence of *salicylic aldehyde.*

The herb of *Spiræa digitata, lobata* and *Filipendula,* also the flowers of *Spiræa Aruncus* yield *salicylic aldehyde* upon distillation. *Hydrocyanic acid,* but no salicylic aldehyde, is obtained from the herb of *Spiræa Aruncus,* from the leaves of *Spiræa japonica,* also from the herb and flowers of *Spiræa*

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[1]) Liebig's Annalen **88** (1853), 284.

[2]) Arch. der Pharm. **204** (1874), 429.

[3]) Chem. Zentralbl. **1899,** II. 259.

sorbifolia. Neither salicylic aldehyde nor hydrocyanic acid could be detected in the distillates of *Spiræa lævigata, acutifolia, ulmifolia* and *opulifolia* (Wicke).

340. Apple Oil.

If fresh apple peelings from *Pirus Malus,* L. are covered with water and then distilled with steam, according to C. Thomæ[1]) but little solid substance passes over. Occasionally oily drops are formed which soon congeal almost entirely. When the distillate is shaken out with ether, a solid mass results which crystallizes when moistened with alcohol. When filtered, a yellow oil results which has the odor of apples.

From numerous rosaceous plants hydrocyanic acid and benzaldehyde have been obtained: from the leaves, twigs and seeds of the peach tree, *Prunus Persica,* Jess., from the fleshy part of the cherry (*Prunus Cerasus,* L.), from the kernel of the plum (*Prunus domestica,* L.), from the bark, leaves, flowers and seeds of *Prunus Padus,* L., and from the young leaves and the flowers of *Prunus spinosa,* L. (Ger. *Schlehe*). An enumeration of all of these plants and parts of plants would lead too far, since there is no practical reason for so doing. Hence reference should be had to C. Wehmer's *Die Pflanzenstoffe* (Jena, Gustav Fischer), where from p. 273 to p. 306 the entire literature may be found. A list of all plants yielding benzaldehyde and hydrocyanic acid will be found on p. 531 of vol. I of this work.

341. Oil of Mountain Ash Berries.

In the preparation of malic acid from mountain ash berries, the fruits of *Sorbus Aucuparia,* Gærtn. (Ger. *Vogelbeere,* family *Rosaceæ*), a pungent odor is noticed that is due to a substance volatile with steam. If the vapors are condensed a colorless oil results, which, when diluted, has a not unpleasant odor and which has the following properties: b. p. 221° (755 mm.)[2]); 136° (30 mm.)[3]); d_{15° 1,068[2]); d_{21° 1,0628[3]); $[\alpha]_j + 40{,}8^\circ$.

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[1]) Journ. f. prakt. Chem. II. **84** (1911), 247; **87** (1913), 142.

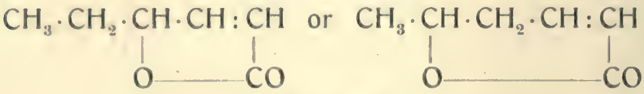
[2]) Liebig's Annalen **110** (1859), 129.

[3]) Berl. Berichte **27** (1894), 344 and **33** (1900), 2140.

The volatile oil of the mountain ash berry was first investigated by A. W. Hofmann[1]) and designated by him as parasorbinic acid. According to O. Dœbner[2]) it is a lactone of the formula $C_6H_8O_2$, more particularly that of γ- or δ-hydroxyhydrosorbinic acid.

$$CH_3\cdot CH:CH\cdot CH:CH\cdot COOH$$

Sorbinic acid.



$$CH_3\cdot CH_2\cdot\begin{array}{c}CH\\|\\O\end{array}\!\begin{array}{c}\cdot CH:\\ \\ \text{———}\end{array}\!\begin{array}{c}CH\\|\\CO\end{array}\quad\text{or}\quad CH_3\cdot\begin{array}{c}CH\\|\\O\end{array}\!\begin{array}{c}\cdot CH_2\cdot CH:\\ \\ \text{————}\end{array}\!\begin{array}{c}CH\\|\\CO\end{array}$$

Sorbin oil.

According to Dœbner, the mature or nearly mature mountain ash berries are the most suitable material for the preparation of the oil. Whereas the immature berries contain malic acid only, the ripening berries contain sorbin oil and the malic acid disappears. At the same time sorbinose (Ger. *Sorbinzucker*), $C_6H_{12}O_6$ and sorbite $C_6H_{14}O_6$ result.

342. Raspberry Oil.

From the press-cakes of the raspberry, *Rubus Idæus,* L. (Ger. *Himbeere,* family *Rosaceæ*), H. Hænsel[3]) obtained a small amount of an oil that had the odor of fermented raspberries: d_{15° 0,8833; $\alpha_D + 2^\circ 8'$; S. V. 193; S. V. after acetylation 215; soluble in 30 parts of 80 p. c. alcohol.

343. Oil of Water-Avens Root.

The volatile oil from the roots of *Geum urbanum,* L. (Ger. *Nelkenwurzel,* family *Rosaceæ*) was examined as early as 1818 by Trommsdorff[4]) and again in 1844 by Buchner[5]). However, they did not determine with any degree of certainty whether the oil, which had a clove-like odor, was identical with the eugenol from clove oil or not.

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[1]) Liebig's Annalen **110** (1859), 129.

[2]) Berl. Berichte **27** (1894), 344 and **33** (1900), 2140.

[3]) Apotheker Ztg. **19** (1904), 854.

[4]) Trommsdorff's Neues Journ. der Pharm. **2** (1818), I. 53.

[5]) Buchner's Repert. f. d. Pharm. **35** (1844), 169.

E. Bourquelot and H. Hérissey[1]) distilled the comminuted fresh root after previous maceration for 12 hours. Thus they obtained 0,1 p.c. of an oil the bulk of which consisted of *eugenol* (benzoyl eugenol).

They ascertained that the root contains a glucoside which is hydrolyzed by an enzyme, likewise present, with formation of eugenol. Inasmuch as repeated experiments to produce the eugenol odor in the extract with other enzymes such as emulsin, invertin, the enzyme from *Aspergillus niger,* v. Tgh. also from other plant powders, were unsuccessful, it may be assumed that the enzyme of the water-avens root is a specific enzyme which has thus far been found only in the root of the closely related species *Geum rivale,* L. *Gein* is the name suggested for the new glucoside, *gease* that for the enzyme.

Upon distillation of the dry root *(Radix caryophyllata)* H. Hænsel[2]) obtained 0,022 p.c. of a reddish-brown oil with an aromatic odor and a burning, bitter taste, $d_{13,5^\circ}$ 1,037; soluble in 90 p.c. alcohol.

344. Oil of Rose.

Oleum Rosarum. — Otto of Rose. — Attar of Rose. — Rosenöl. — Essence de Rose.

Origin. Only a few of the more than 7000 horticultural varieties of the rose are used in the production of the oil. So far as the roses used for distillation are concerned, it is less a matter of shape and appearance than of resistance to climatic conditions and a rich yield of flowers. Both conditions are satisfied by the *Rosa damascena,* Mill. cultivated in the Balkan states and in Germany. This cultural variety is not known in the wild state but is a product of horticulture. Presumably the original plant was a hybrid between *Rosa gallica* and *Rosa canina.*

The Bulgarian rose bush is fairly well protected by thorns which curve only slightly backward. They bear pointed-oval three-pair leaflets and the end leaflets are of pure green colour;

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[1]) Journ. de Pharm. et Chim. VI. **18** (1903), 369; **21** (1905), 481. — Compt. rend. **140** (1905), 870.

[2]) Chem. Zentralbl. **1903**, I. 1137.

Fig. 46.
Rose harvest in Bulgaria.

Fig. 47.
Rose harvest in Bulgaria.

the calices are bare and slightly covered with a white „bloom". Numerous inflorescences contain as many as 27 florets that are arranged somewhat like a false umbel. Completely blown and expanded, the roses do not acquire a diameter of more than 7 cm. Although double, they still reveal a considerable number of antheridia with large yellow anthers. Frequently the outer petals are almost white, the inner ones more and more red, revealing under favorable conditions, a pure rose-red.

In Bulgaria the roses are cultivated in dense hedges of the height of a man. The white rose, *Rosa alba,* L., is used to indicate the limits of the several rose fields. It is said to yield an inferior oil richer in stearoptene[1]).

The rose cultivated in southern France, primarily for the production of rose water and rose pomade, is the *Rosa centifolia,* L.[2]). It is planted in rows but the hedges are not as dense nor as high as those of Bulgaria.

Recently, experiments have been made in the vicinity of Grasse with two rose varieties which possess the advantage of a longer flowering period and of greater productivity. The *Rose à Parfum de l'Hay* has been obtained by Jules Graveraux in Fontenay-aux-Roses (Seine) by crossing the Japanese *Rosa rugosa,* Thb. with a bastard of the *Rosa damascena* and the remontant rose, the *Général-Jacqueminot,* whereas the *Roseraie de l'Hay* is a similar variety produced by Cochet-Cochet in Coubert (Seine-et-Marne).

The first variety has not come up to the expectations held in Grasse, since the odor of the products obtained therefrom is neither delicate nor strong enough. The experiments with the *Roseraie de l'Hay* have not yet been concluded[3]).

Under favorable weather conditions about 3 million kg. of roses are annually harvested and utilized in southern France.

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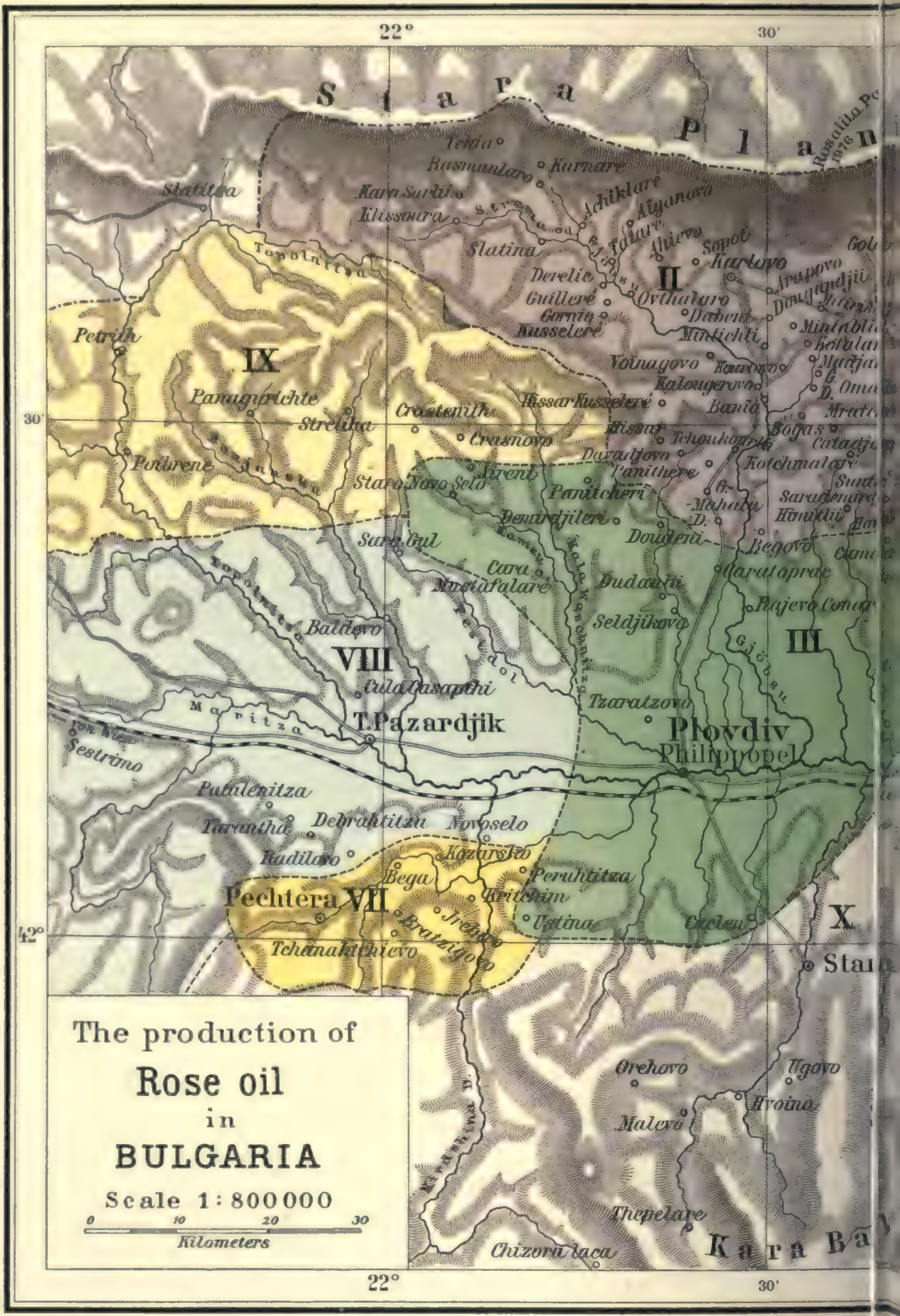
[1]) Hence the Chamber of Commerce of Philippopolis has recommended to the cultivators of roses not to raise any white roses, since they afford a poorer yield as well as an oil of inferior quality. Report of Schimmel & Co. October 1906, 65.

[2]) According to Cochet-Cochet the oil rose of southern France is not *Rosa centifolia,* L. but likewise *Rosa damascena,* Mill. Berichte von Roure-Bertrand Fils October 1911, 70.

[3]) Berichte von Roure-Bertrand Fils October 1911, 73.



The production of Rose oil in BULGARIA

Scale 1:800000


23°
30′
Balkan
Kazanlik
I
Skobelevo
Imitlii
Cheinovo
Urenlii
Bitcherlii
Enina
Hassatl
Seltzi
Gussovo
Bergovetz
Sahrane
Gabarevo
Tundja
Tarnitschane
Imouchlare
P. Banya
Sulitleri
Touria
Alkanlii
Oresovo
Achlatli
Tcharganow
D. Soffoulare
Lahanlii
Urla
Nicolaevo
Maglige
Kazalajderé
Hamzalari
Bagina
Nova Machla
Dalboki
Kososmadé
Tvarditza
Konaré
Tersiobass
Haïnito
Orisari
Kapalnia
Tundsha
IV
N.-Zagora
Kriva Krouchn
Balabanlii
Bosagatch
Smavli
Kispetlii
Colupthi
Djoumalii
Sachovitza
V
St. Zagora
Baraclari
Koulloudja
Ada-Tepé
Sichecebynar
Kolena
Aidanlii
Echerkovo
Mouratlii
Teke
Djambazito
Ahijevo
Caraptcha
Kalfa
Nova-Machla
Caraferen
Hadjioulare
Enichen
Alagun
Buchmanlii
Tchehlare
Mahmoudlare
Kazanka
Babel
Baldjilare
Kolutchevo
Sakarlii
Sudaklii
Derelie
Evdjivlen
Kovantchi
Echerren
VI
Tchirpan
Assaharovo
Thicardji
Enihten
Ahmatovo
Maritza
nach Konstantinopel
Uzun
Chaskovo
Perpelek D.
Sasly D.
Sogutli
42°
Districts:
I Kazanlik
II Karlovo
III Plovdiv
IV Nova-Zagora
V Stara-Zagora
VI Tchirpan
VII Pechtera
VIII Pazardjik
IX Panagurichte
X Stanimaka

Between 1904 and 1911 the price paid for 1 kg. of fresh roses varied between 25 centimes and 2.50 fr.[1]). In recent years a large part of the harvest is subjected to extraction with volatile solvents (Comp. vol. I, p. 251). The yield of concrete oil amounts to from 0,17 to 0,25 p.c.

Spain also has begun to cultivate roses, *e.g.* in Chinchilla (province of Granada), thus far however, on a small scale only.

Concerning the rose cultures started in Kachetia, Government of Tiflis, in the Caucasus, by the Russian government[2]), nothing more has been heard in recent years. In 1902[3]) the amount of rose oil obtained amounted to about 3 kg., in addition to 320 kg. of rose water. 11,5 ha. (= 29 acres) had been cultivated with Bulgarian roses. In other parts of the Transcaucasus, experiments have been made to cultivate roses of Persian origin[4]).

What variety of rose was cultivated in the rose gardens in Shiraz, formerly so famous, is not definitely known. Possibly it was the *Rosa gallica,* the dried petals of which are to-day exported from Persia in large quantities. Whether roses are distilled in Persia at the present time is not known. According to a consular report, about 2,5 kg. of rose oil were exported from Jesd, a Persian city, about the middle of the nineties. It has been suspected that this was not a rose oil but an oil distilled together with sandalwood[5]).

In recent years an Anatolian oil of rose has repeatedly been met with in the market. However, it has been impossible to learn anything more about it. Brussa, Sparta and Burdur in Asia Minor are mentioned as places of production. Neither has it been possible to ascertain whether and to what extent oil of rose is distilled in Damascus and in Marrakesh, Morocco[6]).

In India where the distillation of rose oil has been carried on for about two centuries in Kanauj (Kanouj)[7]), in Gazipour

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[1]) Bericht von Roure-Bertrand Fils October 1911, 72.

[2]) Report of Schimmel & Co. April 1900, 39.

[3]) Berichte von Roure-Bertrand Fils October 1902, 24.

[4]) Chemist and Druggist 70 (1907), 815.

[5]) Report of Schimmel & Co. October 1896, 65; October 1912, 97.

[6]) Jeancard Fils & Cie., Rev. de Grasse 1911, No. 25.

[7]) Comp. sandalwood oil p. 336.

on the Ganges and in other parts of Bengal, *Rosa damascena* is likewise used. However, the oil from these places is never pure but always mixed with sandalwood oil. As already mentioned, sandalwood is commonly distilled together with the roses.

All of these places of production play but a very minor role in the world's commerce of rose oil and need receive but little consideration beside Bulgaria.

Production of Bulgarian Oil of Rose. The cultivation of roses[1]) is carried on particularly in southern Bulgaria in the valley of Kazanlik and Karlovo[2]). Outside of this district there are several plantations in the plains of Philippopolis and more particularly in Brezovo. At the lower altitudes (300 m.) the harvest is relatively early *e.g.,* in Kazanlik (Kezanlik), Brezovo and Karlovo. In the districts of Kalofer (700 m.) and Klissoura (800 m.) it is relatively late. In general the rose fields occupy an intermediate area between the grain fields of the plains and the forests of the mountains. Moreover, a light, stony soil which is not overmoist is selected. The red *Rosa damascena* and

Fig. 48.

Bulgarian rose oil still.

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[1]) P. Jeancard, Journ. Parfum. et Savonn. **20** (1907), 254; Americ. Perfumer **2** (1908), 192.

[2]) Comp. the accompanying map of the Bulgarian rose districts.

the white *Rosa alba* are mostly cultivated. The distiller would prefer to see the latter eliminated, but the farmers adhere to their old practices. The roses are planted in rows 2,5 m. apart. The individual plants are placed in holes from 40 to 50 cm. deep, are covered with a layer of earth 5 to 6 cm. in thickness and with stable manure; the plants have to be hoed twice each year. The yield per hectare of a good plantation runs up to 4000 kg. per year, but as a rule is much less. The gathering of the roses begins late in May or early in June. Frequently there is a scarcity of women to do the picking. The Bulgarians and Turks are somewhat indolent. Instead of beginning to pick before daybreak and interrupting the labor when the sun is high, they start late and gather all day long. The result is that frequently the flowers arrive at the still in a bad condition (scorched and discolored). The temperature in the rose bags occasionally rises to 50°[1]).

The distilling outfit used in Bulgaria is very simple and is the same as that described more than 40 years ago by Baur[2]). The fire-place consists of masonry work, and the fuel is supplied by the near forests of the Balkan mountains. On it rests the copper still *(lambic)* of 110 liters capacity (fig. 48) and 1,1 m. high. The body of the still is conical and provided with two handles by means of which it can be removed from the fire-place. The diameter of the still is 0,8 m. at about the middle of the still and 0,25 m. at the neck. The helmet which is 0,5 m. high and has the shape of a puff-ball fits well into the neck of the still. The joints are luted with clay and strips of cloth. The helmet is provided with an exit tube which slopes toward the

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[1]) A detailed account of the conditions prevailing will be found in the inaugural dissertation of Georg Sjaroff, *Die Rosenkultur und Rosenölindustrie in Bulgarien,* Leipzig 1907. The author, a Bulgarian, treats the cultivation of the roses, the distillation of the oil, its commerce, and the economic aspect of the industry. He supplies statistics concerning the area under cultivation, prices of raw materials and final product; discussing in detail the causes of the low price of the oil which prevailed at that time. Interesting items, based on personal observations, may also be found in a paper by P. Siedler, *Über Rosenkultur und Rosenölgewinnung in Bulgarien.* Berichte d. deutsch. pharm. Ges. **22** (1912), 476.

[2]) Neues Jahrbuch für Pharmacie und verwandte Fächer **27** (1867), 1—20; Jahresb. f. Pharm. **1867**, 350.

ground at an angle of 45°. This connects with the condensing tube, which is a straight tube of the thickness of a thumb and 0,25 m. long. It passes through a tub made of oak or beech wood, filled with water. The condensation water is conducted to the tub by means of a wooden gutter.

A considerable number of these stills are mounted under a roof. According to G. Sjaroff, such an outfit is known as *giulapana.*

Each still is charged with 10 to 15 kg. of freshly picked roses and 75 to 100 or 120 liters of water. The distillation is continued until 2 flasks of 5 liter capacity each have been filled. The water remaining in the still is used for the next distillation. This method is quite irrational because of the large amount of extractive matter and salts that collect in the course of time. Their presence can scarcely be without influence on the delicate perfume.

After sufficient distillate has accumulated, 40 liters of the rose water are transferred to a still and the first five liters of distillate cohobated. At first this second distillate is a white, turbid liquid. Upon cooling it becomes clear, the oily particles separating at the surface. For the purpose of separating the floating oil, the Bulgarians make use of a small funnel-shaped instrument of tin provided with a long handle having a very fine opening at the bottom. This opening permits the water to pass through but not the semi-congealed oil. In this manner oil and water are separated.

According to a quite unreliable and equally improbable account, 3000 kg. of flowers yield 1 kg. of oil in Bulgaria. No doubt, a much larger amount of flowers is needed. *With the requisite amount of palmarosa oil* 3000 kg. of flowers may suffice to produce 1 kg. of "Bulgarian oil of rose"!

After the oil (Bulgarian *güljag*) has been adulterated for a second time with palmarosa oil by the dealer, it is transferred to tin-lined copper flasks *(estagnons)* and then enters the market as Bulgarian oil of rose. For this purpose the palmarosa oil is specially prepared by exposing it to the sun in shallow dishes. The designation "Turkish" as applied to oil of rose is no longer correct. At least in European Turkey no rose oil is produced.

Fig. 49.

Bulgarian Giulapana.

According to the author of the dissertation referred to in foot-note 1, p. 555, several rose oil distilleries on a factory scale with boiler exist at the present time, *viz.,*

1. The factory of Montalan in Karlovo, founded by Chier in 1902. It is provided with 4 stills having a capacity of 2500 liters each.

2. The factory of Garnier in Karasarlii, erected in 1904. The extraction method is followed, the apparatus illustrated and described on p. 256 of vol. I being used.

3. The factory of Batzuroff, located in the outskirts of the village Karnare and erected in 1905. It is equipped with four stills, each heaving a capacity of 9000 liters. The charge consists of from 1500 to 2000 kg. roses.

Production of German Oil of Rose. The first efforts to produce oil of rose in Germany on a factory scale were made by Schimmel & Co. in 1883. At first *Rosa centifolia,* L. grown in the vicinity of Leipzig was used. In 1888 the firm secured a considerable number of rose plants from Bulgaria. With careful handling these were increased rapidly. At the present time about 35 hectares in the neighborhood of Miltitz near Leipzig are covered with this variety. Because of the injury done to the fresh flowers during transportation, the roses must be worked up on the spot. For this reason a new factory building, equipped with the best modern appliances, was erected in the midst of the rose fields. The roses picked in the morning are transferred directly to the large copper stills, each of which has a capacity of 1500 kg. roses in addition to the requisite water. (Vol. I, p. 240, fig. 52). One kg. of oil is obtained from about 5000 to 6000 kg. of flowers.

It goes without saying that the mistakes made in Bulgaria are here avoided. The stills are not heated over direct fire but with steam. For every charge of roses fresh water is taken. As in the case of all other volatile oils, oil of rose is collected in a series of Florentine flasks arranged as cascade.

Thanks to the care exercised in its manufacture, the German oil of rose is far superior to the Bulgarian product. Although its stearoptene content is high, it is twice as intensive as to odor and will go twice as far. So far as stearoptene content and strength of odor are concerned, the *Rosengeraniol* of Schimmel & Co. resembles the Bulgarian oil. For the production

Fig. 50.

Rose fields in Miltitz.

of rose geraniol 2500 kg. of roses and 1 kg. of pure geraniol are distilled together.

Production of Oil of Rose in France. The production of rose oil in southern France differs fundamentally from that in Bulgaria and Germany in this, that the distillation is conducted primarily for the sake of rose water and that rose oil is obtained as a by-product. From 1 kg. roses 1 kg. rose water is obtained. In addition 60 to 70 g. oil are collected from 1000 kg. flowers, the oil separating from the rose water[1]. The quantity of roses collected in France is not inconsiderable, amounting to about one-fifth to one-seventh of the Bulgarian harvest. In good years it runs up to 3 millions of kg.[2]. A large portion of the flowers is extracted with volatile solvents, another portion is worked up into pomade.

Production of Rose Perfume by Extraction. As will be pointed out later (p. 568), the treatment of roses by distillation is not the most rational for the production of this floral perfume. The phenylethyl alcohol which is readily soluble in water cannot be separated by means of cohobation. Hence, oil of rose obtained by distillation contains little or nothing of this important odoriferous constituent[3]. Even before this fact was known, it had been recognized that the rose perfume obtained by the extraction with fat or volatile solvents corresponded much more to the natural perfume than did the volatile oil. The production of rose pomades has been conducted in France for a long time, also in Germany. It was much later that the extraction with petroleum ether was resorted to. (For the description of this process see vol. I, p. 247). As already pointed out on p. 558, this process is also applied in Bulgaria. A similar manufacturing plant exists in Beirut.

Properties. The Bulgarian oil of rose is light yellow in color, occasionally with a greenish tinge. At 21 to 25° it has the consistence of fatty almond oil. Its odor is strong and benumbing, resembling that of roses. The taste is pungent and

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[1] P. Jeancard and C. Satie, Bull. Soc. chim. III. **31** (1904), 934.

[2] Berichte von Roure-Bertrand Fils October **1907**, 59.

[3] The phenylethyl alcohol remains principally in the rose water, hence this reproduces the odor of the roses better than does the oil.

Fig. 51.

Rose harvest in Miltitz.
(In the background the workmen's village of Schimmel & Co.).

balsamic. At about 18 to 21° acicular or lamellar crystals separate which are shiny and iridescent. On account of their low specific gravity they collect at the surface forming a thin film which breaks up readily when shaken. When cooled to a lower temperature the oil congeals to a transparent, soft mass which is again liquefied by the warmth of the hand.

With the higher stearoptene content the specific gravity is lowered. $d_{15^\circ}^{20^\circ}$ 0,856 to 0,870; $d_{15^\circ}^{30^\circ}$ 0,849 to 0,862; $\alpha_D - 1$ to -4°; n_{D20° 1,452 to 1,464[1]; the congealing point, the method for the determination of which is described on p. 572, lies between + 18 and + 23,5°; A. V. 0,5 to 3; E. V. 7 to 16; total geraniol content (*i. e.* of alcohols computed as $C_{10}H_{18}O$) 66 to 75 p.c., in exceptional instances up to 76 p.c.; citronellol content determined by formylation (see vol. I, p. 580) 24 to 37 p.c.; stearoptene content 17 to 21 p.c.

On account of the difficultly soluble paraffins which it contains, oil of rose yields turbid solutions only, even with very large amounts of 90 p.c. alcohol; from these solutions the stearoptene separates gradually. The liquid portion, the so-called eleoptene, yields a clear solution even with 70 p.c. alcohol.

When examined by Schimmel & Co., two oils, presumably distilled from white roses, revealed the following properties: 1. (from Karlovo) d_{30° 0,8696; $\alpha_D - 2^\circ 35'$; n_{D25° 1,46218; congealing point + 18°. 2. (from Kazanlik) d_{30° 0,8526; $\alpha_D - 3^\circ 50'$; n_{D25° 1,45871; congealing point + 19°; A. V. 2,2; E. V. 9,9; E. V. after acetylation 213,9 = 70,1 p.c. alcohol $C_{10}H_{18}O$. Similar constants were revealed by a third oil[2]: d_{15° 0,8723; $\alpha_D - 2^\circ 54'$; E. V. 11,14; E. V. after acetylation 222,44 corresponding to 73,4 p.c. alcohols of the formula $C_{10}H_{18}O$. It was soluble in 1 vol. of 90 p. c. alcohol with abundant separation of paraffin. It congealed at 14° but liquefied again completely at 20°[3].

In connection with an Anatolian oil distilled from red and white Bulgarian roses, Schimmel & Co. ascertained the following

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[1] As to the index of refraction of otto of roses see also E. J. Parry, Chemist and Druggist **63** (1903), 246. — W. H. Simmons, *ibidem* **68** (1906), 20.

[2] Berichte von Roure-Bertrand Fils October **1908**, 28.

[3] Hence the stearoptene content of these three oils does not appear to be unusually high, whereas otherwise the oil of white roses is regarded as rich in stearoptene. Comp. p. 552.

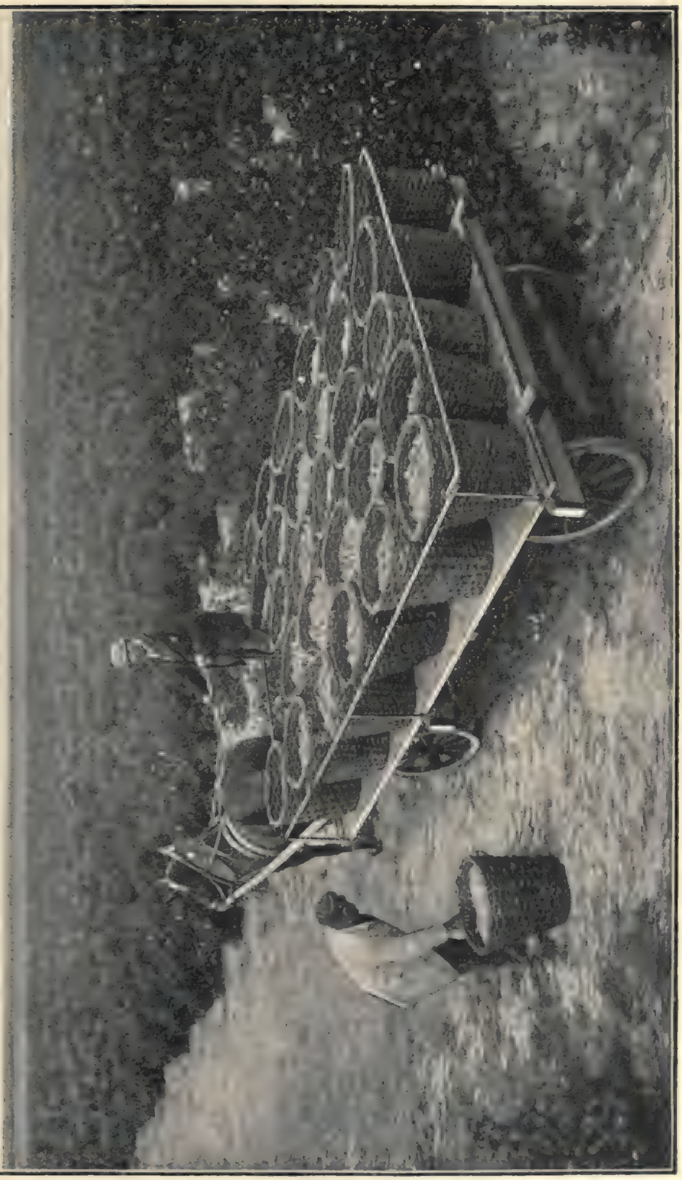

Fig. 52.
Rose harvest in Miltitz.

constants: d_{30° 0,8589; α_D $-2^\circ 20'$; n_{D25° 1,46486; congealing point $+19,5^\circ$; A. V. 1,4; E. V. 9,8; total geraniol content 74 p. c.

On account of its larger stearoptene content, the German oil of rose (from *Rosa damascena,* Mill.), at ordinary temperature, is a soft, greenish mass permeated by crystals. A complete analysis of three samples is recorded in the accompanying table. Its odor is much stronger and more intense than that of the Bulgarian oil. The congealing point lies between 27 and 37°; the specific gravity between 0,838 and 0,850 at 30°; α_D $+1$ to -1°. The stearoptene content fluctuates between 26 and 40 p.c.

	d	α_D	n_D	Cong. Pt.	A.V.	E.V.	Total Geraniol	Citronellol	Stearoptene
1.[1])	0,8438 (30°)	$-0^\circ 44'$	1,45811 (29°)	$+29^\circ$	2,3	4,5	60,4 p.c.	17 p.c.	28,5 p.c.
2.[1])	0,836 (33°)	$-0^\circ 52'$	1,45711 (33°)	$+30^\circ$	0	10,4	54 p.c.	13,7 p.c.	40,0 p.c.
3.[2])	0,8444 (35°)	$-0^\circ 23'$	1,46139 (35°)	$+30^\circ,8$	4,3	5,2	56,8 p.c.		abt. 42 p.c. with S.V. 3,0

The phenylethyl alcohol content of the last oil enumerated in the preceeding table (determined by shaking out with 1 p.c. sodium hydroxide solution[3])) amounted to about 9 p. c. The properties of the oil deprived of phenylethyl alcohol and stearoptene were: d_{15° 0,8885; α_D $-0^\circ 44'$; n_{D20° 1,46565; E. V. after acetylation 266,9 = 91,8 p. c. $C_{10}H_{18}O$; soluble in 1 vol. and more of 70 p.c. alcohol.

An oil distilled at Leipzig from *Rosa centifolia,* L. had the following properties: d_{25° 0,8727; α_D $+0^\circ 49'$; congealing point $+28^\circ$; S. V. 7,8.

According to J. Dupont and J. Guerlain[4]) two French oils distilled in 1895 and 1896 respectively had the following properties: d_{30° 0,8225 and 0,8407; α_{D30° $-6^\circ 45'$ and $-8^\circ 3'$; stearoptene content 35 and 26 p.c. respectively.

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[1]) Report of Schimmel & Co. April **1901**, 48.

[2]) *Ibidem* October **1906**, 67.

[3]) Comp. footnote 3 on page 569.

[4]) Compt. rend. **123** (1896), 700.

Two oils distilled from the *Roseraie de l'Hay* (see p. 552) yielded upon analysis the following constants: —

d_{30°	α_D	n_{D25°	Cong. Pt.	A. V.	E. V.	Total Geraniol
0,8706	— 1° 26′	1,46486	+ 13°	1,8	6,3	91 %
0,8653	— 3° 20′	1,46159	+ 18,6°	1,8	5,6	91,8 %

P. Jeancard and C. Satie1) have examined the French oils obtained by various methods.

1. The oil obtained from the complete roses (inclusive of the calyx) including the oil separated upon the cohobation of the aqueous distillate. Congealing point 25,5°; stearoptene content 33,2 p.c.2). Properties of the liquid portion (eleoptene): d_{15° 0,8790; α_D — 3°; soluble in 2 vol. of 70 p.c. alcohol; total alcohol content 88,55 p.c., citronellol 22,4 p.c.

2. The oil obtained by distilling 1 kg. of roses so as to obtain 1 kg. of rose water. This does not include the oil contained in the rose water (without cohobation). Congealing point + 25,9°; stearoptene content 58,88 p.c.; A. V. 2,24; E. V. 14,7°; total alcohol content 32 p.c.; citronellol 15,10 p.c.

3. An oil obtained from the calyces, antheridia and pistils but without the floral leaves. The yield from 1000 kg. was about 50 g. d_{15° 0,8704; α_D — 41°; congealing point + 8°; stearoptene content 51,13 p.c.; A. V. 6,12; E. V. 22,4; total geraniol content 13,99 p.c.; citronellol 13,56 p.c. The high stearoptene content is noteworthy, also the fact that aside from citronellol other alcohols appear to be conspicous by their absence.

4. An oil distilled from tea roses. Congealing point 23,5°; stearoptene content 72 to 74 p.c. Remarkable are the enormously high stearoptene content and the low congealing point. The stearoptene could be separated into a portion melting at 14°

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1) Bull. Soc. chim. III. 31 (1904), 934.

2) It is to be noted that the stearoptene content was not determined in any of these oils as described on p. 573. J. and S. proceeded according to the following method: 10 g. of oil are weighed in a beaker when 50 cc. of acetone, chilled to — 10°, are added without shaking. The mixture is then filtered through a filter surrounded by a freezing mixture, the residue washed several times and the liquid removed with the aid of a suction pump. The tared filter is dried in a vacuum desiccator over sulphuric acid and weighed.

and into another portion melting at 40°. The stearoptene from the calyces of the ordinary rose (see No. 3 above) appears to be of similar composition.

Upon the analysis of a Russian oil (from Kachetia, comp. p. 553), Roure-Bertrand Fils[1]) obtained the following constants: d_{30° 0,8368; $\alpha_{D26^\circ} - 4^\circ 16'$; congealing point $+23^\circ$; stearoptene content 33,5 p.c.; A. V. 5,7; E. V. 4,7; total geraniol 48,9 p.c.; citronellol 34 p.c.

In connection with a Spanish oil distilled at Chinchilla, Schimmel & Co. observed the following properties: d_{30° 0,8247; $\alpha_D - 1^\circ 23'$; n_{D25° 1,45212; congealing point $+27^\circ$; A. V. 3,3; E. V. 10,7; E. V. after acetylation 135,5 = 41,5 p.c. total geraniol; paraffin content 50 p.c., E. V. of the paraffin 7,0. The constants of another Chinchilla rose oil were found as follows[2]): $d_{15^\circ}^{30^\circ}$ 0,844; $\alpha_D - 2^\circ$; n_D 1,565; m. p. 27 to 28°; paraffin content 33,3 p.c.; m. p. 15° of the paraffin 31,31°.

Concerning rose oils obtained by the extraction method, H. von Soden[3]) makes the following communication: 8000 kg. of French roses yielded 0,052 p.c. of volatile oil which congealed between 5 and 7°; d_{15° 0,967; $\alpha_{D17^\circ} - 1^\circ 55'$; E. V. 4,6; E. V. after acetylation 295. By means of phthalic acid anhydride 75 to 80 p.c. of alcohols were isolated from the oil, 75 p.c. of which consisted of phenylethyl alcohol and 25 p.c. of the other primary alcohols commonly found in oil of rose.

45 kg. of German roses yielded 0,0107 p.c. of ethereal extract oil with a congealing point of $+12^\circ$; d_{19° 0,984; $\alpha'_{D17^\circ} + 0^\circ 9'$; A. V. 3; E. V. 4; E. V. after acetylation 313,5; content of phenylethyl alcohol 75 p.c., of aliphatic alcohols (primarily) 25 p.c.

Composition. Not long after the introduction of elementary analysis the first combustions of rose oil and its stearoptene were made by Saussure in 1820[4]). A second analysis by R. Blanchet[5]) soon followed. Whereas the combustion of the oil revealed little more than its oxygen content, that of the

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[1]) Berichte von Roure-Bertrand Fils October **1902**, 24.

[2]) Perfum. and Essent. Oil Record **3** (1912), 3.

[3]) Journ. f. prakt. Chem. II. **69** (1904), 265.

[4]) Annal. de Chim. et Phys. II. **13** (1820), 337.

[5]) Liebig's Annalen **7** (1833), 154.

stearoptene revealed its hydrocarbon character. Blanchet regarded the substance as a terpene $C_{10}H_{16}$. It was not until 1869 that Flückiger[1]) looked upon it as a representative of the paraffin series. The molecular weight determination made later by F. B. Power[2]) under his direction yielded results that agreed with the formula $C_{16}H_{34}$. R. Bauer[3]) who made numerous observations on the distillation of Turkish oil of roses in Bulgaria and who made detailed reports thereon from 1867 to 1872, claimed that the odorless stearoptene could be converted into fragrant eleoptene by oxydation, also that reversely, the eleoptene could be artificially reduced to stearoptene. These remarkable claims have not been substantiated by later investigations. About the same time (1872), Gladstone[4]) occupied himself with the study of the liquid portion of the oil, the boiling point of which he found to be 216°. The first detailed investigation of rose oil was made by C. U. Eckart[5]). As principal constituent of German as well as Bulgarian oil he found, in 1890, an alcohol of the formula $C_{10}H_{18}O$ to which he assigned the name rhodinol. Although he observed a great similarity between the new alcohol and geraniol, Eckart declared rhodinol to be different from geraniol. He also proposed a formula to express this difference structurally. It is possibly largely due to the incorrect boiling point, which was found at 216° in correspondence with Gladstone's observation, instead of at 229°, that Eckart did not recognize the geraniol which he had in hand.

Shortly thereafter, namely in 1893, W. Markownikoff and A. Reformatzky[6]) claimed that the formula $C_{10}H_{20}O$ should be assigned to the principal constituent of Bulgarian oil of rose and gave to it the name roseol. At the same time, however,

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[1]) Pharmaceutical Journ. II. **10** (1869), 147. — Zeitschr. f. Chem. **13** (1870), 126; Jahresber. f. Chem. **1870**, 863.

[2]) Flückiger, *Pharmakognosie*. III. ed., p. 170.

[3]) Neues Jahrb. f. Pharm. **27** (1867), 1 and **28** (1867), 193; Jahresber. d. Pharm. **1867**, 350. — Dingler's polyt. Journ. **204** (1872), 253.

[4]) Journ. chem. Soc. **25** (1872), 12. — Pharmaceutical Journ. III. **2** (1872), 747; abstract Jahresber. f. Chem. **1872**, 816.

[5]) Arch. der Pharm. **229** (1891), 355. — Berl. Berichte **24** (1891), 4205. — Th. Poleck, Berl. Berichte **23** (1890), 3554.

[6]) Journ. f. prakt. Chem. II. **48** (1893), 293.

Barbier[1]) had arrived at the conclusion that Eckart's formula $C_{10}H_{18}O$ was the correct one. This conclusion was still farther verified by Tiemann and Semmler[2]) who recognized the identity of Eckart's rhodinal with citral, the aldehyde $C_{10}H_{16}O$ corresponding to geraniol. The conflicting results obtained in the investigations of Eckart on the one hand and of Markownikoff and Reformatzky on the other hand caused Bertram and Gildemeister[3]) to take up the investigation of oil of rose. They ascertained that the bulk of both German and Bulgarian oils of rose consists of geraniol $C_{10}H_{18}O$, the alcohol discovered by Jacobsen in 1870 in palmarosa oil (b. p. 229 to 230°) and that rhodinol is impure geraniol[4]).

However, geraniol is not the only alcohol contained in oil of rose. Hesse[5]) suspected that the alcohol reuniol $C_{10}H_{20}O$, found by him in pelargonium oil, might also be contained in rose oil. Tiemann and Schmidt[6]) proved the identity of reuniol with citronellol, the reduction product of citronellal.

Another important alcoholic constituent is phenylethyl alcohol. It is found in small amounts only (abt. 1 p. c.) in the oil distilled according to the ordinary methods and can be obtained by cohobation only if special methods are employed.

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[1]) Compt. rend. **117** (1893), 177.

[2]) Berl. Berichte **26** (1893), 2708.

[3]) Journ. f. prakt. Chem. II. **49** (1894), 185.

[4]) A lively controversy has arisen as to whether the alcohol $C_{10}H_{18}O$ should be named geraniol in accordance with the well-established name given to it by Jacobsen, or rhodinol, the name given to an impure compound by Eckart. Without going into the merits of this controversy, the literature thereon may here be referred to: H. Erdmann and P. Huth: *Zur Kenntnis des Rhodinols oder Geraniols.* Journ. f. prakt. Chem. II. **53** (1896), 42. — J. Bertram and E. Gildemeister: *Über Geraniol und Rhodinol. Ibidem* II. **53** (1896), 225. — A. Hesse: *Über die vermeintliche Identität von Reuniol, Rhodinol und Geraniol. Ibidem* II. **53** (1896), 238. — H. Erdmann: *Untersuchungen über die Bestandteile des Rosenöls und verwandter ätherischer Öle. Ibidem* II. **56** (1897), 1. — Bertram and Gildemeister: *Die Bestandteile des Rosenöls und verwandter ätherischer Öle. Ibidem* II. **56** (1897), 506. — Th. Poleck: *Zur Rhodinolfrage. Ibidem* II. **56** (1897), 515 and Berl. Berichte **31** (1898), 29. — Bertram and Gildemeister: *Zur Rhodinolfrage. Ibidem* **31** (1898), 749.

[5]) Journ. f. prakt. Chem. II. **50** (1894), 472.

[6]) Berl. Berichte **29** (1896), 922.

It was discovered simultaneously by two investigators, though independently of each other, *viz.,* by H. von Soden and W. Rojahn[1]) and by H. Walbaum[2]). In the so-called concrete oils obtained by the extraction of fresh or dried rose petals with ether or petroleum ether it occurs in much larger amounts[3]), likewise in the ethereal oil obtained from the rose pomades (abt. 46 p. c.)[4]) and in the oil extracted from rose water (abt. 35 p. c.)[1]).

An alcoholic constituent of minor importance is *l*-linalool[5]) (oxidation to citral; m. p. of naphthocinchoninic acid 197 to 199°). Essential as constituent is an odoriferous nonylic aldehyde (m. p. of pelargonic acid 252 to 253°) found by Schimmel & Co.[5]). Probably this is accompanied by higher and lower homologues. In this connection traces of citral were also found in oil of rose (m. p. of naphthocinchoninic acid 195 to 197°). In addition there should be mentioned eugenol[6]) which is present to the extent of about 1 p. c.; also a primary sesquiterpene alcohol which combines with phthalic acid anhydride and which possibly is identical with farnesol[7]). Finally, nerol (m. p. of diphenyl urethane 52 to 53°) should be mentioned. According to von Soden and Treff[6]), rose oil contains from 5 to 10 p. c. of this alcohol.

The alcohols are contained in rose oil mostly as such. In small part only are they present as esters. The eleoptene of Bulgarian oil of rose contains about 90 p. c. of alcohols computed as $C_{10}H_{18}O$. Normal Bulgarian oil (including the stearoptene) contains, on the average, from 2,5 to 3,5 p. c. of esters computed as geranyl acetate, German oils from 1,6 to 3,6 p. c.

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[1]) Berl. Berichte **33** (1900), 1720.

[2]) *Ibidem* 1903, 2299. — Walbaum and Stephan, *ibidem* 2302.

[3]) From the water left in the still after distillation of roses v. Soden and Rojahn separated an oil by means of ether extraction from which they isolated phenylethyl alcohol in the following manner: 200 g. of oil were shaken with 5 kg. of a 5 p.c. solution of sodium hydroxide. In addition to the acids and phenols some of the phenylethyl alcohol went into solution and could be recovered in a very pure state by shaking out the clear solution with ether.

[4]) v. Soden and Rojahn, Berl. Berichte **33** (1900), 3063; **34** (1901), 2803.

[5]) Report of Schimmel & Co. October **1900**, 54.

[6]) Berl. Berichte **37** (1904), 1094.

[7]) See vol. I, p. 399.

As becomes apparent from the investigations of Dupont and Guerlain[1]), the esters are more strongly optically active than is the mixture of the underlying alcohols. Whereas the liquid portions of a French oil of rose was lævorotatory to the extent of 10° 30′ before saponification, after saponification the angle was but —7° 55′. The acids combined with the alcohols as esters have not yet been investigated. Dupont and Guerlain are of the opinion that the esters play an important role in the production of the perfume.

As shown by Flückiger[2]), the stearoptene of rose oil belongs to the hydrocarbons of the paraffin series C_nH_{2n+2}. However, it does not consist of a single hydrocarbon but at least of two, and probably of a series of homologous paraffins. This becomes apparent from the fact that when larger amounts of rose oil stearoptene are treated properly, they can be separated into fractions melting at 22° and at from 40 to 41°[3]).

According to Schimmel & Co.[4]) the ethyl alcohol, which was found by Eckart in rose oil, is formed only when the roses have become heated and begin to ferment during transportation to the still. If the floral leaves are distilled as soon as picked the oil contains no ethyl alcohol.

Examination. In connection with so costly a product as oil of rose the danger of adulteration is very great. Hence in the course of time numerous empirical methods of examination have been proposed. Most of these pertained to the detection of palmarosa oil, the so-called Turkish geranium oil. Even formerly these tests did not enjoy special confidence. This, however, was altogether shaken when it was shown that geraniol is the principal constituent of palmarosa oil as well as of rose oil. It is true, the possibility was not excluded that some minor constituent of the palmarosa oil might yield specific reactions with the reagents suggested and thus reveal the presence of the foreign oil. However, the investigation of palmarosa oil in this

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[1]) Compt. rend **123** (1896), 750.

[2]) See footnote 2, p. 567.

[3]) Report of Schimmel & Co. October **1890**, 54. — Eckart, Dupont and Guerlain, *loc. cit.*

[4]) Report of Schimmel & Co. October **1892**, 41.

direction has yielded no tangible results[1]). Moreover, it should be remembered that the Bulgars treat the palmarosa oil before they use it as adulterant. Thus *e.g.* they attempt to impart to the palmarosa oil a more rose-like odor by shaking it with lemon juice and by exposing it to the sun.

In addition to palmarosa oil, the genuine geranium oil, also its constituents geraniol and citronellol, come into consideration. If the adulteration has been made skillfully, not only do the various proposed color reactions with iodine, sulphuric acid[2]) and magenta sulphurous acid fail, but the more rational chemical and physical methods of investigation as well. This is partly due to the similarity between the chemical constituents of the oil of rose itself and those of its adulterant. Moreover, the character of oil of rose varies so considerably because of differences in climate, meteorological conditions, character of soil, and method of distillation. This is particularly true of its paraffin content; hence a comparison of the physical constants which, even in a normal oil, vary so considerably, do not always lead to the detection of an adulterant.

It is for this reason that it is impossible to state with any degree of certainty that the Bulgarian oil of rose of commerce is the pure distillate from roses. Various indications would seem to favor the doubt. First of all, the large importation of palmarosa oil into Bulgaria arouses suspicion. Its use seems to become apparent when one considers that, as a rule, the exportation of oil of rose from Bulgaria is greater than the production. (Comp. the curve on p. 576.) Moreover the differences between Bulgarian and German oil are too great to be explained away by climatic differences. It is also queer that especially fine oils, occasionally exhibited by Bulgarian distillers, reveal the greatest similarity with German oil as to odor, congealing point and stearoptene content.

On the other hand the product obtained by the distillation of 2500 kilos of roses with 1 kilo of geraniol[3]) cannot be differen-

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[1]) E. Gildemeister and K. Stephan, Arch. der Pharm. **234** (1896), 321.

[2]) G. Panajotow, Berl. Berichte **24** (1891), 2700. — Report of Schimmel & Co. April **1892**, 45. Comp. also Jedermann, Zeitschr. f. analyt. Chemie **36** (1897), 96 and Report of Schimmel & Co. April **1897**, 34.

[3]) Report of Schimmel & Co. October **1896**, 66.

tiated from the commercial Bulgarian oil of rose. Intensity of odor, congealing point and stearoptene content are identical.

In order to guard against crude adulterations, the specific gravity, angle of rotation, index of refraction, stearoptene content, saponification value and the content of alcoholic components should be determined.

If the results of such an investigation are in harmony with the constants of good average oils, and if the odor is delicate and of sufficient strength, the oil in question may be regarded without suspicion. However, no chemist can undertake to guarantee the purity of an oil on the strength of its physical and chemical examination.

SPECIFIC GRAVITY. Inasmuch as the oil is permeated with crystals at 15°, the density determination must be made at 20, 25 or 30°. The addition of palmarosa oil scarcely alters the density, that of alcohol lowers it. The presence of the latter may be indicated by taking the specific gravity before as well as after shaking the oil with water[1]). Sandalwood oil, used in the distillation of rose oil in India, is indicated by its greater density.

OPTICAL ROTATION. The optical rotation is scarcely influenced by the presence of geraniol or palmarosa oil, but by that of gurjunbalsam oil (for its detection see p. 575). It is noteworthy that the angle of rotation of the French oil is much greater than that of German or Bulgarian oil.

CONGEALING POINT. The congealing point of oil of rose is that degree of temperature at which the first crystals appear when the oil is subjected to slow cooling. According to P. N. Raikow[2]), who defines the congealing point as the point of supersaturation of the eleoptene with the stearoptene, the determination is carried out in the following manner:

About 10 cc. of oil of rose are transferred to a test tube with a diameter of 15 mm. A thermometer is suspended in the oil in such a manner that it touches neither the bottom nor the sides. With the aid of the hand the contents of the test tube are warmed to a temperature 4 to 5° above the point of super-

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[1]) Report of Schimmel & Co. October 1908, 108.

[2]) Chem. Ztg. 22 (1898), 149.

saturation and well shaken. The tube is then fastened to a support and allowed to stand and cool until the first crystals separate. The degree of temperature is read off on the thermometer, the oil is again warmed and well shaken and the congealing point determined once more.

As to good Bulgarian oils of commerce, the congealing point or the crystallization point[1]), as it has been aptly named, as a rule fluctuates between 18 and 23°, however, variations upwards as well as downwards have been observed. Formerly oil of rose was valued in accordance with its congealing point. Although the odorless paraffin is valueless, an oil was higher priced the higher its congealing point. Originally this conclusion was based on the correct assumption that the addition of palmarosa oil must bring about a lowering of the congealing point. When later the congealing point was raised artificially by the addition of spermaceti, this method lost in importance. It has already been pointed out that the genuine, normal Bulgarian oil of rose is much richer in stearoptene than the commercial oil.

DETERMINATION OF THE STEAROPTENE CONTENT[2]). 50 g. of oil and 500 g. 75 p.c. alcohol are heated to from 70 to 80°. Upon cooling the solution to 0° the stearoptene separates well nigh quantitatively. It is removed by filtration and is treated in like manner with 200 g. of 75 p.c. alcohol. This operation is repeated until the stearoptene is odorless. As a rule two such treatments of the crude stearoptene are sufficient.

DETERMINATION OF POSSIBLE SPERMACETI IN THE STEAROPTENE. From 3 to 5 g. of stearoptene are boiled with 20 to 25 g. of 5 p.c. alcoholic potassa for a short time in a flask connected with a reflux condenser. The alcohol is then evaporated and water is added to the residue. Upon cooling, the bulk of the stearoptene separates at the surface as a solid, crystalline mass. The alkaline liquid is poured off, the stearoptene melted with some hot water and again allowed to cool. The water is again poured off and the operation repeated until the wash water is neutral. The combined aqueous liquids are shaken out twice with ether in order to remove any suspended

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[1]) P. Siedler, Berichte d. deutsch. pharm. Ges. **22** (1912), 489.

[2]) Report of Schimmel & Co. April 1889, 37.

stearoptene. The alkaline solution separated from the ether is acidulated with dilute sulphuric acid and again shaken out with ether. Upon evaporation of the ether no residue of fatty acids should remain. For the purpose of control the recovered stearoptene is dried at 90° and weighed. Invariably a small loss will be observed due to volatilization while drying.

It is simpler to determine any spermaceti content by saponifying with half-normal potassium hydroxide solution and titrating back with half-normal sulphuric acid. The saponification value of spermaceti is 128 to 130, that of the natural rose oil stearoptene about 3 to 7.

SAPONIFICATION. The ester value of good commercial oils fluctuates between 7 and 16, the acid value between 0,5 and 3. Palmarosa oil has an E. V. of from 12 to 50, the true geranium oils one of from 31 to 100. Hence the addition of these foreign oils may be indicated by an increase in the E. V.

ACETYLATION. For a complete analysis, rose oil should be acetylated in order to determine the alcohol (geraniol and citronellol) content. Naturally the amount of these alcohols is inversely proportional to the stearoptene content. Good oils of rose contain from 66 to 75 p.c. of alcohols computed as geraniol. Palmarosa oil contains from 75 to 95 p.c. of geraniol[1]).

DETECTION OF SPECIFIC ADULTERANTS. In Bulgaria guaiac wood oil from *Bulnesia Sarmienti* with its agreeable tea-rose-like odor is also used as adulterant[2]). Its presence can be recognized microscopically by the guaiol crystals which separate from the oil upon cooling. Under the microscope guaiol appears as long needles with a canal-like groove in the middle. The crystals of rose oil stearoptene are smaller and thinner and reveal sharply articulated shapes[3]). The presence of guaiac wood oil in rose oil can be definitely established by the isolation of the guaiol which melts at 91°.

Guaiac wood oil increases the specific gravity, the optical rotation and the congealing point of the rose oil to which it

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[1]) E. Gildemeister and K. Stephan, Arch. der Pharm. **234** (1896), 326.

[2]) Report of Schimmel & Co. October 1898, 38.

[3]) F. Dietze, Süddeutsche Apoth. Ztg. **38** (1898), 672 and 680.

has been added. It decreases the ester value but very little. Upon evaporation such an oil leaves a resinous residue[1]).

According to communications received by Schimmel & Co.[2]), a mixture of salol and antipyrine is sometimes added to increase the congealing point of oil of rose. Presumably their presence has not been definitely established.

According to E. J. Parry[3]) nonylic and decylic aldehydes have recently been used as adulterants of rose oil. They are added in the form of a 5 p.c. alcoholic solution. Parry has examined such a solution that had been sent to him from Bulgaria. He describes it as colorless, permeated with crystals of paraffin, the odor reminding of oranges. Specific gravity 0,813 at 30°; index of refraction 1,3655 at 20°. The isolated aldehyde had the specific gravity of 0,835 and an index of refraction of 1,4226 at 20°. After recrystallization the oxime melted at 68,5°. Since nonylic and decylic aldehydes occur as natural constituents of the oil, their addition could not be detected in the small amounts of oil subjected to examination. However, the alcohol added at the same time can readily be detected. The test for alcohol[4]) is all the more desirable since it is occasionally added to counteract the increase in specific gravity produced by the addition of geraniol, palmarosa oil or gurjun balsam oil. Hence the specific gravity should always be determined both before and after the oil has been shaken with water (and subsequently dried). If the density of the oil has been increased by this operation, the alcohol should be isolated from the water after this has been filtered through a moist filter. The alcohol can be identified by the well known methods recorded on pages 349 and 612 of vol. I.

Recently Schimmel & Co.[5]) found that gurjun balsam oil had been used as adulterant. Its detection can be caused in the following manner. The stearoptene is separated by means of dilute alcohol, which also precipitates the gurjun balsam oil,

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[1]) F. Dietze, Süddeutsche Apoth. Ztg. **38** (1898), 672 and 680.

[2]) Report of Schimmel & Co. October **1902**, 75.

[3]) Chemist and Druggist **77** (1910), 531.

[4]) Report of Schimmel & Co. October **1908**, 108; April **1910**, 92; April **1911**, 99.

[5]) *Ibidem* April **1912**, 109; October **1912**, 96.

and its optical rotation ascertained. Whereas the normal stearoptene is inactive and solid at room temperature, the stearoptene which includes the gurjun balsam oil is optically dextrogyrate and is liquid at ordinary temperature.

In order to prove chemically the presence of gurjun balsam oil, the paraffin is separated as completely as possible by freezing. The residue is then oxidized in acetone solution with permanganate according to the method of E. Deussen and H. Philipp[1]). Those components which have not been attacked by the permanganate are removed by fractional distillation at 104 to 105° (5 mm.) and the distillation residue is treated with semicarbazide. If gurjun balsam oil be present the semicarbazone of the gurjunene ketone results which, after re-crystallization from hot alcohol, melts at 234°.

Production and Commerce. So far as the world's commerce in rose oil is concerned only that from Bulgaria comes into consideration. The oils produced in southern France, Saxony, Asia Minor and Russian Transcaucasia, whether by distillation or other methods, are quantitatively of minor importance. With the exception of a few years, the Bulgarian statistics of the commerce in oil of rose reveal the peculiar phenomenon that the amount of oil exported considerably exceeds the amount produced. Moreover, this difference is of such a nature that it cannot be explained away by assuming that these excess amounts represent the overproduction of previous years. In the Report of Schimmel & Co. for October 1908 the accompanying curve was published. It represents the amounts of oil produced, also the amounts of oil exported by the individual countries and totals. As a result of the publication of this discrepancy, the Bulgarian statistician has become cautious in the publication of his export figures. In the statistics for recent years we find the following data concerning production and exportation: —

	1908	1909	1910	1911	1912
Production (kg.)	2652	4319	3148	3950	2987
Exportation (kg.)	4612	6054	?	?	?

The excess of oil exported over that produced is probably accounted for by the assumption that the natural oil is extensi-

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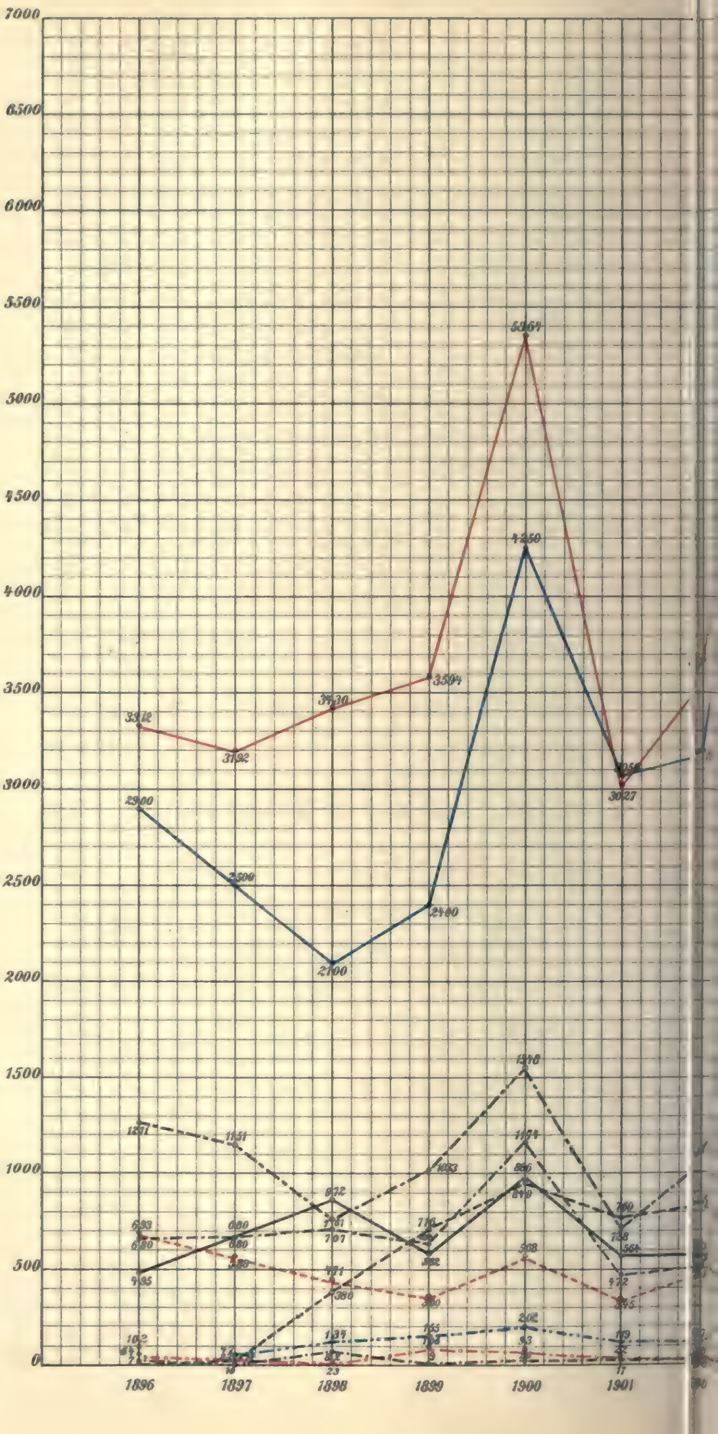
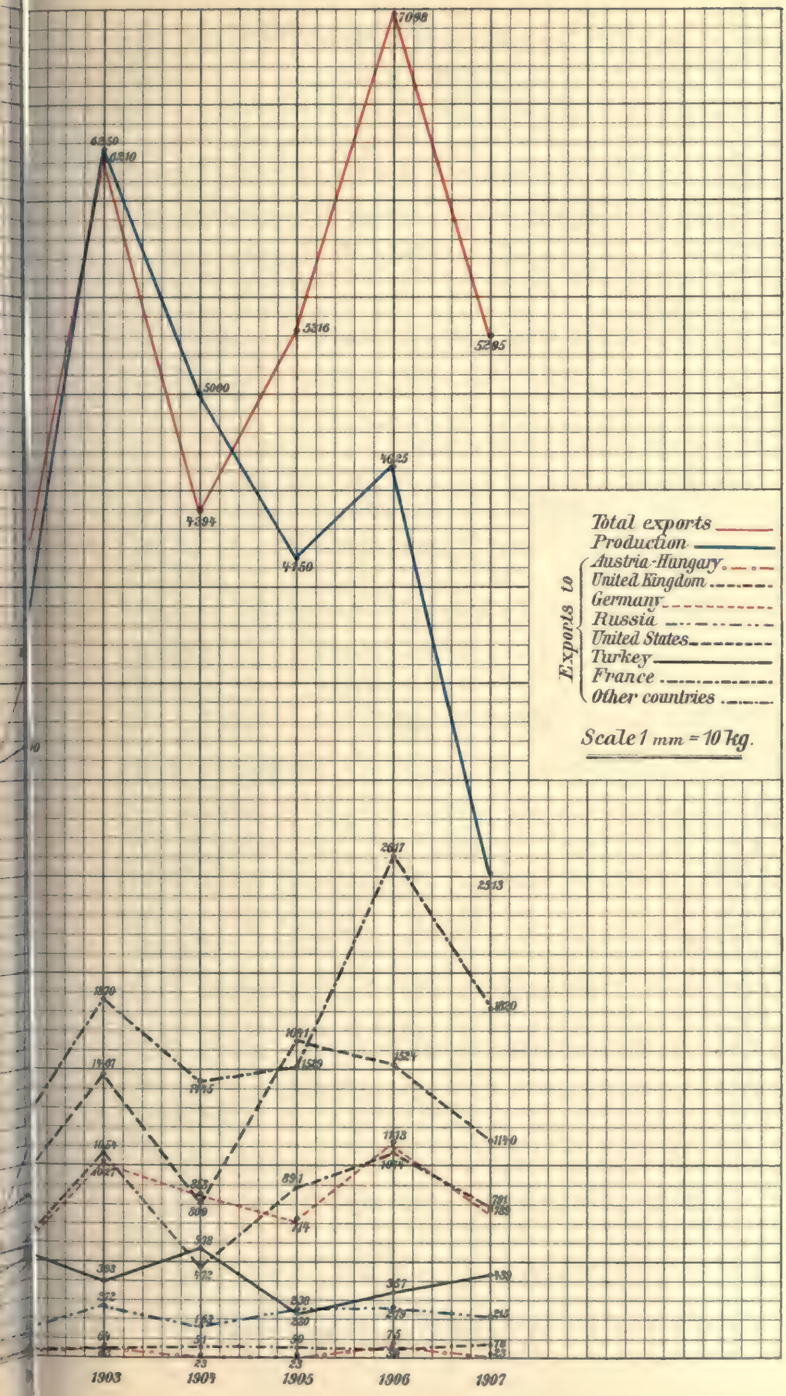
[1]) Liebig's Annalen **367** (1909), 56; **374** (1910), 105.

Production of rose oil in Bulgaria, compared with the total exports in the years 1896 to 1907, and countries of destination.



6250
6210
5000
4394
5316
7098
5295
4625
4150
2513
2637
1820
1870
1407
1445
1661
1529
1524
1140
1054
1027
863
809
891
714
1118
1074
791
789
528
393
472
439
357
372
163
338
330
279
215
64
51
59
75
78
23
23
23
40
1903
1904
1905
1906
1907
Total exports
Production
Exports to
Austria-Hungary
United Kingdom
Germany
Russia
United States
Turkey
France
Other countries
Scale 1 mm = 10 kg.

vely mixed with the adulterants enumerated in the previous paragraphs (palmarosa oil, gurjun balsam oil, alcohol &c.). In spite of regulations against their importation and other well-meant rules that are difficult to enforce, it must be assumed, judging from current literature, that the profitable business of adulteration continues undiminished. In this respect the sealing of the oil by the Bulgarian Export Revenue Office, has caused but little change. Originally it was, no doubt, conceived as guaranty for the purity of the oil. At present the sealed flasks are merely an indication that the oil is of Bulgarian origin.

345. Oil of Haw.

The dried fruit of the rose (Ger. *Hagebutte*), when deprived of its seeds, yielded upon distillation 0,038 p.c. of an oil the odor of which strongly resembled of that of the haws[1]. d_{20° 0,90733; α_{D19° (in 10 p.c. benzene solution) + 0,40°; A.V. 22,1. The oil contains an aldehyde and when dissolved in alcohol separates a stearoptene.

346. Bitter Almond Oil.

Oleum Amygdalarum amararum. — Bittermandelöl. — Essence d'Amandes Amères.

Origin. The almond tree, *Prunus Amygdalus,* Stokes (*Amygdalus communis,* L.), which belongs to the family of *Rosaceæ,* is cultivated in Europe, Asia and northern Africa, and recently also in California. In the course of time several cultural varieties have resulted, which, however, differ merely in the size of their fruits and seeds. Those trees which yield bitter almonds reveal no constant botanical differences from those that produce sweet almonds. Probably all almond trees originally produced bitter almonds and it may be that continuous cultivation resulted in the sweet variety.

Production. Of the bitter almond oil of commerce only a very small amount is obtained from bitter almonds. For its technical production the seeds of the apricot, *Prunus Armeniaca,* L., are used almost exclusively. Its oil in no way

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[1] H. Hænsel, Chem. Zentralbl. 1906, I. 1497.

differs from that of the bitter almond[1]). The apricot kernels, that is the seeds without the hard shells, were formerly imported into Europe almost exclusively from Asia Minor and Syria, the home of the tree. They were designated peach kernels[2]). More recently other countries, more particularly Morocco, California and Japan have acquired importance as producers[3]).

Before the kernels are used for the production of the volatile oil they must be deprived of their fatty oil. They are ground in a roller mill to a coarse powder and exposed to a pressure of 350 atmospheres in a hydraulic press. Upon cold expression the bitter almonds yield about 50 p.c., the apricot kernels about 35 to 38 p.c. of fatty oil.

By means of a chaser mill (vertical millstones) the press cakes are reduced to a fine powder and are then ready for the production of the volatile oil. This does not occur as such in the seeds, but results upon fermentation in a similar manner as do mustard oil and oil of wintergreen. In the presence of water the glucoside amygdalin, which is present in the bitter almond and in the apricot kernel, is changed by the enzyme, emulsin, to benzaldehyde, hydrocyanic acid and glucose.

The reaction is expressed by means of the following equation:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water}}{H_2O} = \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\substack{\text{Hydrocyanic}\\\text{acid}}}{CNH} + \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

As to the immediate products which result in this reaction, a lively controversy has arisen between K. Feist[4]), L. Rosenthaler[5]), S. J. M. Auld[6]) and Bourquelot and Hérissey[7]) which

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[1]) Comp. G. de Plato, On the transformation of hydrocyanic acid during the ripening process of the almond. Annali della R. Staz. chim.-agr. sperim. II. **4** (1910), 117; Report of Schimmel & Co. October **1911**, 19.

[2]) The kernels of the peach, *Prunus Persica*, Jess., likewise yield an oil of equal value to that of bitter almond oil.

[3]) Comp. O. Tunmann, *Der Drogenhandel Hamburgs.* Apotheker Ztg. **26** (1911), 579.

[4]) Arch. der Pharm. **246** (1908), 206, 509; **247** (1909), 226, 542; **248** (1910), 101.

[5]) *Ibidem* **246** (1908), 365, 710. — Biochem. Zeitschr. **14** (1908), 238; **15** (1909), 71, 257. — Arch. der Pharm. **248** (1910), 105.

[6]) Journ. chem. Soc. **93** (1908), 1251, 1276; **95** (1909), 927.

[7]) Journ. de Pharm. et Chim. VII. **6** (1912), 246.

cannot here be entered into. It has been shown that emulsin is no definite chemical compound but a mixture of enzymes to which different names have been assigned. Leaving out of consideration the formation of the glucosecyanhydrin, the system amygdalin-emulsin, according to Rosenthaler's elaborate investigations[1]), presents the following reaction possibilities.

I. Amygdalin, when reacted upon by amygdalase[2]) yields mandelic nitrile glucoside and glucose.

II. When acted upon by prunase[3]), mandelic nitrile glucoside is resolved into *d*-benzaldehyde cyanhydrin and glucose.

III. *d*-Benzaldehyde cyanhydrin, when acted on by *d*-hydroxynitrilase[4]) resolves itself into benzaldehyde and hydrocyanic acid.

IV. Under the influence of a *d*-hydroxynitrilase[5]), benzaldehyde and hydrocyanic acid combine so as to form d-benzaldehyde cyanhydrin.

V. Benzaldehyde and hydrocyanic acid likewise combine to form inactive benzaldehyde cyanhydrin.

VI. By means of *d*-hydroxynitrilase, inactive benzaldehyde cyanhydrin can be broken down asymmetrically with formation of *l*-benzaldehyde cyanhydrin. As a result of the use of an emulsin rich in this enzyme, the benzaldehyde cyanhydrin formed upon the hydrolysis of the amygdalin may be strongly lævogyrate.

Inasmuch as the emulsin loses its activity at boiling temperature the fermentation must be completed at a temperature

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[1]) Arch. der Pharm. **248** (1910), 534; **251** (1913), 85. — Additional literature will be found in vol. I of this text-book, p. 534, footnote 3; also in the Report of Schimmel & Co. April **1913**, 20.

[2]) According to Caldwell, Courtauld, H. E. and E. F. Armstrong and Horton; comp. H. Euler, *Allgemeine Chemie der Enzyme,* p. 17. According to G. Bertrand and A. Compton (Bull. Soc. chim. IV. **9** [1911], 1071) emulsin consists of amygdalinase and amygdalase. At moderatly increased temperatures both act with about equal readiness on amygdalin. For a test period of 15 hrs. the best temperature for the action of the enzymes on amygdalin is $+40°$; for a period of 2 hrs. it is $+56°$ for amygdalase and $+58°$ for amygdalinase.

[3]) H. E. and E. F. Armstrong and E. Horton, Proceed. Royal Soc. London, B. **85** (1912), 359, 363; Chem. Zentralbl. **1912**, II. 1292.

[4]) Arch. der Pharm. **248** (1910), 534.

[5]) *Ibidem* **251** (1913), 56, 85.

below 60° before the distillation is begun. Hence the almond powder is made into a mash with 6 to 8 parts of water at from 50 to 60° and is allowed to stand for about 12 hrs. After which time the oil formed is distilled over with steam.

According to the directions of M. Pettenkofer[1]), 12 parts of almond powder deprived of its fatty oil are stirred into 100 to 120 parts of boiling water and the mixture kept at the boiling temperature of water for 15 to 30 minutes. It is then set aside to cool. To the cooled mixture 1 part of fresh bitter almond powder, mixed with 6 to 7 parts of water, is added and the mixture allowed to macerate for 12 hours.

It is claimed that the amygdalin is brought into solution better by treating the bulk of the almond powder with boiling water. The emulsin of one part of the almond powder suffices to hydrolyze the amygdalin of 12 parts of the powder.

During the process of distillation care should be exercised not to allow the poisonous vapors of hydrocyanic acid to escape into the laboratory. In order to prevent this the condensation should be very effective, the connection between condenser and receiver should be sealed with either bladder or parchment paper and any hydrocyanic acid that does not condense should be conducted by means of a tube from the end of the receiver out into the open air.

Inasmuch as benzaldehyde is readily soluble in water, more particularly in water containing hydrocyanic acid, the bulk of the oil is obtained only after cohobation of the aqueous distillate.

The yield of oil from bitter almonds varies from 0,5 to 0,7 p.c., from apricot kernels 0,6 to 1 p.c.

Inasmuch as in many applications the presence of the hydrocyanic acid is objectionable, the oil may be deprived thereof. This is done by shaking the oil with milk of lime and ferrous sulphate when the hydrocyanic acid is precipitated in the form of calcium ferrocyanide. The benzaldehyde remaining is rectified by means of water vapor. If the operation has been conducted carefully no trace of hydrogen cyanide remains. Its absence can be ascertained by means of the Prussian blue test recorded on p. 534 of volume I.

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[1]) Liebig's Annalen **122** (1862), 81.

In place of the oil deprived of its hydrocyanic acid, the much cheaper artificial benzaldehyde is sometimes used. Because of the disagreeable odor and taste, due to the presence of chlorinated products, this artificial benzaldehyde can be used only in the production of cheaper soaps and not in the manufacture of liqueurs and perfumery. It is produced by boiling benzyl chloride with lead or copper nitrate or by heating the benzylidene chloride with sodium hydroxide or milk of lime.

Benzaldehyde prepared in this way can be recognized by its chlorine content which may be determined according to the combustion method described in vol. I, p. 609.

Properties. Bitter almond oil containing hydrocyanic acid is a strongly refractive liquid which is at first colorless but later turns yellow. Its odor is that of the chewed bitter almonds. On account of the poisonous hydrocyanic acid content, smelling the oil should be avoided or at least done cautiously! d_{15° 1,045 to 1,070. A higher density may be attributed to a larger hydrogen cyanide content or more correctly benzaldehyde cyanhydrin (comp. p. 582 under Composition). Freshly prepared bitter almond oil is neutral. Later it acquires an acid reaction due to the oxidation of benzaldehyde to benzoic acid.

α_D is mostly $\pm 0^\circ$. In isolated instances the oil is slightly dextrogyrate. As high as $+0^\circ 9'$ has been observed; n_{D20° 1,532 to 1,544. The magnitude of the index of refraction is inversely proportional to the hydrocyanic acid content. The oil is relatively soluble in water, one part of oil being soluble in somewhat more than 300 parts of water. However, the oil is much more soluble in 1 to 2 vol. or more of 70 p.c. alcohol, also in 2,5 vol. or more of 60 p.c. alcohol. In the course of time the solubility of the oil in 60 p.c. alcohol diminishes. The hydrocyanic acid content of the oil varies, that of crude oils being greater than that of the rectified oils. Thus in connection with a crude oil (d_{15° 1,090; n_{D20° 1,52986) 11 p.c. of CNH, and in connection with a rectified oil (d_{15° 1,053; n_{D20° 1,54497) only 0,56 p.c. CNH were observed. This demonstrates conclusively that the oil used for medicinal purposes should contain a definite amount of hydrocyanic acid. According to the U. S. Pharmacopœia the oil should contain from 2 to 4 p.c. The method for its determination is described on p. 603 of vol. I.

If the oil is distilled over direct fire special precaution should be exercised because of the formation of hydrogen cyanide vapors. Under these conditions there passes over at first an oil richer in hydrogen cyanide, later one that is weaker. The residue contains benzoin, a polymerization product of benzaldehyde resulting from the action of the hydrocyanic acid.

Bitter almond oil deprived of hydrocyanic acid, or natural benzaldehyde is a colorless, optically inactive liquid; b. p. 179°; d_{15° 1,050 to 1,055 (a higher specific gravity may be due to a greater benzoic acid content); n_{D20° 1,542 to 1,546; soluble in 1 to 2 vol. and more of 70 p.c. alcohol. The pure benzaldehyde is much more prone to oxidation by atmospheric oxygen than is the oil containing hydrocyanic acid which acts as a preservative. The access of air readily converts the aldehyde into benzoic acid. For details see under Storage on p. 584.

Composition. Bitter almond oil consists of benzaldehyde, hydrocyanic acid and benzaldehyde cyanhydrin (phenylhydroxyacetonitrile or mandelic acid nitrile). Upon the hydrolysis of the amygdalin in the process of fermentation, benzaldehyde and hydrocyanic acid result which upon prolonged contact combine to form benzaldehyde cyanhydrin.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Hydrocyanic acid}}{CNH} = \underset{\text{Benzaldehyde cyanhydrin}}{C_6H_5CH(OH)CN}$$

The proof that bitter almond oil really contains benzaldehyde cyanhydrin was supplied by Fileti[1]). Upon the reduction of bitter almond oil he obtained phenylethylamine, whereas a freshly prepared mixture of hydrocyanic acid and benzaldehyde yielded methylamine only.

Benzaldehyde cyanhydrin is readily decomposed. Even when boiled with water vapor, or in vacuo, it is resolved into its components. Hence it can be found only after the distillation of the oil. It is formed especially when the oil is allowed to remain in prolonged contact with water rich in hydrocyanic acid, a condition that obtains at times in the course of the production.

Inasmuch as benzaldehyde cyanhydrin has a relatively high specific gravity, *viz.,* 1,124, the density of the oil increases with

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[1]) Gazz. chim. ital. 8 (1878), 446; Berl. Berichte 12 (1879), 296.

the hydrocyanic acid content. Whereas normal oils with a specific gravity of 1,052 to 1,058 contained from 1,6 to 4 p.c. of hydrocyanic acid, oils with a density of from 1,086 to 1,096 contained from 9 to 11,4 p.c. An experiment made to clear up this situation revealed that the specific gravity of a pure benzaldehyde when allowed to stand over an aqueous 20 p.c. solution of hydrocyanic acid had increased from 1,054 to 1,074[1]).

Concerning the equilibrium benzaldehyde + hydrocyanic acid $\rightleftarrows$ benzaldehyde cyanhydrin see the paper by P. H. Wirth[2]).

Inasmuch as both odor and taste of benzaldehyde from bitter almonds are supposed to be better than those of the best artificial product, it may be assumed that the former contains some other unknown constituent. F. D. Dodge[3]) tried to isolate such a constituent by dissolving 60 g. of bitter almond oil deprived of hydrocyanic acid in 100 cc. of ether and adding 200 g. of a concentrated bisulphite solution. After 18 hours the resulting bisulphite addition product was removed by filtration, washed with ether and the ethereal solution evaporated in a vacuum desiccator after it had been shaken with some soda solution. Treated in this manner, a residue of 0,2 p.c. of a yellow oil was obtained. It was heavier than water and had a pleasant, characteristic odor, but could not be identified. Artificial benzaldehyde treated in like manner yielded traces of an oil without decided odor.

Adulteration and Examination. The qualitative detection of hydrocyanic acid has been described in vol. I, p. 533, the quantitative determination in vol. I, p. 603.

The detection of foreign oils in bitter almond oil is accomplished readily by converting the benzaldehyde into its bisulphite addition product and separating this from the non-aldehydic admixtures.

5 g. of the oil to be investigated and 45 g. of sodium bisulphite solution are transferred to a 100 cc. test tube and the mixture thoroughly shaken. Then 60 g. of water are added

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[1]) Report of Schimmel & Co. April 1893, 8.

[2]) Arch. der Pharm. 249 (1911), 382.

[3]) 8th International Congress of Applied Chemistry, Washington and New York, 1912, vol. 17, p. 15.

and the test tube is placed in hot water. If the oil is pure a clear solution results. Foreign substances collect at the surface and can be separated for the purpose of further investigation.

In order to test for nitrobenzene (oil of mirbane) either the original oil or the oil that floated on the bisulphite solution may be taken. It is dissolved in twenty times its weight of alcohol and the solution diluted with water until the turbidity remains permanent. Some zinc and dilute sulphuric acid are added and the mixture allowed to react for several hours. The solution is then filtered, freed from alcohol by evaporation and boiled for a short time with a drop of potassium bichromate solution. If any nitrobenzene was present it will have been reduced to aniline and this identified by its violet color after the oxidation with the bichromate.

The most common adulteration of bitter almond oil, whether deprived of its hydrogen cyanide content or not, consists in the addition or substitution of artificial benzaldehyde. Inasmuch as this frequently contains chlorinated products, the detection of chlorine may serve as a proof of the presence of artificial benzaldehyde. For this purpose the combustion method described in vol. I, p. 609 is best employed.

However, inasmuch as benzaldehyde free from chlorine occurs in commerce, a negative chlorine test is by no means a sign of the purity of an oil. But in all cases in which chlorine is found, it may be regarded as a positive indication of adulteration with artificial benzaldehyde.

An addition of alcohol, which is said to occur not infrequently, may be ascertained in the ordinary manner.

As to the several methods for the determination of benzaldehyde in bitter almond oil see Dodge, footnote 3, p. 583 and the Report of Schimmel & Co. April 1913, 23.

Storage. If a small amount of benzaldehyde be exposed to the air in a capsule, crystals of benzoic acid will soon separate and after a time the entire oil will have changed to a crystalline mass. The same change takes place when benzaldehyde is stored in bottles that are but partly filled. Hence to prevent such change, benzaldehyde should be kept in completely filled, well stoppered bottles. As has been shown by special experiments[1]), an addition of 10 p.c. of alcohol acts as a preservative. If but 5 p.c. of alcohol be added the oxidation takes place more rapidly than in the undiluted oil.

Bitter almond oil containing hydrocyanic acid is much less readily oxidized than the oil freed from its acid content. The hydrocyanic acid acts as a preservative in like manner as do the 10 p.c. of added alcohol.

347. Cherry Laurel Oil.

Oleum Laurocerasi. — Kirschlorbeeröl. — Essence de Laurier-Cerise.

Origin and Production. *Prunus Laurocerasus* L., a native of Persia and the Caucasus, is frequently cultivated in moderate climates, more particularly as an ornamental plant.

As to its properties, the oil distilled from the cherry laurel leaves closely resembles that of the bitter almonds and can be distinguished only by its slightly different odor. The method of preparation is the same as that for bitter almond oil. The cut leaves are mashed with water, the mixture allowed to stand for some time and then distilled with steam. According to Umney[2]) the yield amounts to about 0,05 p.c.

As with the bitter almonds, the oil results upon the hydrolysis of a glucoside, the prulaurasin[3]), by emulsin. This glucoside crystallizes in thin, colorless needles, has a slightly bitter taste, melts at 120 to 122° and is readily soluble in water, alcohol and acetic ether, but is well-nigh insoluble in ether and deviates the plane of polarized light to the left, ($[\alpha]_D$ — 62,69°). Prulaurasin has the formula $C_{14}H_{17}NO_6$ and is hydrolyzed by emulsin into hydrocyanic acid (8,59 p.c.), glucose (61,24 p.c.) and benzaldehyde.

According to older statements the oil and hydrocyanic acid were supposed to exist in part as such in the leaves and not to owe their formation to the glucoside. However, C. Ravenna

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[1]) Report of Schimmel & Co. April 1895, 11.

[2]) Pharmaceutical Journ. III. 5 (1875), 761.

[3]) H. Hérissey, Compt. rend. 141 (1905), 959. — Journ. de Pharm. et Chim. VI. 23 (1906), 5. — The following papers have reference to laurocerasin as the glucoside was formerly known: Lehmann, Neues Repert. f. d. Pharm. 23 (1874), 449. — Pharm. Zeitschr. f. Russl. 24 (1885), 353, 369, 385, 401; Berl. Berichte 18 (1885), 569, Abstracts. — K. Jouck, Arch. der Pharm. 243 (1905), 421.

and M. Tonegutti[1]) have proven that the leaves do not contain free hydrocyanic acid.

Properties. Cherry laurel oil can be distinguished from bitter almond oil only by the odor. This distinction becomes more apparent after the benzaldehyde has been combined with sodium acid sulphite. As to all other properties there is almost perfect agreement between the two oils. d_{15° 1,050 (in a few instances as low as 1,0457 has been observed) to 1,066; α_D mostly inactive, occasionally slightly active, $+0^\circ 12'$ to $-0^\circ 46'$; n_{D20° 1,540 to 1,543; soluble in 2,5 to 4 vol. of 60 p.c. alcohol (the solubility in 60 p. c. alcohol diminishes with age) and in 1 to 2 vol. of 70 p.c. alcohol; A. V. 1,6 to 2,8; hydrocyanic acid content 0,4 to 3,6 p.c., seldom higher (up to 8 p.c. and more!).

In as much as cherry laurel oil is very poisonous because of its hydrogen cyanide content, this fact should be taken into consideration when it is used.

Composition. Like bitter almond oil, cherry laurel oil contains benzaldehyde, hydrocyanic acid and benzaldehyde cyanhydrin (phenyl hydroxyacetonitrile)[2]). Naturally the same quantitative variations occur here as in the case of bitter almond oil (see this).

According to W. A. Tilden[3]), the oil contains traces of another substance in addition to those already mentioned. It is probably due to this that the oil owes the peculiar odor that differentiates it from bitter almond oil. If the oil be shaken out with sodium acid sulphite solution, a dark colored liquid remains which, upon oxidation with chromic acid, yields benzoic acid. Tilden suspects the presence of benzyl alcohol.

Adulteration and Examination. Cherry laurel oil is subject to the same adulterations practiced on bitter almond oil. The admixtures can be tested for as indicated for bitter almond oil on p. 584.

348. Oil from Cherry Pits.

Ground cherry stones (pits and hard shells), after maceration yielded 0,016 p.c. of volatile oil which had the following properties:

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[1]) Chem. Zentralbl. **1910**, II. 892.

[2]) Fileti, Gazz. chim. ital. 8 (1878), 446; Berl. Berichte 12 (1879), 296.

[3]) Pharmaceutical Journ. III. 5 (1875), 761.

$d_{15°}$ 1,0532; $\alpha_D \pm 0°$; $n_{D20°}$ 1,53888; soluble in 2,5 vol. and more of 60 p.c. alcohol. The hydrocyanic acid content amounted to 0,27 p.c. The oil was colorless to light yellow in color and had an odor similar to that of bitter almond oil, yet with a pronounced difference[1]).

349. Wild Cherry Bark Oil.

The bark of *Prunus virginiana,* Mill. (*Prunus serotina,* Poir.), a native of North America has long been used in the preparation of aromatic beverages and of domestic remedies. It was made official in the first edition of the U. S. Pharmacopœia. That the distillate of the bark contained an oil with hydrocyanic acid was recognized by St. Procter[2]) in 1834. In 1838 Wm. Procter[3]) ascertained that the oil was not contained in the bark as such but results in a manner similar to that of bitter almond oil. More detailed investigations of the bark were undertaken by F. B. Power jointly with H. Weimar[4]) and C. W. Moore[5]).

After having been mashed, the powdered bark yields 0,2 p.c. of oil that resembles that of bitter almonds. It consists largely of benzaldehyde and is rich in hydrocyanic acid[6]). Specific gravity 1,045 to 1,050.

According to Power and Moore the bark contains l-mandelonitrile glucoside (amygdonitrilglucoside), the same glucoside which Hérissey[7]) had isolated several years previously from the closely related *Prunus Padus,* L.

These investigators obtained, though in very small amounts, l-mandelonitrile glucoside (m. p. 145 to 147° from acetic ether; $[\alpha]_D - 29{,}6°$) from the water soluble portion of the alcoholic extract of the bark. The acetyl derivative of the glucoside, the tetracetyl l-mandelonitrile glucoside, melted at 136 to 137° after having been recrystallized from alcohol; $[\alpha]_D - 24{,}0°$ (in acetic ester).

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[1]) Report of Schimmel & Co. April 1913, 111.

[2]) Americ. Journ. Pharm. 6 (1834), 8.

[3]) *Ibidem* 10 (1838), 197.

[4]) Pharm. Rundschau (New York) 5 (1887), 203.

[5]) Journ. chem. Soc. 95 (1909), 243.

[6]) Schimmel's Report April 1890, 48.

[7]) Journ. de Pharm. et Chim. VI. 26 (1907), 194. — Arch. der Pharm. 245 (1907), 475, 641.

Upon distilling the alcoholic extract with water vapor they isolated, in addition to benzoic acid, a volatile oil. The yield, however, was so small that the boiling point only (100 to 120° under 5 mm. pressure) could be determined. The odor was pleasantly aromatic, but quite distinct from that of benzaldehyde. The bark contained 0,075 p.c. of hydrocyanic acid.

The leaves of this species likewise yield an aqueous distillate that contains hydrocyanic acid[1]).

350. Oil of Prunus sphærocarpa.

When distilled the bark of *Prunus sphærocarpa,* Ser. (family *Rosaceæ*), a tree rather common in most of the Brazilian states, yields, according to Th. Peckolt[2]), 0,046 p.c. of a volatile oil with the odor of bitter almond oil; d_{18° 1,0409. The flowers also have the odor of benzaldehyde. From the seeds the same investigator isolated 0,910 p.c. of crystalline amygdalin. From the leaves and bark he obtained amorphous substances only, which, however, reacted with emulsin.

The fresh leaves yielded a distillate rather weak in hydrogen cyanide its content varying according to the months in which the material was collected. Thus the material collected early in March (summer) yielded 0,085 p.c. of hydrogen cyanide, that collected early in September (winter) 0,0016 p.c., and that collected early in December (spring) 0,005 p.c.

Family: LEGUMINOSÆ.

351. Oil of Cassie Flowers from Acacia Farnesiana.

Origin. *Acacia Farnesiana,* Willd., which is probably indigenous to the West Indies[3]) and probably likewise to West Africa[4]), is a

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[1]) Flückiger, *Pharmakognosie des Pflanzenreiches,* Berlin 1891. 3rd ed., p. 765.

[2]) Berichte der deutsch. pharm. Ges. 20 (1910), 594.

[3]) Engler-Prantl, *Die natürlichen Pflanzenfamilien,* Part. III, Section I, 3d Div., p. 112.

[4]) E. de Wildeman, Publication de l'État Indépendant du Congo 1906. *Notices sur des plantes utiles et intéressantes de la flore du Congo.* II. Brussels 1906, p. 105.

leguminous shrub which is at present widely distributed over the warmer climates of all continents, thus in Egypt, Australia, the Hawaiian Islands, the Philippines, and North and South America. In southern France, Algeria, Syria (Beirut), northern India (Naini Tal, on the southern slope of the Himalayas) and in New Caledonia the fragrant flowers are used in the production of perfume.

In southern France the shrub is known as *Cassier du Levant, Cassillier de Farnèse, Cassier ancien* or simply *Cassier*. In favorable localities it is cultivated from seeds on a large scale.

In southern France the collection of flowers begins when the plants are three years old[1]). Each plant yields 500 to 600 g. of flowers which are collected twice weekly during the months of September, October, and November and occasionally during December. During recent years 150 000 kg. of cassie flowers have been harvested annually in France and Algiers[2]). In 1910 one kg. of flowers demanded a price of 3 fr.[3]).

Whereas in northern India, cassie pomade has been made from the flowers for many years, no attempt has been made to utilize the flowers of *Acacia Farnesiana*[4]) in the tropics proper.

Production. Inasmuch as a volatile oil cannot be obtained from cassie flowers by distillation, the flowers are extracted either with hot fat (pomade) or more frequently with petroleum ether. The cassie extract of commerce obtained according to the latter method is a dark brown mass of salve- or wax-like consistence.

Properties. The oil proper has been prepared but rarely. Schimmel & Co.[5]) prepared it by shaking out 115 kg. cassie pomade three times with alcohol. From the united washings the alcohol was removed carefully by distillation. The residue, which still contained large amounts of fat, was distilled with water vapor. The aqueous distillate, which contained most of

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[1]) Comp. also L. Mazuyer, Journ. Parfum. et Savonn. **21** (1908), 254.

[2]) See footnote 4, p. 588.

[3]) Berichte von Roure-Bertrand Fils April **1911**, 76.

[4]) The second species which is cultivated in southern France because of its flowers, but which is less highly prized, is *Acacia Cavenia*, Hook. et Arn. See p. 591.

[5]) Report of Schimmel & Co. April **1904**, 23.

the odoriferous principles in solution, yielded upon extraction with ether 315 g. of a dark colored oil. For further purification it was next treated with soda solution when 28 g. of fatty acids (caprinic acid?) which probably originated in the fat used, also a small amount of salicylic acid, were obtained. The oil, rectified a second time with water vapor, was heavier than water, light yellow in color and possessed a pleasant but strong odor of cassie flowers. The yield amounted to 197 g. = 0,171 p.c. of the pomade. The following constants were observed: d_{15° 1,0475; $\alpha_D \pm 0^\circ$; n_{D20° 1,51331; S. V. 176.

H. von Soden[1]) extracted 1000 kg. of cassie flowers with petroleum ether and after removal of the waxy constituents obtained 840 g. = 0,084 p.c. of volatile oil which congealed at 18 to 19°; d_{27° 1,040; α_{D25° $-0^\circ 40'$; A. V. 42,50; E. V. 114 = 30,9 p.c. methyl salicylate.

In connection with an oil obtained in like manner by Schimmel & Co.[2]) from a French cassie flower extract the following constants were observed: d_{15° 1,0575; α_D $-0^\circ 30'$; n_{D22° 1,51500; A. V. 25,4; E. V. 229. The yield amounted to 5,65 p.c. of the extract.

Composition. The principal constituents of the oil of cassie flowers were made known by an investigation in the laboratory of Schimmel & Co.[3]). An oil obtained from Indian cassie flower pomade was used, the constants of wich have been enumerated above under "Properties". By shaking the oil with dilute sodium hydroxide solution about 11 p.c. of methyl salicylate (b. p. 224 to 226°; d_{15° 1,1770) were removed, also a small amount of *p*-cresol (m. p. of the anisic acid, obtained by the oxidation of its *p*-cresol methyl ether, 180°). The oil deprived of its phenols contained benzaldehyde (m. p. of semicarbazone 214°), benzyl alcohol (m. p. of acid phthalic ester 105 to 106°; m. p. of phenyl urethane 177°), a ketone having the odor of menthone (b. p. 200 to 205°; d_{15° 0,9327; α_D $-3^\circ 50'$; m. p. of semicarbazone 177 to 178°), anisic aldehyde (m. p. of anisic acid 180°), decylic aldehyde

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[1]) Journ. f. prakt. Chem. II. 69 (1904), 270.

[2]) Report of Schimmel & Co. April 1907, 27.

[3]) *Ibidem* October 1899, 58; April 1901, 18; April 1903, 17. — H. Walbaum, Journ f. prakt. Chem. II. 68 (1903), 235. — Report of Schimmel & Co. April 1904, 23. — G. I. P. 139635 and 150170.

(m. p. of semicarbazone 97°), cuminic aldehyde (m. p. of semicarbazone 200°). A constituent of the greatest importance, so far as the odor is concerned is a ketone with a violet odor that boils at 133° under 15 mm. pressure (m. p. of *p*-bromphenyl hydrazone 103 to 107°). The presence of geraniol and linalool, though not positively proven, is rendered probable.

According to Haarmann and Reimer[1]) the higher boiling portions of the oil contain a sesquiterpene alcohol $C_{15}H_{26}O$ named farnesol (Comp. vol. I, p. 399).

352. Cassie Flower Oil from Acacia Cavenia.

Origin and Production. In addition to *Acacia Farnesiana,* described on p. 588, *Acacia Cavenia,* Hook. et Arn.[2]) is likewise cultivated in southern France. This species demands less care and yields a larger harvest of flowers the odor of which, however, is not so delicate. The trade name of *A. Cavenia* is *Cassier Romain,* presumably because this shrub was brought to Cannes from Italy about 100 years ago. As stated, one of the advantages is that *A. Cavenia* is less sensitive and demands less care than *A. Farnesiana,* which must be trimmed annually in March, whereas *A. Cavenia* demands no such treatment.

The plant is reproduced by cuttings. As soon as these have taken root they are transplanted[3]). During the first summer after transplanting, the shrubs bear flowers. In 1910 the price of 1,5 fr. pro kg. was paid for these in Grasse[4]).

The perfume is obtained according to the same method by which that of *A. Farnesiana* is produced.

Composition[5]). The extract investigated had been obtained by extraction of the flowers with petroleum ether. From this the oil was obtained by distillation with water vapor and shaking

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[1]) Chem. Zentralbl. **1904**, I. 975. G. I. P. 149603.

[2]) In Grasse the perfume of *Acacia dealbata,* Lk., known there as *mimose,* is extracted and utilized, whereas *A. floribunda,* Willd. (*A. longifolia,* Willd.) and *A. Melanoxylon,* R. Br. are not suited to this purpose. Berichte von Roure-Bertrand Fils April **1904**, 60.

[3]) L. Mazuyer, Journ. Parfum. et Savonn. **21** (1908), 254.

[4]) Berichte von Roure-Bertrand Fils April **1911**, 76.

[5]) H. Walbaum, Journ. f. prakt. Chem. II. **68** (1903), 235. — Report of Schimmel & Co. October **1903**, 19.

out the aqueous distillate with ether. When shaken with dilute sodium hydroxide solution the oil yielded 5,5 p. c. phenols, 8,8 p.c. non-phenols and 1,1 p.c. salicylic acid, computed with reference to the extract. In another instance 3 p.c. of phenols, 4,5 p.c. of non-phenols and 1,66 p.c. salicylic acid were obtained.

The mixture of phenols consists of 90 p.c. of eugenol (m. p. of benzoyl compound 69 to 70°). The salicylic acid found (m. p. 156°) is present in the oil as methyl ester. The following substances were also identified; benzaldehyde (m. p. of semicarbazone 214°), benzyl alcohol (m. p. of phenylurethane 77 to 78°), geraniol (m. p. of diphenyl urethane 81°), anisic aldehyde (m. p. of anisic acid 184°; of semicarbazone 203 to 204°), eugenol methyl ether (m. p. of veratric acid 178°), and a ketone with a violet-like odor. Presumably linalool and decylic aldehyde are also present.

353. Oil of Copaiba.

Oleum Balsami Copaivae. — Copaivabalsamöl. — Essence de Baume de Copahu.

Origin. Copaiba balsam, known in Europe since the beginning of the 16. century, is yielded by a number of species of *Copaifera* (family *Leguminosæ*) which are indigenous to the territory of the Amazon and its tributaries as far north as Guayana, Venezuela and Columbia. The principal balsam trees are *Copaifera officinalis,* L., *C. guyanensis,* Desf., *C. coriacea,* Mart., *C. Langsdorffii,* Desf., *C. confertiflora,* Benth., *C. oblongifolia,* Mart., and *C. rigida,* Benth. The Bolivian balsam is derived from *Copaiba paupera,* Herzog[1]). In order to obtain the balsam a cavity is cut into the trunk with the aid of an axe, or holes are drilled to the center of the trunk with a two inch bit and the balsam collected with the aid of tin tubes[1]). Occasionally the trees are so rich in balsam that the resin ducts burst of their own accord and then the balsam exudes from the longitudinal cleavages. As much as 30 l. or more of balsam are at times obtained from a single tree[2]).

Commercially, copaiba balsam is differentiated according to the ports of export. Of these the Maracaibo balsam (derived

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[1]) Schweiz. Wochenschr. f. Chem. u. Pharm. 47 (1909), 373.

[2]) Th. Peckolt, *Untersuchung der Copaifera Langsdorffii,* Desf., Pharm. Rundsch. (New York) 10 (1892), 234.

principally from *Copaifera officinalis*) and the Para balsam are the most important. The latter is rather limpid and since it yields the largest amount of oil, up to about 85 p.c., is preferred for the distillation of the oil. Maracaibo balsam has a thicker consistence and yields from 35 to 58 p.c. of oil. The following yields[1]) have been obtained from other commercial varieties; Angostura (Brazil) 52 to 55 p.c., Bahia (Brazil) 44 to 62 p.c., Maranham or Maranhão (Brazil) 27 to 56 p.c., Maturin (Venezuela) 41 to 55 p.c., Cartagena (Columbia) 40 to 64 p.c., Bolivia 23 p.c., Surinam 41 to 72 p.c.

Properties. Oil of copaiva balsam is a colorless, yellowish or blueish liquid with the characteristic pepper-like odor of the balsam and a bitter, grating and persistent taste. It is mostly soluble in an equal volume of absolute alcohol.

The properties of the oils of the several commercial varieties of balsam vary considerably. This is particularly true of the optical rotation. The data recorded in the following compilation are limit values. However, the observations are not numerous, hence the limits may have to be changed as a wider range of materials is included.

OIL FROM PARA BALSAM.

d_{15° 0,886 to 0,910; α_D —7 to —33°; n_{D20° 1,493 to 1,502; A.V. 0 to 1,9; E.V. 0 to 4 (in one instance 13); soluble in 5 to 6 vol. of 95 p.c. alcohol.

OIL FROM MARACAIBO BALSAM.

d_{15° 0,900 to 0,905; α_D —2° 30′ to —12°; n_{D20° about 1,498; A.V. 0,9 to 1,0; E.V. 1 to 1,6; soluble in 5 to 6 vol. of 95 p.c. alcohol.

OIL FROM BAHIA BALSAM.

d_{15° 0,888 to 0,909; α_D — 8 to —28°; n_{D20° 1,494 to 1,497; A.V. 0,5 to 7,9; E.V. to 4 (in one instance 14,9); soluble in 5 to 10 vol. of 95 p.c. alcohol.

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[1]) Partly observations by Schimmel & Co. and by Evans Sons Lescher & Webb Ltd. Comp. Report of Schimmel & Co. April **1905**, 24; April **1908**, 36; April **1909**, 41; April **1910**, 147; April **1911**, 136. See also E. Praël, Arch. der Pharm. **223** (1885), 740.

OIL FROM MARANHAM BALSAM.

d_{15° 0,896 to 0,905; α_D — 1° 30′ to — 22°.

OIL FROM CARTAGENA BALSAM.

d_{15° 0,894 to 0,910; α_D — 2° 30′ to — 23°.

OIL FROM MATURIN BALSAM. (4 investigations.)

d_{15° 0,899 to 0,904; α_D — 7° 30′ to — 10° 10′; n_{D20° 1,497 to 1,500; A. V. 0 to 0,6; E. V. 0,9 to 3,6; soluble in 5 to 6 vol. of 95 p.c. alcohol.

OIL FROM ANGOSTURA BALSAM. (1 investigation.)

d_{15° 0,9161; α_D — 2° 20′; n_{D20° 1,50169; A. V. 10,9; E. V. 0; soluble in 5,5 vol. of 95 p.c. alcohol.

OIL OF BALSAM FROM BRITISH GUAYANA. (1 investigation.)[1]

d 0,924; α_D — 9°. Oil content of the balsam determined by evaporation at 100°, 52,1 p.c.

OIL OF BALSAM FROM DUTCH GUAYANA. (Surinam, from *Copaifera guayanensis.*)[2]

d_{15° 0,903 to 0,906; α_D — 7° 30′ to — 10° 30′; A. V. 0; E. V. 6,7; acetyl value 28,4[3]).

OIL FROM BOLIVIAN BALSAM. (1 investigation.)[4]

d_{15° 0,916; α_D + 18°; n_{D20° 1,5048; A. V. 1,07; S. V. (cold) 1,6; soluble in 9 vol. of 95 p.c. alcohol.

Composition. R. Blanchet[5]), also E. Soubeiran and H. Capitaine[6]) obtained a solid chlorhydrate upon passing hydrogen chloride into the oil. In one instance its melting point was found at 77°, in another at 54°. The analyses agreed with the formula $(C_{10}H_{16}2HCl)x$. Later investigators failed to obtain a solid chlorhydrate from either Para or Maracaibo oil[7]). When

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[1]) E. W. Bell, Pharmaceutical Journ. 65 (1900), 98.

[2]) J. F. Pool, Jahresb. d. Pharm. 1897, 74.

[3]) L. van Itallie and C. H. Nieuwland, Arch. der Pharm. 242 (1904), 539; 244 (1906), 161.

[4]) C. Hartwich, Schweiz. Wochenschr. f. Chem. u. Pharm. 47 (1909), 373.

[5]) Liebig's Annalen 7 (1833), 156.

[6]) *Ibidem* 34 (1840), 321.

[7]) Brix, Monatsh. f. Chem. 2 (1882), 507. — J. C. Umney, Pharmaceutical Journ. III. 24 (1893), 215.

oxidizing both oils with nitric acid, neither L. Posselt[1]) nor E. G. Strauss[2]) obtained results worth mentioning. S. Levy and P. Engländer[3]) were more successful when they oxidized the Para balsam oil with potassium dichromate and sulphuric acid. They obtained a crystalline acid that melted at 140°, which further investigation revealed to be identical with asymmetric dimethyl succinic acid $C_6H_{10}O_4$. Inasmuch as only the small yield of 1½ p.c. of the oil used was obtained, it appears doubtful whether the acid owes its formation to the principal constituent of the oil or to some minor constituent.

Upon oxidation of Maracaibo balsam, Brix obtained small amounts of terephthalic acid. When distilling absolutely dry Maracaibo oil over sodium he obtained a blue distillate the composition of which corresponded with the formula $C_{20}H_{32} + H_2O$.

However, none of these investigations revealed a true insight into the composition of the oil. Wallach[4]) was the first to demonstrate that the bulk of the oil consists of caryophyllene, a sesquiterpene $C_{15}H_{24}$ (see Vol. I, p. 331) that also occurs in oil of cloves. If fraction 250 to 270° is treated with glacial acetic and sulphuric acid, caryophyllene hydrate, the handsome crystals of which melt at 96°, results.

From the caryophyllene of copaiba oil E. Deussen and A. Hahn[5]) succeeded in obtaining the nitrosochloride and the nitrosate of the inactive hydrocarbon designated α-caryophyllene.

In order to clear up the contradictions of the earlier investigators Schimmel & Co.[6]) examined the products resulting from the action of hydrochloric acid on the oil.

As already stated, the melting point of the hydrochloride is recorded by Blanchet as 77°, by Soubeiran and Capitaine as 54°, whereas Brix and Umney failed to obtain a solid chlorhydrate.

The oil to be examined (150 g.; d_{15° 0,9036; $\alpha_D - 9°58'$) was fractionated into three equal parts:

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[1]) Liebig's Annalen **69** (1849), 67.

[2]) *Ibidem* **148** (1868), 148.

[3]) *Ibidem* **242** (1887), 189. — Berl. Berichte **18** (1885), 3206, 3209.

[4]) Liebig's Annalen **271** (1892), 294.

[5]) Chem Ztg. **34** (1910), 873.

[6]) Report of Schimmel & Co. Oktober **1910**, 184.

I. B. p. 113 to 115° (6 mm.); d_{15° 0,8989; α_D — 8°7′
II. B. p. 115 to 119° (6 mm.); d_{15° 0,8960; α_D — 10°1′
III. B. p. 119 to 133° (6 mm.); d_{15° 0,8968; α_D — 11°58′.

The chlorhydrates were prepared according to the well-known method by passing the hydrogen chloride into the well-cooled ethereal solution. From the last fraction only was it possible to obtain a solid hydrochloride without great difficulty. The residues of the other two fractions had to be chilled thoroughly for a long time and the oily mass, permeated with crystals, had to be spread on porous plates. The melting points of the several chlorhydrates varied from 60 to 90°, hence did not differ materially from those obtained by Blanchet and by Soubeiran and Capitaine. Separation was brought about by fractional crystallization. The bulk of the crystals occurred as fine needles, melted at 113 to 115° ($[\alpha]_D$ — 34°28′ in a 2,5 p.c. chloroform solution) and the melting point was not lowered when mixed with l-*cadinene* dihydrochloride. The chlorhydrate that melted at 65 to 70° and which was obtained in smaller amount ($[\alpha]_D + 18°35′$ in a 2,1 p.c. chloroform solution) was identical with *caryophyllene* dihydrochloride. The yield of cadinene dihydrochloride amounted to 4 to 5 p.c., that of caryophyllene dihydrochloride about ½ p.c. Hence it becomes apparent that β-caryophyllene occurs in the oil in addition to inactive caryophyllene, first found by Wallach and characterized as α-caryophyllene by Deussen and Hahn, and *l*-cadinene. However, the presence of other sesquiterpenes has not yet been excluded.

Later E. Deussen and B. Eger[1]) verified the presence of β-caryophyllene in the several copaiba balsam oils by preparing what they call β-nitrocaryophyllene, a compound of the formula $C_{12}H_{19}N_3O_6$. On account of its insolubility in most organic solvents, this compound is well suited for the identification of β-caryophyllene. For its preparation 2 to 3 g. of the oil to be examined are dissolved in ether and oxides of nitrogen are passed into this solution which is not cooled but protected against light, until crystals no longer separate. After the precipitate has been washed with ether it is weighed. In this manner Deussen and Eger obtained from 9,5 to 16 p.c. of

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[1]) Liebig's Annalen **388** (1912), 136. — Chem. Ztg. **36** (1912), 561.

β-nitrocaryophyllene from four Para copaiba oils, 3 to 6 p.c. from two Maracaibo oils and 8 to 9 p.c. from a Maturin oil. If the oils are adulterated with gurjun balsam oils the amounts are correspondingly less.

In a Surinam copaiba balsam oil, van Itallie and Nieuwland[1]) found cadinene (m.p. of the dichlorhydrate 116 to 117°; $[\alpha]_D$ in chloroformic solution $-36°5'$) also a sesquiterpene alcohol $C_{15}H_{26}O$ that melted at 113 to 115° and which, when treated with anhydrous formic acid yielded a sesquiterpene with the following properties: b.p. 252° (759 mm.); $d_{15°}$ 0,952; $\alpha_D -61,7°$; $n_{D15°}$ 1,5189. In addition to cadinene other sesquiterpenes occur in the oil, but caryophyllene could not be identified.

Adulteration. Copaiba balsam oil as such is adulterated but rarely, if ever. However, the adulteration of the balsam with gurjun balsam, or African copaiba or Illurin balsam has been observed. Gurjun balsam is distinguished from copaiba balsam by means of a number of color reactions. As in the case with most of these reactions, the results are more or less questionable. Of these tests the following has proven the most reliable. If to a solution of 4 drops of copaiba balsam in 15 cc. glacial acetic acid, 4 to 6 drops of concentrated nitric acid be added, a pure copaiba balsam remains unchanged, whereas in the presence of gurjun balsam the glacial acetic acid solution is colored a purplish-red[2]). The oils of the two balsams behave in like manner. A further indication of the presence of gurjun balsam oil is obtained by means of Turner's reaction. According to Deussen and Eger[3]) one drop of the material to be examined is dissolved in 3 cc. of glacial acetic acid and 2 drops of a freshly prepared 1 p.c. solution of sodium nitrite are added. This solution is carefully poured over concentrated sulphuric acid. If within 5 minutes the glacial acetic acid solution is colored a deep violet the presence of gurjun balsam oil may be assumed.

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[1]) Footnote 3, p. 594.

[2]) Comp. Utz, Chem. Zentralbl. **1908**, II. 1212; Report of Schimmel & Co. April **1909**, 41. — The color reactions of the copaiba balsams are discussed in detail by A. Eibner in a contribution entitled: *Über Copaivabalsame und Copaivaöle.* Technische Mitteil. f. Malerei **24** (1908), Nos. 22 and ff.

[3]) Chem. Ztg. **36** (1912), 561.

Exact proof of the presence of this adulterant, however, is supplied by the preparation of the gurjunene-ketone semicarbazone. According to E. Deussen and H. Philipp[1]) that portion of 170 g. of oil which distils over below 145° under 10 to 12 mm. pressure is resolved into three fractions of 50 g. each, the residue above 145° being ignored. The acetone solution of each of these fractions is oxidized with potassium permanganate. To those that yield Turner's reaction semicarbazide solution is added. Aside from the melting point of 234° when re-crystallized from hot alcohol, the high optical rotation is characteristic of the semicarbazone. Dissolved in concentrated aqueous chloralhydrate solution, the specific angle of rotation is $+317°$.

Inasmuch as gurjun balsam oil is strongly lævogyrate, it increases the rotation of the copaiba balsam oil to which it has been added as adulterant. In order to counteract this effect, the oil from the dextrogyrate copaiba balsam has been added. Moreover, gurjun balsam oil has a higher specific gravity than copaiba balsam oil. This fact also may assist in the detection of the former.

T. T. Cocking[2]) has observed that the oil of unadulterated balsam invariably has a slightly higher rotation than the first 10 p.c. distilled distilled therefrom in vacuum. Hence this may serve as a means to detect additions of gurjun balsam as well as of African balsam. Parry[3]) claims that this observation does not hold true, but Cocking[4]) maintains the correctness of his original position. It would seem, therefore, that this method should be further tested out in connection with material of unquestioned purity.

354. African Copaiba Balsam Oil.

The "Illurin balsam" or African copaiba balsam, which first made its appearance in the London market, is obtained from western Africa, more particularly from the Niger countries, it is said. The botanical source has not been ascertained but the

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[1]) Liebig's Annalen **369** (1909), 57. — Chem. Ztg. **36** (1912), 561.

[2]) Chemist and Druggist **77** (1910), 119.

[3]) *Ibidem* **80** (1912), 19.

[4]) *Ibidem* 128, 204.

Oxystigma Mannii, Harms (*Hardwickia Mannii,* Oliv.) is regarded as the parent plant[1]).

Properties. Upon distillation the balsam yields 37 to 46,5 p.c. of oil[2]): d_{15° 0,917 to 0,929; $\alpha_D + 5^\circ 45'$ to $+ 30^\circ$; A. V. 0,5 to 9,3; E. V. 0 to 5,6; E. V. after acetylation (1 determination) 10; soluble in 98 p.c. alcohol, but the addition of more than 2 vol. produces faint opalescence; soluble in 95 p.c. alcohol in the ratio of 1:10 with opalescence[3]).

Composition. When passing hydrogen chloride into the oil Umney[4]) did not succeed in obtaining a solid chlorhydrate. Upon passing hydrogen chloride into the ethereal solution of a dextrogyrate oil, H. von Soden[5]) obtained a dihydrochloride that melted at 116 to 119°; $\alpha_D - 3^\circ$ in a 10 p.c. benzene solution. The regenerated hydrocarbon had the following properties: b. p. 274,5 to 276° (743 mm.); d 0,928; $\alpha_D - 94^\circ$. These properties agree well with those of *l*-cadinene.

Similar results were obtained by Schimmel & Co.[6]). 90 p.c. of an oil prepared by themselves distilled between 267 and 276°. In a vacuum of 5,5 to 6 mm. pressure it distilled between 118 and 125°. By passing hydrogen chloride into the ethereal solution, they obtained 37,5 p.c. of a chlorhydrate that crystallized in long needles melting at 117 to 118° ($[\alpha]_D - 37^\circ 27'$ in a 5,022 p.c. chloroform solution). The hydrocarbon, regenerated with the aid of sodium ethylate, boiled at 271 to 273° ($[\alpha]_D - 105^\circ 30'$). The addition of hydrogen chloride again yielded the chlorhydrate melting at 117 to 118° ($[\alpha]_D - 36^\circ 48'$ in a 4,73 p.c. chloroform solution). Whether African copaiba balsam contains *l*-cadinene or whether the dextrogyrate sesquiterpene is converted into a derivative of *l*-cadinene by the action of hydrogen chloride will have to be ascertained by further investigation. Probably the

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[1]) Umney, Pharmaceutical Journ. III. **22** (1891), 449 and **24** (1893), 215. — H. Solereder, Arch. der Pharm. **246** (1908), 72. — Engler and Prantl, *Die natürlichen Pflanzenfamilien,* Supplement to Part II—IV, 1897, p. 195.

[2]) Comp. C. M. Kline, Americ. Journ. Pharm. **77** (1905), 185.

[3]) Observed in connection with a single oil. Report of Schimmel & Co. October **1908**, 48.

[4]) *Loc. cit.*

[5]) Chem. Ztg. **33** (1909), 428.

[6]) Report of Schimmel & Co. October **1909**, 46.

relationships are similar to those observed in connection with West Indian sandalwood oil, the dextrogyrate sesquiterpene of which was converted into *l*-cadinene by Deussen[1]) through the chlorhydrate.

In the lowest fraction (b. p. 128 to 129,5° under 15 mm. pressure) of African copaiba balsam oil, E. Deussen[2]) proved the presence of 13 p.c. of β-caryophyllene by passing nitrous acid gas into its ethereal solution. The oil that had not been fractionated yielded 1,65 p.c. of so-called nitro-β-caryophyllene corresponding to a content of 0,87 p.c. of β-caryophyllene.

355. Bubimbi Bark Oil.

The bark of *Scorodophlœus Zenkeri,* Harms (family *Leguminosæ*) is used as a spice by the natives of Kamerun. Its odor is very strong, persistent and, in the long run, unbearable. It reminds one of that of *Marasmius alliatus* (Schäff.), Schröt. (Ger. *Knoblauchpilz*).

From a small sample of the bark, C. Hartwich[3]) obtained 0,0107 p.c. of volatile oil by adding salt to the aqueous distillate and shaking out with ether. The oil was brownish in color and had a very disagreeable odor. After standing a short time the oil congealed to small crystalline needles in which the presence of sulphur was detected but not that of nitrogen.

356. Hardwickia Balsam Oil.

Kingiodendron pinnatum (Roxb.), Harms (*Hardwickia pinnata,* Roxb.[4]), family *Leguminosæ*) is a stately tree closely related to the *Copaifera* species. It is native to India. The balsam obtained from it is used for medicinal as well as technical purposes (for painting the woodwork of houses). According to D. Hooper[5]) it is obtained in South Kanara in the

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[1]) Arch. der Pharm. **238** (1900), 149.

[2]) Liebig's Annalen **388** (1912), 142. — Comp. also Copaiba balsam oil, p. 592.

[3]) Apotheker Ztg. **17** (1902), 339.

[4]) *Hardwickia binata,* Roxb., which had erroneously been mentioned as the parent plant (Report of Schimmel & Co. April **1905**, 85), yields no volatile oil. Comp. also H. Solereder, Arch. der Pharm. **246** (1908), 71 and Ed. Schaer, Handelsbericht von Gehe & Co. **1913**, 182.

[5]) Pharmaceutical Journ. **78** (1907), 4.

following manner: About 3 feet above the ground a deep cavity is made into the trunk. Only large trees with a circumference of 5 to 6 feet are tapped. The balsam begins to flow at once. The trees are completely exhausted toward the end of four days. A healthy, strong tree with a circumference of 8 feet yields about 12 gals. (= 53 l.) of balsam.

When distilled with water vapor the balsam[1]) yields from 25 to 50 p.c. of a colorless volatile oil with the following properties: $d_{15°}$ 0,904 to 0,906; α_D —7° 42′ to —8° 24′; A. V. 0,85; E. V. 2,88; soluble in about 5 vol. and more of 95 p.c. alcohol.

357. Cativo Balsam Oil.

Upon the distillation of the balsam of *Prioria copaifera* Grisebach with water vapor, G. Weigel[2]) obtained 2 p.c. of a volatile oil that distilled with difficulty and probably consisted of higher boiling terpenes (sesquiterpenes?).

358. Supa Balsam Oil.

Sindora Wallichii, Benth. (family *Leguminosæ*), the plant from which the supa balsam[3]) is derived, is found all over the Philippine Islands. A freshly wounded tree yields about 10 l. of balsam. This is a mobile, homogeneous liquid, light yellow in color, with a slight fluorescence and a faint but characteristic odor: $d_{30°}^{30°}$ 0,9202; $\alpha_{D30°}$ —31,3°; when cooled below 20° it separates white, flocculent crystals that constitute about 5 p.c. of the oil. They melt at 63 to 64° and are a hydrocarbon. Supa balsam dissolves in all of the ordinary solvents but alcohol. It absorbs atmospheric oxygen and finally solidifies. When distilled with steam a colorless oil is obtained: $d_{30°}^{30°}$ 0,9053; $\alpha_{D30°}$ —21°; the bulk of the oil distills between 143 and 149° under 40 mm. pressure; when repeatedly distilled under 760 mm. pressure the

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[1]) For the properties of the balsam see G. Weigel (Pharm. Zentralh. 47 [1906], 773), D. Hooper *(loc. cit.)* and Schimmel & Co. (Report of Schimmel & Co. April 1907, 109).

[2]) Pharm. Zentralh. 44 (1903), 147.

[3]) A. M. Clover, Philippine Journ. of Sc. 1 (1906), 191. Clover refers to the balsam as wood oil, a designation likewise applied to gurjun balsam and to other balsams derived from the *Dipterocarpaceæ*.

oil distils between 255 and 267° without appreciable residue. If, however, the balsam is first distilled without water vapor in vacuum, 73 p. c. pass over consisting of little water and mostly of an oil which under 40 mm. pressure passes over below 170° without, however, revealing a definite boiling point. This oil distills within a range of seven degrees and presumably consists of a mixture of sesquiterpenes. Of these cadinene was identified by means of its hydrochloride (m. p. 117 to 118°) by passing hydrogen chloride into the glacial acetic acid solution of the distillate. The regenerated cadinene boiled between 164 and 165° (38 mm.); α_{D30° -78° (-39° in a 50 mm. tube). The inaction of both sodium and phosphorus pentoxide in benzene on the oil revealed the absence of alcoholic substances.

359. Copal Oils.

In the course of the investigation of copals derived from leguminous plants[1]) their volatile oils were also prepared. However, the information concerning them is very meagre. As to their composition not the least is known and in most instances not even their physical constants have been ascertained.

Zanzibar copal from *Trachylobium verrucosum* (Gärtn.), Oliv. The volatile oil[2]) boils in the main between 200 and 215°, apparently with decomposition.

Sierra Leone copal[3]), probably from *Copaifera Guibourtiana,* Benth. (*Guibourtia copallifera,* Benn.). The oil[4]) distils largely between 147 and 160°.

Loango copal. Under diminished pressure (? mm.) the oil[5]) distills principally at 160°.

Benin copal yields 2,7 p. c. of volatile oil[6]) that distils between 180 and 256°.

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[1]) Comp. also the oils derived from coniferous copals, p. 9.

[2]) Stephan, Arch. der Pharm. **234** (1896), 560.

[3]) According to Tschirch (*Die Harze und die Harzbehälter,* Leipzig **1906**, II. Ed. Vol. II, p. 755) the West African copals or copaiba-copals are derived from *Cæsalpinioidæ,* many also from *Copaifera* species.

[4]) M. Willner, Arch. der Pharm. **248** (1910), 285.

[5]) *Ibidem* 273.

[6]) M. Kahan, *ibidem* 439.

Kameroon copal from *Copaifera Demeusii,* Harms[1]). A light yellow oil[2]); b. p. 145 to 155°; d 0,830.

Angola copal contains 2 p.c. of volatile oil[2]); b.p. 140 to 160°; d 0,853.

Brazil copal[3]), principally from *Hymenæa Courbaril,* L. and other species of *H.* Volatile oil 2,66 p.c.; b. p. 245 to 255°[4]).

Columbia copal. Derived from the same species as the previous one. Oil yield 6,6 p.c.; b. p. 210 to 220° in vacuum (? mm.)[4]).

360. Sappan Leaf Oil.

According to van Romburgh, the leaves of *Cæsalpinia Sappan,* L., the leguminous tree which supplies the sappan wood used for dyeing, yields 0,16 to 0,2 p.c. of an almost colorless volatile oil: d_{28° 0,825; $\alpha_D + 37^\circ 30'$ to $+50^\circ 30'$. The bulk of the oil boils at 170°. The odor is pepper-like and reminds of phellandrene. The amount of phellandrene nitrite which separates when the oil is treated with sodium nitrite and glacial acetic acid, is so large as to lead to the assumption that the bulk of the oil consists of *d*-phellandrene. During the distillation of the leaves van Romburgh observed the occurrence of methyl alcohol[5]).

361. Tolu Balsam Oil.

Oleum Balsami Tolutani. — Tolubalsamöl. — Essence de Baume de Tolu.

Origin and Production. The viscid balsam that exudes from incissions into the trunk of the tolu balsam tree, *Myroxylon (Toluifera) Balsamum var. α genuinum,* Baill. (family *Leguminosæ*) hardens in the course of time to a solid mass which softens at about 30° and melts between 60 and 65°. It is in this form in which it is mostly found in commerce. Upon distillation with water vapor, the solid tolu balsam yields from 1,5 to 7 p.c. of oil. Slow distillation yields an oil lighter than water, rapid distillation with high tension vapors yields more oil that is denser.

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[1]) H. Harms, Notizbl. bot. Gart. Berlin-Dahlem **5** (1910), 175; Apotheker Ztg. **25** (1910), 1038.

[2]) H. Rackwitz, Arch. der Pharm. **245** (1907), 420, 424.

[3]) Tschirch, *loc. cit.* p. 770.

[4]) St. Machenbaum, Arch. der Pharm. **250** (1912), 10, 17.

[5]) Report of Schimmel & Co. April **1898**, 53.

Properties. The very agreeably aromatic odor of the oil reminds of hyacinths: d_{15° 0,945 to 1,09; α_D — 1°20′ to + 0°54′; n_{D20° 1,544 to 1,560; A. V. 5 to 34; E. V. 177 to 208; soluble in 1 vol. or more of 90 p. c. alcohol, with 80 p. c. alcohol it generally does not yield a clear solution.

Composition. The older statements[1] concerning its composition are not only contradictory in part but supply but very imperfect information.

According to Kopp, the hydrocarbon which boils at about 170° and which has an elemi-like odor is a terpene (probably phellandrene?). Inasmuch as E. Busse[2] has observed the benzyl esters of benzoic and cinnamic acids in the balsam, these are very likely also contained in the oil. As a matter of fact the oil has a high ester number and from the saponification liquid, crystalline acids (probably cinnamic and benzoic acids) can be separated.

According to F. Elze[3] farnesol is contained in tolu balsam oil.

362. Peru Balsam Oil.

Oleum Balsami peruviani. — Perubalsamöl. — Essence de Baume de Pérou.

Origin. Peru balsam, which is used extensively in pharmacy and perfumery, is obtained from artificial wounds of a tree which, according to the recent investigations of H. Harms[4], is *Myroxylon Balsamum var. β. Pereiræ* (Royle), Baill.

The balsam is obtained in the following manner[5]. The gray bark, full of ridges, is loosened near the ground. After several days some balsam will have secreted which is absorbed by rags laid on the wound. By means of the flame of a torch the wound is scorched, with the result that in the course of the next eight days considerable balsam will be secreted. This is collected by means of fresh rags. Later the burnt surface is irritated by means of incisions and scratches. When the

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[1] Deville, Annal. de Chim. et Phys. III. **3** (1841), 151; Liebig's Annalen **44** (1842), 304. — Kopp, Journ. de Pharm. et Chim. III. **11** (1847), 425. — E. A. Scharling, Liebig's Annalen **97** (1856), 71.

[2] Berl. Berichte **9** (1876), 830.

[3] Chem. Ztg. **34** (1910), 857.

[4] Notizbl. bot. Gart. Berlin-Dahlem **5** (1908), 95.

[5] P. Preuß, Berichte d. deutsch. pharm. Ges. **10** (1900), 306.

secretion has again diminished, the surface is again scorched by means of a torch. After the exudation has ceased altogether, the bark is removed and comminuted. Like the rags it is boiled with water to remove any adhering balsam.

Production and Properties. Inasmuch as the Peru balsam oil, also known as cinnamein, is very difficultly volatile with water vapor, it is separated by shaking out the balsam with carbon disulphide, ether, petroleum ether or similar solvents. It is a reddish-brown, somewhat viscid liquid: d_{15° 1,102 to 1,121; slightly dextrogyrate, up to $+2^\circ 30'$; n_{D20° 1,573 to 1,579; A. V. 25 to 45; E. V. 200 to 250; soluble in 0,3 to 4 vol. or more of 90 p.c. alcohol. The diluted solution is frequently opalescent either immediately or after standing.

Composition. The bulk of Peru balsam oil consists of a mixture of the benzyl esters of cinnamic and benzoic acids. An oil examined by Tschirch and Trog[1]) consisted principally of benzyl benzoate, whereas in several oils examined by H. Thoms[2]) the cinnamic ester predominated. In one instance the mixture of acids, obtained upon cold saponification of the cinnamein with alcoholic potassium hydroxide, consisted of cinnamic and benzoic acids in the ratio of 40 : 60. The acid mixture also contained an acid melting at 79 to 80°, presumably a dihydrobenzoic acid. Combined with these acids, Thoms discovered an alcohol $C_{13}H_{22}O$, which he named peruviol, the odor of which reminded of honey and narcissus. It had the following properties: b. p. 139 to 140° (7 mm.); $d_{17,5^\circ}$ 0,886; $\alpha_D + 13^\circ$.

By acting on peruviol with cinnamyl chloride, only a small amount of a crystalline ester with the odor of hyacinth resulted. When oxidized with alkaline permanganate in the cold, a mixture of lower fatty acids resulted.

E. Schmidt[3]) demonstrated the presence of small amounts of vanillin. According to F. Elze[4]) farnesol is also present. Cinnamic alcohol, the presence of which was claimed by

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[1]) Arch. der Pharm. **232** (1894), 70.

[2]) *Über Cinnameïn oder Perubalsamöl.* Arch. der Pharm. **237** (1899), 271.

[3]) Tagebl. d. Naturforscher-Vers. Straßburg **1885**, 377.

[4]) Chem. Ztg. **34** (1910), 857.

M. Delafontaine[1]), apparently does not occur in Peru balsam oil any more than does stilbene which J. Kachler[2]) claimed to have found[3]).

363. Oil of Myroxylon peruiferum.

From the leaves of *Myroxylon peruiferum,* L., a leguminous tree closely related to the Peru balsam tree, Th. Peckolt[4]) obtained a small amount of oil with a faint but pleasant and peculiar odor the specific gravity of which was 0,874 at 14°.

From the bark two oils were obtained, one with a specific gravity of 1,139 at 15°, the other with a specific gravity of 0,924 at 17°.

The oil from the wood had an odor that was faintly sassafras-like, and a specific gravity of 0,852 at 15°.

364. Quino-Quino Balsam Oil.

Quino-Quino balsam resembles Peru and tolu balsams. It has been described by C. Hartwich and A. Jama[5]). The resin which had been obtained in Florida and Pampa grande (Bolivia) by Dr. Herzog, was derived from *Myroxylon Balsamum var. γ punctatum* (Klotzsch)[6]), Baill., a tree that grows in Peru, southern Brazil and eastern Bolivia and which is known as *quina-quina.* The balsam is used as incense and as varnish. As to its chemical composition it resembles tolu and Peru balsams: A. V. 80,30; S. V. 134,09; vanillin content about 0,044 p.c. It

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[1]) Zeitschr. f. Chem. N. F. 5 (1869), 156; Chem. Zentralbl. **1869**, 902.

[2]) Berl. Berichte **2** (1869), 512.

[3]) The formation of Peru balsam, Kronstein (Deutsche med. Wochenschr. **36** [1910], 2339; Apotheker Ztg. **25** [1910], 1023) attributes to the polymerization of allyl cinnamate. He has demonstrated that this ester, upon prolonged heating, is converted into a resin which is related both physically or chemically to Peru balsam. Hence it is possible that the secretory ducts contain allyl cinnamate in the monomolecular condition and which, upon polymerization, yields Peru balsam, whereas such substances, like free cinnamic acid and benzyl cinnamate, which cannot be polymerized, remain in their original condition.

[4]) Zeitschr. d. allg. österr. Apoth. Ver. **17** (1879), 49; Jahresb. f. Pharm. **1879**, 59.

[5]) Schweiz. Wochenschr. f. Chem. u. Pharm. **47** (1909), 625, 641.

[6]) Harms, Notizbl. bot. Gart. Berlin-Dahlem **5** (1908), 97.

differs from the other two balsams by its lower cinnamein content, which amounts to 5,83 p.c. (whereas Peru balsam contains 56 to 64 p.c. and tolu balsam 7,5 p.c.). The cinnamein has the same qualitative composition but differs quantitatively, benzyl benzoate predominating almost exclusively with only traces of benzyl cinnamate.

A balsam examined by J. D. Riedel[1]) differed somewhat in its properties. It is described as a thick, tenaceous extract with the odor of coumarin which, when exposed to the air, evaporates to a resin that can be pulverized. S. V. 184,8. 10,1 p.c. of a constituent resembling cinnamein were isolated. It was semi-solid and its S. V. was 99,9. The balsam did not contain cinnamic acid.

Hartwich and Jama[2]) regard the difference in the consistence of the two balsams as accidental. The other difference they account for by assuming that whereas their own balsam was obtained by making incisions into the trunk, the balsam examined by Riedel was obtained from the fruit. They base their assumption on the analogy with Peru balsam. In this case the fruits likewise yield a product that has the odor of coumarin and is free from cinnamic acid. They are further of the opinion that the odor of a sample obtained by them from Riedel did not have the odor of coumarin but of piperonal. However, they do not attempt to decide whether this compound or vanillin is present.

365. Cabriuva Wood Oil.

Myrocarpus fastigiatus, Fr. All. is a leguminous tree that attains a height of 8 m. or more, which is a native of Brazil. It is called *cabriuva.* The yellowish-white flowers arranged in the form of a corymb are very fragrant, the odor reminding of a mixture of vanilla and frankincense or tolu balsam. The wood is one of the most valuable Brazilian woods.

The oil from the wood has been examined by Schimmel & Co.[3]). It was light yellow in color and had a faint, not unpleasant odor: d_{15° 0,9283; $\alpha_D - 8^\circ 29'$.

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[1]) Riedel's Mentor **1912**, S. 33.

[2]) Schweiz. Wochenschr. f. Chem. u. Pharm. **50** (1912), 312.

[3]) Report of Schimmel & Co. April **1896**, 64.

From 100 kg. of the sawdust of the wood, Peckolt[1]) obtained 4,3 g. of oil which he designates *Oleo essencial de Cabureiba ou Oleo pardo* and the specific gravity of which was 0,925 at 13°.

366. Myrocarpus Balsam Oil or Cabureiba Balsam Oil.

Myrocarpus balsam is one of the obsolete balsams of the older pharmacopœias. E. Schaer[2]) is of the opinion that it is identical with the Cabureiba balsam described by the Dutch physician Willem Piso about the middle of the 17th century in his *Historia naturalis Brasiliæ* IV. 5, 57, also with the *Baume du Pérou en coques* of Guibourt's *Histoire naturelle des drogues simples.*

The *Myrocarpus fastigiatus,* Allem. and the *M. frondosus,* Allem., both of which are natives of central Brazil, yield a balsam from natural wounds and from incisions. For its collection, fruits of the size of a walnut, that have been hollowed out and which are obtained either from certain palms or certain *Myrtaceæ,* are used. After having been allowed to dry for several days the fruits are sealed with a plant wax. The balsam itself is reddish-brown and, aside from its tough consistency, greatly resembles Peru and tolu balsams as to appearance, odor and other properties. Schaer found it to contain benzoic acid, free as well as combined with aromatic alcohols. Cinnamic acid and vanillin he could not find.

In the ethereal extract A. Tschirch and J. O. Werdmüller[3]) found benzoic acid (m. p. 121°) but could not detect any cinnamic acid. In the saponification liquid of the resin, vanillin was found.

The volatile oil which may be supposed to possess properties similar to those of Peru balsam, has not yet been isolated.

367. Oil of Cyclopia genistoides.

Upon the distillation of the leaves of *Cyclopia genistoides,* R. Br. (family *Leguminosæ*) H. Hænsel[4]) obtained 0,101 p.c. of

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[1]) *Katalog der National-Ausstellung in Rio* **1866**, 48.

[2]) Arch. der Pharm. **247** (1909), 176.

[3]) *Ibidem* **248** (1910), 431.

[4]) Chem. Zentralbl. **1906**, II. 1496.

a light brown oil with an intense odor. At room temperature, the oil was permeated with paraffin crystals (heptacosane) that melts at 53 to 54°; $d_{15°}$ 0,8737; $\alpha_D + 0{,}36°$ in 10 p.c. benzene solution.

368. Broom Oil.

The dried flowering herb of *Genista tinctoria,* L. (family *Leguminosæ*) yielded upon distillation 0,0237 p.c. of an oil that was solid at ordinary temperature and which melted at 36°: $d_{33°}$ 0,8980. It begins to boil at 80°, between 80 and 100° about 5 p. c. pass over, between 100 and 200° 10 p. c., the balance between 200 and 280°[1]).

369. Carqueja Oil.

This oil is supposed to be obtained from *Genista tridentata* (family *Leguminosæ*) a plant that grows wild in Brazil and is used as a popular remedy in a variety of ways[2]).

Carqueja oil is yellowish and has a somewhat narcotic, camphor-like, not pleasant odor: $d_{15°}$ 0,9962; $\alpha_D - 31°15'$ at 17°; S. V. 190,5. When distilled three-fourths of the oil passed over between 200 and 300°, acetic acid being formed. In the first fraction a small amount of cineol was detected. The residue consisted of a thick, tough mass.

370. Oil of Spartium scoparium.

The dried, flowering herb of *Spartium scoparium,* L. (Ger. *Besenginster,* family *Leguminosæ*) yields upon distillation 0,031 p.c. of a dark brown oil with a strong odor which when cooled to 0° congeals in part[3]). $d_{15°}$ 0,8673; A. V. 58,6; E. V. 29,4. It contains furfurol, palmitic acid (m. p. 60 to 61°) and a paraffin that melts at 48 to 49°[4]).

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[1]) H. Hænsel, Pharm. Ztg. 47 (1902), 819.

[2]) Report of Schimmel & Co. April 1896, 64.

[3]) H. Hænsel, Apotheker Ztg. 24 (1909), 283.

[4]) The flowers of *Spartium junceum,* L. (Fr. *Genêt d'Espagne,* Ger. *spanischer Ginster*) which also belongs to the *Genisteæ,* are extracted in Grasse with volatile solvents for the preparation of perfume.

371. Commock Oil.

From the air-dried roots of *Ononis spinosa,* L. (Ger. *Hauhechel,* family *Leguminosæ*) H. Hænsel[1]) obtained 0,0066 p.c. of a liquid oil with an acid reaction. d_{15° 0,9917. From the aqueous distillate additional oil to the extent of 0,0132 p.c. was obtained.

372. Fenugreek Oil.

According to H. Hænsel[2]), the comminuted seeds of *Trigonella Fœnum-græcum,* L. (family *Leguminosæ*) yield 0,014 p.c. of a brown oil with an intense odor: $d_{13,2^\circ}$ 0,870; α_D in 10 p.c. alcoholic solution $+0,8^\circ$.

373. Melilot Oil.

Upon distillation the dried flowers of *Melilotus officinalis,* Desr. (family *Leguminosæ*) yield 0,0133 p.c. of volatile oil which contains coumarin (m. p. 67°)[3]).

374. Clover Oils.

1. OIL FROM THE FLOWERS OF *TRIFOLIUM INCARNATUM.*

The flowers of *Trifolium incarnatum,* L. have been distilled by H. Rogerson[4]) who obtained 0,029 p.c. of a pale yellow oil with reference to the dried clover and 0,006 p.c. with reference to the fresh flowers. The oil, which has a strong odor boiled between 120 and 180° (15 mm.); $d_{20^\circ}^{20^\circ}$ 0,9597; $\alpha_D - 1^\circ 48'$. Furfurol was the only constituent that could be identified.

2. OIL FROM THE FLOWERS OF *TRIFOLIUM PRATENSE.*

From the flowers of the red clover, *Trifolium pratense,* L., F. B. Power and A. H. Salway[5]) obtained an oil with a rather unpleasant odor. Computed with reference to the dry flowers the yield was 0,028 p.c., with reference to the fresh flowers 0,006 p.c. $d_{20^\circ}^{20^\circ}$ 0,9476; $\alpha_D + 4^\circ 10'$. Furfurol was identified.

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[1]) Apotheker Ztg. **25** (1910), 303.

[2]) *Ibidem* **18** (1903), 51.

[3]) H. Hænsel, *Ibidem* **15** (1900), 516.

[4]) Journ. chem. Soc. **97** (1910), 1004.

[5]) *Ibidem* 232.

375. Oil of Psoralea bituminosa.

More particularly when rubbed the herb of *Psoralea bituminosa,* L. (family *Leguminosæ*) gives off a strong asphalt-like odor. The leaves were formerly officinal as *Herba trifolii bituminosi* and were used as a remedy for a variety of ailments.

Upon distillation of 20,5 kg. of dry herb, Schimmel & Co.[1]), obtained 10 g. = 0,048 p. c. of an oil which was semisolid at ordinary temperature but which revealed no trace of the original bituminous odor. From it fatty acids could be isolated which melted between 38 and 40° (lauric acid?). The sp. gr. of the oil was 0,8988 at 25°; A. V. 57,18; E. V. 12,25.

376. Oil of Amorpha fruticosa.

According to Vittorio Pavesi[2]), the leaves and fruits of *Amorpha fruticosa,* L. (family *Leguminosæ*) which is frequently cultivated in gardens for decorative purposes, contain two distinct oils. Upon distillation with water vapor the fruits yielded 0,15 to 0,35 p.c., the leaves 0,05 to 0,08 p.c. of volatile oil light yellow in color, with a bitter taste and with the following constants:

Fresh oil from the leaves: $n_{D17,5^\circ}$ 1,50083; $n_{D18,5^\circ}$ 1,50928.
Old oil from the leaves: $n_{D17,5^\circ}$ 1,50036; $n_{D18,5^\circ}$ 1,50892.

Oil from the unripe fruits:	d_{15° 0,9019;	$n_{D17,5^\circ}$ 1,49951	optical rotation slightly lævogyrate.
Oil from the ripe fruits:	d_{15° 0,9055;	$n_{D17,5^\circ}$ 1,50036	

Fraction 150 to 200° (750 mm.), (80 to 120° under 30 mm. pressure) of the leaf oil contains a terpene that has not been further characterized. In the higher boiling fraction (b. p. 250 to 265°; d_{15° 0,91661; n_{D15° 1,50559) cadinene could be identified by means of its chlorhydrate melting at 117°. In large part, however, the fraction consists of a sesquiterpene (d_{15° 0,916; n_{D15° 1,50652) which resembles clovene, found by Wallach as companion of cadinene, and which also may be regarded as a new sesquiterpene to which Pavesi has given the name amorphene.

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[1]) Report of Schimmel & Co. October **1903**, 76.

[2]) Annuario della Soc. chimica di Milano **11** (1904), fascicles 1 and 2. — Rendiconti del R. Ist. Lomb. di sc. e lett. II. **37** (1904), 487; Report of Schimmel & Co. October **1904**, 9.

377. Indigofera Oil.

According to van Romburgh, the leaves of *Indigofera galegoides*, DC. (family *Leguminosæ*) contain a substance (probably amygdalin) which reacts with emulsin forming hydrocyanic acid and benzaldehyde. Upon distilling the fresh herb, mashed with water, 0,2 p.c. of oil were obtained.

Indigofera oil is light yellow and has the odor of bitter almond oil but differs from it by an herbaceous odor. Sp. gr. 1,046[1]).

In addition to benzaldehyde and hydrocyanic acid, the oil contains traces of ethyl alcohol and small amounts of methyl alcohol. The presence of the latter was demonstrated by its conversion into methyl iodide and into methyl oxalate melting at 54°.

When previous to the distillation the leaves were digested with water at 50° for 24 hours, the first distillate contained large amounts of ethyl alcohol in addition to methyl alcohol. The ethyl alcohol apparently is formed when the leaves are soaked in water[2]).

378. Oil of Robinia Pseudacacia.

Verschaffelt[3]) had pointed out that the odor of the flowers of *Robinia Pseudacacia*, L. (family *Leguminosæ*) indicated the presence of methyl anthranilate. That the flowers contain this ester was demonstrated by F. Elze[4]). He extracted the flowers with a readily volatile solvent and obtained a dark brown oil (yield not mentioned) with a peculiar basic odor which, however, faithfully reproduced the fragrance of the flowers upon dilution. The oil had the following constants: b. p. 60 to 150° (5 mm.); d_{15° 1,05; it contained 9 p.c. ester computed as methyl anthranilate. Its alcoholic solution had a decided blueish fluorescence.

The following constituents were identified: anthranilic acid methyl ester (m. p. 25°), indol (m. p. 52°), traces of pyridine-like bases, heliotropin (m. p. 37°; m. p. of semicarbazone 235°), benzyl

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[1]) Report of Schimmel & Co. October 1894, 73.

[2]) Verslag's Lands Plantentuin te Buitenzorg 1894, 44; Report of Schimmel & Co. April 1896, 70.

[3]) Chem. Weekblad 1908, No. 25.

[4]) Chem. Ztg. 34 (1910), 814.

alcohol (d_{15° 1,048), linalool (oxidation to citral) and α-terpineol (m. p. of phenyl urethane 111°). In addition aldehydes and ketones, with a decided odor of peach, and probably also nerol are present.

379. Licorice Oil.

Upon the distillation of the root of *Glycyrrhiza glabra,* L. (family *Leguminosæ*) H. Haensel[1]) obtained a small amount of volatile oil. From the Spanish root a yield of 0,03 p.c. and from the Russian root 0,035 p.c. were obtained. The oil from the Spanish root deviated the ray of polarized light to the left, that of the Russian oil to the right.

380. Oil of Dalbergia Cumingiana.

As *kaju laka* the wood of *Dalbergia Cumingiana,* Benth. (family *Leguminosæ*) plays an important role in Dutch East India[2]). At first it is colorless, but that of older trees becomes red and heavier. The aromatic odor given off when the wood is burned is due to a volatile oil which at first is colorless and has an odor resembling somewhat that of cineol. The oil has been produced in Buitenzorg[3]) with a yield of 0,5 p.c.; d_{26° 0,891; α_{D26° —4° 31′; E. V. 5; E. V. after acetylation 116. The oil began to boil at 260° and up to 310° had distilled over only in part. Further heating caused decomposition. A test for aldehydes gave negative results.

Family: GERANIACEÆ.

381. Rose Geranium Oil.

Oleum Geranii. — Geranium- or Pelargoniumöl. — Essence de Géranium Rose.

Origin. For the purpose of distillation three species of the genus *Pelargonium* and their cultural varieties are principally

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[1]) Pharm. Zentralh. **40** (1899), 533.

[2]) W. G. Boorsma, *Über Aloeholz und andre Riechhölzer.* Bull. du Dép. de l'Agricult. aux Indes Néerl. **1907** No. 7 (Pharmacologie III), p. 25; Report of Schimmel & Co. October **1908**, 21.

[3]) Jaarb. dep. Landb. in Ned.-Indië, Batavia **1906**, 45; Report of Schimmel & Co. October **1908**, 49.

cultivated, *viz., Pelargonium odoratissimum,* Willd.[1]), *P. capitatum,* Ait., and *P. roseum,* Willd. (family *Geraniaceæ*). The last-named is regarded as a variety of *P. Radula,* Ait.[2]). According to L. Ducellier[3]), *Pelargonium graveolens,* Ait. (*P. terebinthinaceum,* Cav.) is cultivated exclusively for the distillation of the volatile oil.

The oil is located principally in the leaves, stems and petioles being devoid of oil which is likewise wanting in the flowers of *P. odoratissimum*[4]), whereas, according to Blandini[5]), the oil content of the flowers is greater than that of the leaves. As a rule, however, the leaves only are used in the production of oil. The harvest begins shortly before the flowering period when the leaves begin to turn yellow and when the lemon-like odor gives way to the rose-like odor.

The plants grown on dry soil are said to give less oil, but an oil of finer quality than those cultivated on soil that is irrigated.

The reports found in literature as to the yield of oil vary considerably. In France the leaves of *P. odoratissimum* yield 0,1[6]) to 0,2 p.c.[4]), in Corsica 0,125 to 0,166 p.c.[7]). In Réunion where *P. capitatum* is cultivated, the leaves of this species yield 0,1 to 0,14 p.c.[8]) of oil. The distillation conducted in Italy (Portici) on an experimental scale, yielded much higher results: the leaves yielded 0,7 to 0,8 p.c. and the flowers 1,5 to 1,98 p.c.[5]). In Sicily but 0,07 p.c. of oil were obtained.

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[1]) According to the Index Kewensis *P. odoratissimum* (Sol.) Ait.

[2]) J. C. Sawer, Odorographia. London **1892**, vol. I, p. 42.

[3]) The excellent monograph by this author on "Le Géranium rosat, sa culture en Algérie", Algiers 1913, appeared too late to receive consideration in the preparation of this treatise.

[4]) E. Charabot and G. Laloue, Compt. rend. **136** (1903), 1467.

[5]) Bull. de l'Office du Gouvern. de l'Algérie **12** (1906), 277; Report of Schimmel & Co. April **1907**, 54. — The publication of Blandini, who made his cultural experiments at the agricultural school at Portici, were known to the author only through the abstract referred to above. In as much as his statements concerning the oil yield of leaves and flowers differ materially from those made by other authors, the firm of Schimmel & Co. directed a request for information to this institute. However, no answer was received to the two requests made.

[6]) Berichte von Roure-Bertrand Fils April **1901**, 17.

[7]) R. Gattefossé, Parfum. moderne **3** (1910), 73.

[8]) de Cordemoy, Rev. cultures coloniales **14** (1904), 170.

According to J. de Cordemoy[1]), *Pelargonium capitatum,* Ait. is cultivated in Réunion. In recent years its cultivation has been considerably increased. Altitudes of from 400 to 1200 m. are selected. In the higher altitudes the winters are too severe, the plants being ruined by frost. A soil rich in humus, such as exists in newly broken ground, is best adapted to the cultivation of rose geranium. For the production of the oil, the distillers use very simple stills of which about 250 are found in the entire colony. About 700 to 1000 kg. of leaves yield 1 kg. of oil. The exhausted leaves are very serviceable as fertilizer.

In Algiers the oil of rose geranium is mostly distilled in regions surrounding the cities. Boufarik, in the plains of Mitidja, about 35 km. distant from the city of the same name, is the commercial center. The most important factory is reported to be located in an old monastery of the Trappists order.

According to Robert Gattefossé[2]), the cultivation of rose geranium is still greatly neglected in Corsica. *Pelargonium odoratissimum,* which grows in northern Corsica, might well be planted successfully in other favorable parts of the island. In May, August and October the working rural population of several communities of the peninsula of Cape Corso is busy with the harvesting and distillation of these fragrant plants.

About half a century ago the cultivation of this plant was introduced from the Provence and was quickly taken up in the communities of Erbalunga, Sisco and Brando. The cultivation is somewhat expensive since the soil requires to be carefully cultivated twice, *viz.,* in March and July, and the irrigation is laborious. In March propagation is accomplished by means of cuttings. For the purpose of harvest the plant is cut off about 5 cm. above the ground. 800 kg. of the first cutting yield 1 kg. of oil; the second is better, only 600 kg. being required; the last cutting yields but little herb and oil. As to quality, the oil is comparable with the Spanish oil and the oil obtained in the vicinity of Grasse.

The annual production amounts to from 600 to 700 kg. However, it has exceeded 1300 kg., but the high price of labor

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[1]) Rev. cultures coloniales 14 (1904), 170.

[2]) Parfum. moderne 3 (1910), 73.

and the low prices offered by the jobbers discouraged the cultivators. The community of Erbalunga owns more than 200 hectares of rose geranium plants which yield, on the average, 5000 kg. of fresh material pro hectare.

Climate, locality and soil seem to impart a special vitality to the plants, since cuttings from the peninsula of Cape Corso are much sought for planting elsewhere. In 1909 more than 350000 cuttings were sold at 15.— francs per thousand.

In France the cultivation of rose geranium *(P. odoratissimum)* is carried on in the vicinity of Grasse, more particularly in the valley of Laval and in the neighborhood of the two small cities Pegomas and Mandelieu[1]). The total production of oil amounts to 2000 to 3000 kg.[2]). Whereas in warmer countries such as Algiers, the plant may survive for from 6 to 8 years and admits of three cuttings annually, in southern France rose geranium must be planted new each year since it is killed by frost. Moreover, but one harvest is possible annually, this taking place between August 20th and the end of September. The plant is propagated by cuttings which are wintered in hot beds and transplanted into the open in March and April[3]).

According to estimate, Spain produces in Valencia and Andalusia about 600 to 1000 kg. of oil annually. Under favorable climatic conditions 2 to 3 harvests are possible.

Properties. Oil of rose geranium is a colorless, greenish or brownish liquid with a pleasant, rose-like odor: d_{15° 0,89 to 0,907; α_D — 6 to — 16°. With the exception of the Spanish oil, the several varieties are as a rule soluble in 2 to 3 vol. of 70 p. c. alcohol, forming a clear solution. However, the addition of more solvent usually produces turbidity due to the separation of paraffin. According to Jeancard and Satie[4]) the A. V. fluctuates between 1,5 and 12, increasing upon standing when the oil is kept in but partly filled bottles. The E. V. fluctuates between 34 and 99, corresponding to between 14,3 and 41,7 p. c. of geranyl tiglinate.

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[1]) Berichte von Roure-Bertrand Fils April **1901**, 17; October **1907**, 36.

[2]) *Ibidem* October **1906**, 28.

[3]) Jeancard and Satie, Bull. Soc. chim. III. **31** (1904), 43.

[4]) Bull. Soc. chim. III. **23** (1900), 37.

The several varieties of oil differ from each other more or less, a fact that finds a ready explanation, in part at least, in the different botanical source of the material distilled (compare under yield on p. 614).

1. Réunion geranium oil. $d_{15°}$ 0,888 to 0,896; $\alpha_D - 7° 50'$ to $- 13° 50'$; $n_{D20°}$ 1,462 to 1,468; A. V.[1] 1,5 to 12; E. V. 50 to 78 = 21 to 33 p. c. geranyl tiglinate[2]); E. V. after acetylation 206 to 233 = 67 to 77,6 p. c. alcohol $C_{10}H_{18}O$; total alcohol including alcohol as ester (comp. vol. I, p. 576) 60 to 71 p. c.

2. African geranium oil. $d_{15°}$ 0,892 to 0,904; $\alpha_D - 6° 30'$ to $- 12°$; $n_{D20°}$ 1,465 to 1,472; A. V. 1,5 to 9,5; E. V. 34 to 70 = 14,3 to 29,5 p. c. tiglinate; E. V. after acetylation 203 to 230 = 66 to 76,4 p. c. alcohol $C_{10}H_{18}O$; total alcohol content including alcohol as ester 62 to 71,5 p. c.

3. French geranium oil. $d_{15°}$ 0,896 to 0,905; $\alpha_D - 7° 30'$ to $- 10° 15'$; A. V. 6 to 10; E. V. 46 to 66 = 19,4 to 28 p. c. tiglinate; E. V. after acetylation 217 to 228 = 71,3 to 75,6 p. c. alcohol $C_{10}H_{18}O$. Citronellol content 37 to 40 p. c.[3]).

4. Spanish geranium oil. $d_{15°}$ 0,897 to 0,907; $\alpha_D - 7° 30'$ to $- 11°$; A. V. 3 to 11; E. V. 64 to 99 = 27 to 42 p. c. tiglinate; E. V. after acetylation 204 to 234 = 66 to 78 p. c. alcohol $C_{10}H_{18}O$.

5. Corsican oil. Of this variety only a few samples have been investigated. $d_{15°}$ 0,896 to 0,901; $\alpha_D - 8$ to $- 10° 30'$; A. V. 3,6 to 5; E. V. 56 to 63 = 23,6 to 26,5 p. c. tiglinate.

6. The German oil[4]), which has been distilled occasionally, is not an article of commerce. Yield 0,16 p. c. $d_{15°}$ 0,906; $\alpha_D - 16°$; tiglinate content 27,9 p. c.; E. V. after acetylation 212 = 69,3 p. c. alcohol $C_{10}H_{18}O$.

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[1]) The acid value of these oils has been determined according to the customary method (see vol. I, p. 572) and not according to the method proposed by Jeancard and Satie (footnote 4, p. 616). According to the latter, 10 cc. of half-normal potassium hydroxide solution are added to 3 g. of the oil and the excess of alkali is titrated back with acid. This method of procedure may result in a partial saponification of the ester, hence in too large an acid value.

[2]) For the computation of the geranyl tiglinate content the table on p. 631 of vol. I may be utilized.

[3]) The properties of the French oil have been studied in detail by Jeancard and Satie. Bull. Soc. chim. III. **31** (1904), 43.

[4]) Report of Schimmel & Co. April **1894**, 33.

7. Oil from Palestine¹). $d_{15°}$ 0,896; $\alpha_D - 8° 20'$; A. V. 9,8; E. V. 68,6; citronellol content 45,7 p. c.

Transportation in tin cans, in which geranium oil is mostly shipped, causes it to assume a brown color and an odor reminding of rotten eggs. The odor, however, is readily removed by exposing the oil for several days in shallow dishes to the air. Naturally, the oil should be transferred to glass containers as soon as possible.

Composition. The principal constituent of geranium oil is geraniol²), $C_{10}H_{18}O$, common to all commercial varieties.

In addition to geraniol a second alcohol, $C_{10}H_{20}O$, citronellol, has been identified by F. Tiemann and R. Schmidt³). It is particularly abundant in the Réunion oil. Mixtures of these two alcohols were formerly regarded as definite chemical compounds. Such was the case with the *"rhodinol de pelargonium"* of P. Barbier and L. Bouveault⁴) and the *"Reuniol"* of Hesse⁵).

The relative amounts of geraniol and citronellol in the several commercial oils have been determined by Tiemann and Schmidt³). Of the 70 p.c. of total alcohols of Spanish geranium oil, 65 p.c. consist of geraniol and 35 p.c. of citronellol. Of the 75 p.c. of total alcohols of the African geranium oil, four-fifths are geraniol and one-fifth citronellol. Réunion geranium oil yields 80 p.c. of alcohols, consisting half and half of geraniol and citronellol respectively. In all of the oils the citronellol existed as a mixture of the dextrogate and lævogyrate modifications.

The above results, however, cannot be regarded as exact, since according to recent investigations other alcohols are present, *viz.*, linalool, borneol (?), terpineol, phenylethyl alcohol, menthol and an amyl alcohol (?). According to Tiemann and Schmidt's assay method⁶) some of these are determined as geraniol, others as citronellol.

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¹) C. Satie, Americ. Perfumer 1 (1907), No. 12, p. 12.

²) Gintl, Jahresb. d. Chem. 1879, 941; J. Bertram and E. Gildemeister, Journ. f. prakt. Chem. II. 49 (1894), 191.

³) Berl. Berichte 29 (1896), 924.

⁴) Compt. rend. 119 (1894), 281 and 334.

⁵) Journ. f. prakt. Chem. II. 50 (1894), 472 and 53 (1896), 238.

⁶) By treating the oil with phosphorus trichloride. This reagent converts citronellol (other alcohols likewise) into a phosphorous acid ester, and geraniol is converted into geranyl chloride and a hydrocarbon.

According to C. Satie[1]), French oil contains from 37 to 43 p.c. of citronellol, African likewise 37 to 43 p.c. and Réunion oil 50 to 65 p.c. These amounts were determined by means of the formylation method with formic acid (comp. vol. I, p. 580), without, however, paying any attention to the length of formylation. As was shown later, this factor is of great importance, hence the above data may have to be modified.

The presence of linalool, which was suspected by Barbier and Bouveault[2]), was proven by Schimmel & Co.[3])[4]) by means of its phenylurethane melting at 65 to 66°. The fraction used for the preparation of this derivative had the following properties: d_{15° 0,872; $\alpha_D - 1^\circ 40'$; n_{D20° 1,4619.

The rose-like odor of geranium oil is due partly to a small content of phenylethyl alcohol (m. p. of phenylurethane 80°)[4]). Terpineol is present in somewhat larger amounts, *viz.,* the inactive α-terpineol[4]) melting at 34 to 35°[5]). It was identified by means of its nitrosochloride (m. p. 114 to 115°), its phenylurethane (m. p. 109 to 111°) and the ketolactone (m. p. 62 to 63°) prepared from the trihydroxy terpane. While purifying the terpineol, traces of menthol were found, also traces of an alcohol with a peculiar odor reminding somewhat of borneol[4]). Finally, an alcohol that produced an irritation causing coughing should be mentioned. Its phenylurethane melted at 41 to 43°[6]). All of these alcohols are present partly free, partly as esters.

The acids separated from the mother liquid after saponification boiled between 100 and 210° and congealed in part. The silver content of its silver salt, also its dibromide melting at 87°, reveal its identity with tiglic acid[7]). The liquid acid mixture apparently contains valeric, butyric[7]) and acetic acids[8]).

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[1]) Americ. Perfumer **1** (1907), No. 12, p. 12.

[2]) Compt. rend. **119** (1894), 281.

[3]) Report of Schimmel & Co. April **1904**, 55.

[4]) *Ibidem* October **1910**, 69.

[5]) *Ibidem* October **1911**, 52.

[6]) *Ibidem* April **1904**, 55.

[7]) *Ibidem* April **1894**, 32. It would be of interest to reinvestigate the statement that the aqueous distillate of *Pelargonium roseum* contains pelargonic acid (Pless, Liebig's Annalen **59** [1846], 54) and to ascertain whether the acid was not a mixture which accidentally happened to have the composition of pelargonic acid.

[8]) Barbier and Bouveault, *loc. cit.*

The non-alcoholic constituents belong to a variety of classes of chemical compounds. In the lowest boiling fractions of both the Réunion and African oils, Schimmel & Co.¹) found a sulphur-compound, the dimethyl sulphide. Though present in minimal amounts only, it exerts a marked influence on the odor of the oil. It was identified by its boiling point, *viz.,* 37°, and by its characteristic reactions with mercuric and platinic chlorides.

Of terpenes the presence of *l*-α-pinene²) (m. p. of nitrolbenzylamine 122 to 123°) and of traces of phellandrene²) (probably β-phellandrene, m. p. of nitrite 114 to 115°) was demonstrated.

In the lower fractions Flatau and Labbé³) discovered *l*-menthone (m. p. of semicarbazone 179,5°). From an oil obtained by cohobation of the aqueous distillate, Charabot and Laloue⁴) isolated citral with the aid of acid sodium sulphite.

From the last fractions of the oil a crystalline substance that melted at 63° and that had the properties of rose oil stearoptene was isolated. Judging from the behavior of the geranium oils toward 70 p.c. alcohol, the paraffin occurs most abundantly in in the Spanish variety.

The green color of individual oils, more particularly of those from Réunion, is due to a liquid ($[C_{10}H_{17}]_2O$?) that boils at 165 to 170° under 10 mm. pressure⁵).

Adulteration and Examination. Geranium oil is adulterated with turpentine oil, cedar-wood oil and gurjun balsam oil⁶). Additions of these oils are recognized by their insolubility in 70 p.c. alcohol and by the lowering of the ester value of the adulterated oils. In order to render the detection of such adulterations more difficult, the ester content has been increased by the addition of artificial esters of benzoic acid⁷), oxalic acid⁸) and phthalic acid⁹).

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¹) Report of Schimmel & Co. April **1909**, 55.

²) *Ibidem* April **1904**, 55.

³) Bull. Soc. chim. **19** (1898), 788.

⁴) Compt. rend. **136** (1903), 1467.

⁵) Barbier and Bouveault, *loc. cit.*

⁶) Report of Schimmel & Co. April **1908**, 56; October **1911**, 53.

⁷) *Ibidem* October **1905**, 36.

⁸) Parry, Perfum. and Essent. Oil Record **2** (1911), 83.

⁹) Report of Schimmel & Co. April **1913**, 66.

Fatty oil, the presence of which is indicated by its insolubility in 70 p.c. alcohol, remains behind when the oil is distilled with water vapor, hence its presence can be proven without difficulty.

An oil adulterated with gingergrass oil has also been observed[1]).

Production and Commerce. The African oil and that from Réunion are the most important of the commercial oils.

The following amounts have been exported:

from Réunion:		from Algiers:	
Year	Amount in kg.	Year	Amount in kg.
1901	13 953		
1902	17 193		
1903	25 323	1903	31 200
1904	27 660	1904	63 600
1905	38 334	1905	52 600
1906	31 645	1906	54 600
1907	31 247	1907	38 700
1908	34 360	1908	46 600
1909	59 788	1909	41 000
1910	61 792	1910	33 800
1911	44 620	1911	28 500
1912	43 138	1912	24 900

As already pointed out, southern France produces annually 2000 to 3000 kg., Spain 600 to 1000 kg. and Corsica 600 to 1300 kg. of oil.

Family: TROPÆOLACEÆ.

382. Oil of Garden Nasturtium.

The odor of *Tropæolum majus,* L. (Ger. *Kapuzinerkresse,* family *Tropæolaceæ*), having an odor similar to that of the cress, induced A. W. Hofmann[2]) to examine the oil[3]). For the preparation of the oil 300 kg. of herb with flowers and immature seeds were distilled with water vapor. The aqueous distillate rich in oil was shaken out with benzene upon the evaporation of which 75 g. (= 0,025 p.c.) of oil were obtained.

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[1]) Report of Schimmel & Co. October **1911**, 53.

[2]) Berl. Berichte **7** (1874), 518.

[3]) The oil was first prepared by Müller, Liebig's Annalen **25** (1838), 207.

It distilled over between 160 and 300° but left a not inconsiderable residue. Only the first fractions, which had a disagreeable odor, contained traces of sulphur.

By far the largest fraction of the oil distilled at 231,9°. This fraction was a strongly refractive liquid with a specific gravity of 1,0146 at 18°. When treated with alkali it gave off ammonia abundantly. According to analysis the oil consists of the nitrile of phenylacetic acid. According to this investigation the garden cress oil contains as principal constituent the same constituent as the herb of *Lepidium sativum,* L.

In addition to small amounts of a hydrocarbon that was not investigated, the nitrile of phenylacetic acid was found in the lower as well as in the higher fractions.

Very different were the results obtained by Gadamer[1]) in a later investigation. He prepared the oil both by ether extraction of the juice, which had been obtained by expression of the comminuted herb, also by distillation of the carefully comminuted garden cress. In the latter instance the oil was obtained by shaking out the aqueous distillate with ether. 4 kg. of herb yielded 1,3 g. = 0,0325 p.c. of a brownish oil which had the pungent odor of cress which became especially noticeable when warmed. With ammonia the oil yields, well-nigh quantitatively, benzylthiourea melting at 162°. This reveals that the oil thus obtained, *i. e.* the normal garden cress oil, consists almost entirely of benzyl mustard oil.

This mustard oil owes its origin to the hydrolysis of a glucoside, the glucotropæolin, $C_{14}H_{18}KNS_2O_9 + xH_2O$, by means of an enzyme. Inasmuch as glucoside and enzyme exist in separate cells of the plant, the formation of benzyl mustard oil takes place only when the cell tissues have been ruptured and both substances can be brought into contact with each other. If the cell membranes are not ruptured previous to distillation, the enzyme is rendered inactive by the heat before it can hydrolyze the glucoside. Under the latter conditions the glucoside is decomposed into phenylacetic acid nitrile (benzyl cyanide) during the process of distillation.

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[1]) Arch. der Pharm. **237** (1899), 111. — Berl. Berichte **32** (1899), 2336.

Thus the results of A. W. Hofmann can be explained when one assumes that the material used by him was not comminuted sufficiently previous to distillation.

The seeds of the garden cress likewise contain glucotropæolin¹). When treated in the appropriate manner they yield a volatile oil which contains sulphur²).

Family: ERYTHROXYLACEÆ.

383. Oil of Coca Leaves.

From time immemorial the coca leaves have been used for chewing by the natives of the South American Cordilleras³). It is only in recent times, however, that, because of their alkaloidal content⁴), they have acquired significance in medicine⁵).

The volatile oil contained in the leaves was first observed and prepared by Niemann⁶) and Lossen⁷) in 1860.

According to their stage of development, the coca leaves⁸) from *Erythroxylon Coca,* Lam. *var. Spruceanum,* Brck. (family *Erythroxylaceæ*) contain varying amounts of volatile oil. Thus van Romburgh⁹) obtained 0,13 p.c. from young, undeveloped leaves, and but 0,06 p.c. from the fully developed ones. It consists principally of methyl salicylate with traces of acetone and methyl alcohol.

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¹) H. ter Meulen, Recueil trav. chim. des P.-B. **24** (1905), 480.

²) F. J. Bernays, Buchner's Repert. f. d. Pharm. 88 (1845), 387; Pharm. Zentralbl. **1845**, 735.

³) Pedro Cieza de Leon, *Parte primera de la Chronica del Peru.* Sevilla 1553. Royal Commentaries of the Incas. By the Inka Garcilasso de la Vega. Translated by Clemens R. Markham. London, Hakluyt Society, 1871. Vol. 2, Chap. 15, p. 371. — W. H. Prescott, History of the conquest of Peru. J. B. Lippincott & Co. 1881. Vol. 1, p. 143. — Wittmack, Berichte d. deutsch. Bot. Ges. **4** (1886), 25. — Kew Bull. **1889**, Nr. 33, p. 222.

⁴) Berichte d. deutsch. pharm. Ges. **9** (1899), 38.

⁵) Pharm. Rundsch. (New York) **2** (1884), 262.

⁶) *De foliis Erythroxyli,* Dissertatio. Göttingen 1860.

⁷) *Über die Blätter von Erythroxylon Coca* Lam., Dissert., Göttingen 1862.

⁸) Comp. C. Hartwich, *Beiträge zur Kenntnis der Cocablätter,* Arch. der Pharm. **241** (1903), 617.

⁹) Recueil trav. chim. des P.-B. **13** (1894), 425. — Verslag 's Lands Plantentuin te Buitenzorg **1894**, 43; Report of Schimmel & Co. October **1895**, 50 and April **1896**, 69.

384. Oil from Erythroxylon monogynum.

The bastard sandal, *Erythroxylon monogynum,* Roxb., is a shrub or small tree which grows in the western parts of the East Indies and in Ceylon. From the wood the natives prepare an oil which they obtain by placing pieces of the wood in an earthenware pot which is heated over direct fire. The volatile product is collected in a second pot inverted over the first one. It is known as *Dummele* and is used for varnishing boats[1]).

By means of steam distillation of the wood, Schimmel & Co.[2]) obtained 2,56 p.c. of an oil which constituted a sticky mass of crystals and the odor of which reminded of that of guaiac wood oil. The specific gravity is less than 1; A. V. 6,77; E. V. 1,56; m. p. 42 to 45°; E. V. after acetylation 131; soluble in 1 vol. of 90 p.c. alcohol with but faint turbidity which disappears upon the addition of more alcohol.

For the purpose of investigating the crystalline constituent, the last fraction of the oil was subjected to distillation *in vacuo.* Fraction 212 to 216° (8 mm.) was dissolved in petroleum ether and the ethereal solution subjected to a low temperature. After two subsequent recrystallizations from petroleum ether, shiny needles, melting at 117 to 118° ($[\alpha]_D$ in 13 p.c. chloroform solution $+32^\circ 28'$) were obtained, the analysis of which yielded results in agreement with the formula $C_{20}H_{32}O$. The substance is an alcohol the acetate of which melts at 72 to 73° and which has the formula $C_{22}H_{34}O_2$.

Family: ZYGOPHYLLACEÆ.

385. Guaiac Wood Oil.

Oleum Ligni Guajaci. — Guajakholzöl. — Essence de Bois de Gayac.

Origin and Production. According to Grisebach[3]), *Bulnesia Sarmienti,* Lor., is a tree 40 to 60 ft. high which belongs to the family *Zygophyllaceæ* and which is native to the Argentine province Gran Chaco along the middle course of the Rio Berjemo.

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[1]) Watt, Commercial Products of India. London 1908, p. 525.

[2]) Report of Schimmel & Co. April 1904, 97.

[3]) Abhandl. d. Königl. Ges. d. Wissensch. zu Göttingen. Vol. 24, p. 75.

The wood, which is very similar to the common guaiac wood from *Guaiacum officinale,* L., has been an article of commerce since 1892 under the name of *Palo balsamo.* It is solid and tough and when exposed to the air assumes a greenish-blue color thus indicating the presence of guaiac resin. When distilled, the wood yields 5 to 6 p.c. of an oil which was first prepared in 1891 by Schimmel & Co.[1]), and placed upon the market as guaiac wood oil[2]).

Properties. Guaiac wood oil is a very viscid liquid. When standing at ordinary temperature, it solidifies gradually to a crystalline mass, white or yellowish in color. Having solidified, it melts again between 40 and 50°. The odor of the oil is very pleasant, reminding of violets and of tea. 0,965 to 0,975; α_D — 3 to — 8°; n_{D30° 1,503 to 1,504; A. V. 0 to 1,5; E. V. 0 to 5; E. V. after acetylation 100 to 153; soluble in 3 to 5 volumes or more of 70 p.c. alcohol.

Composition. The crystalline constituent of the oil is a sesquiterpene hydrate $C_{15}H_{26}O$, known as guaiac alcohol or guaiol[3]). This is a tertiary alcohol[4]) which is odorless and crystallizes in large transparent crystals which melt at 91°[5]). Under ordinary pressure it boils at 288°, in a vacuum of 10 mm. at 148°. Its chloroformic solution is lævogyrate. With dehydrating agents a hydrocarbon $C_{15}H_{24}$ is formed with which is admixed an intensely blue substance. When boiled with acetic acid anhydride a liquid acetyl derivative is formed which boils at 155° under 10 mm. pressure.

The odoriferous substance has not yet been examined.

In perfumery guaiac wood oil is used to produce the tea rose odor. In Bulgaria it has occasionally been employed as an adulterant of oil of rose (p. 574).

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[1]) Report of Schimmel & Co. April **1892**, 55; April **1893**, 42; April **1898**, 26; October **1898**, 29 and October **1908**, 73.

[2]) The name "champaca oil" was later applied to this product though it has no similarity with the genuine champaca oil from *Michelia Champaca,* L. (Report of Schimmel & Co. April **1893**, 42.)

[3]) Wallach, Liebig's Annalen **279** (1894), 395.

[4]) A. Gandurin, Berl. Berichte **41** (1908), 4359.

[5]) The name champacol (Chem. Ztg. Repert. **17** [1893], 31) for this alcohol is as little justified as the name champaca oil for the oil.

386. Guaiac Resin Oil.

From the officinal guaiac resin from *Guaiacum officinale,* L., (family *Zygophyllaceæ*) O. Dœbner and H. Lücker[1]) obtained 0,66 p.c. of an volatile oil which gradually became solid.

By distilling the resin with high-tension steam, H. Hænsel[2]) obtained but 0,03 p.c. of a dark brown, aromatic oil which was not completely soluble in 96 p.c. alcohol and which possessed the following properties: d_{15° 0,9417; A. V. 77; E. V. 12,8; when heated with ammoniacal silver solution it yielded a mirror.

According to E. Pætzold[3]) the oil is neither a constituent of the wood nor of the resin, but of the bark with which the resin is mostly contaminated.

Family: RUTACEÆ.

387. Japanese Pepper Oil.

The fruits of *Xanthoxylum piperitum,* DC. (family *Rutaceæ*) known as *Piper japonicum* (Japanese *sansho*) yield 3,16 p.c. of a volatile oil when distilled with water vapor. It is of a yellow color and has a pleasant odor reminding of lemons. d_{15° 0,973; boiling temperature 160 to 230°.

The principal constituent of the oil is citral $C_{10}H_{16}O$[4]).

An oil distilled by J. Stenhouse[5]) and presumably derived from *Xanthoxylum piperitum,* was obtained from *X. alatum* as was demonstrated later[6]). (See p. 628.)

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[1]) Arch. der Pharm. **234** (1896), 608.

[2]) Apotheker Ztg. **23** (1908), 279.

[3]) *Beiträge zur pharmakognostischen und chemischen Kenntnis des Harzes und Holzes von Guajacum officinale,* L. *sowie Palo balsamo.* Inaug. dissert. Strasburg 1901.

[4]) Report of Schimmel & Co. October **1890**, 61.

[5]) Pharmaceutical Journ. I. **17** (1857), 19. — Liebig's Annalen **104** (1857), 236.

[6]) Hanbury, Science Papers p. 229. — E. M. Holmes, Perfum. and Essent. Oil Record **3** (1912), 37.

388. Oil of Xanthoxylum Hamiltonianum.

According to Helbing[1], the seeds of *Xanthoxylum Hamiltonianum,* Wall. (*Fagara Hamiltoniana* [Wall.], Engl.)[2] yielded 3,84 to 5 p.c. of a volatile oil with a specific gravity of 0,840. It is colorless and has a pleasant persistent odor reminding of that of a mixture of geranium and bergamot oils.

389. Oil of Xanthoxylum ochroxylum.

According to M. Leprince[3] the bark of *Xanthoxylum ochroxylum,* DC. (family *Rutaceæ*), known in Venezuela as *Bosuga blanca,* yields, when extracted with petroleum ether, 6 p.c. of an oil with a density of 0,945 at 15°. Its taste is pungent and astringent, the odor is fresh. At ordinary pressure the oil cannot be distilled and it is saponifiable only in small part. Presumably it is a mixture of fatty and volatile oils.

390. Wartara Oil.

In India the fruits of *Xanthoxylum acanthopodium,* DC. and *X. alatum,* Roxb. are known as wartara[4] seeds.

According to the *Pharmacographia Indica* of Dymock, Warden and Hooper (vol. I, p. 257) this drug has long been used as spice and medicament in the Orient. By Sanskrit writers the carpels of the fruit are named *Tumburu,* which means coriander. The Arabs appear first to have obtained the fruits from northern India. Ibn Sina describes it as an open-mouthed *(Fághireh)* berry of the size of a vetch containing a seed resembling that of the hemp. Háji-Zein el Attár, in 1368, gives a similar description of the *Fághireh* and mentions that the Persians call the fruit *Ḳabábeh-i-kushádeh, i. e.* open-mouthed cubeb.

Upon the distillation of the fruits of *X. acanthopodium,* DC., Schimmel & Co.[5], obtained approximately 2 p.c. of a volatile

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[1] Jahresb. f. Pharm. 1887, 157 and 1888, 128.

[2] Originally *Evodia fraxinifolia* was regarded as the parent plant of this oil.

[3] Bull. Sciences pharmacol. 18 (1911), 343.

[4] The designation wartara is possibly a corruption of Fagara. Both genera *Fagara* and *Xanthoxylum* are so closely related that some botanists regard them as one genus.

[5] Report of Schimmel & Co. April 1900, 49 and October 1911, 49.

oil the odor of which reminded distinctly of coriander. d_{15° 0,871 to 0,874; + 5° 30′ to + 6° 31′; S. V. 27,1. With 1 vol. of 80 p. c. alcohol it formed a clear solution. When distilled under a pressure of 14 mm. the following fractions were obtained.

Fraction	Boiling temperature	d_{22°	$\alpha_{D18,5^\circ}$	Amount of distillate in cc.
1	65 to 70°	0,841	+ 0° 26′	45
2	70 „ 80°	0,846	+ 4° 17′	9
3	80 „ 90°	0,856	+ 11° 38′	34
4	90°	0,865	+ 13° 43′	19
5	90 to 100°	0,865	+ 12° 39′	27
6	100 „ 130°	0,939	— 6° 2′	7

Under atmospheric pressure fraction 1 boiled between 175 and 176°. With bromine it afforded a good yield of a tetrabromide that melted at 125°, hence consisted almost entirely of pure dipentene.

From fractions 3 to 5 a liquid with the properties of *d*-linalool was obtained. Its specific gravity was 0,868, its angle of rotation + 14° 20′, its b. p. 78° (14 mm.). The identity of the substance with linalool was proven by its conversion into citral and *l*-terpineol. The citral obtained upon oxidation with chromic acid mixture yielded the characteristic naphthocinchoninic acid melting at 197 to 200°. When treated with formic acid the linalool yielded *l*-terpineol m. p. 35° (m. p. of phenyl urethane 113°).

The highest boiling fractions occasionally congeal to long needles[1]) which, after recrystallization from alcohol, melt at 36° and boil at 256° (745 mm.). This is methyl cinnamate as demonstrated by the analysis of the silver salt of the cinnamic acid isolated therefrom.

391. Oil of Xanthoxylum alatum.

Origin and Production. In the London market the fruits of *Xanthoxylum alatum*, Roxb., are offered under the name of "Chinese wild pepper". The shrub which belongs to the family *Rutaceæ* occurs in northern Bengal, also in China.

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[1]) Report of Schimmel & Co. April 1901, 59.

Upon distillation of these fruits Schimmel & Co.[1]), obtained 3,7 p. c. of oil which has a lemon yellow color and a peculiar odor reminding of water fennel. Upon continued distillation an additional 0,9 p. c. of a crystalline substance were obtained. The attempt to dissolve these crystals, in the proportion recorded above, in the oil had to be abandoned since the bulk thereof crystallized out again at a temperature between 25 and 30°. Hence the properties of oil and solid substance were determined separately.

The oil revealed the following properties: d_{15° 0,8653; α_D — 23° 35′; n_{D20° 1,48131; A. V. 0,9; E. V. 10,3; E. V. after acetylation 33,6; soluble in 2,6 vol. or more of 90 p. c. alcohol. After several recrystallizations from alcohol, the solid substance was obtained in colorless and odorless needles or in laminæ which melted at 83° and which were optically inactive. They are extremely soluble in ether, chloroform and acetone, less so in benzene, alcohol and petroleum ether.

For one distillate Umney[2]) determined d 0,889; α_D — 23°.

Composition. In the oil F. W. Semmler and E. Schossberger[3]) found a terpene (b. p. 50 to 60° at 9 mm.; d_{20° 0,840; α_D — 26°; n_D 1,47457), which they named xanthoxylene, but which may prove identical with *l*-sabinene. It yields a monochlorhydrate (b. p. 83 to 87° under 10 mm. pressure; d_{20° 0,959; α_D — 11°; n_D 1,4824), which, upon reduction with sodium and alcohol, yields a hydrocarbon $C_{10}H_{18}$ with the following properties: b. p. 52 to 58° (9 mm.); d_{20° 0,8275; α_D — 17°; n_D 1,4582. When ozonized xanthoxylene yields a ketone, the semicarbazone of which melts at 123°, whereas sabinene ketone semicarbazone melts at 141°.

According to Semmler and Schossberger, the solid constituent mentioned above is the dimethyl ether of phloracetophenone[4]), $C_{10}H_{12}O_4$, the monobromo derivative, $C_{10}H_{11}BrO_4$, of which melts at 187°, the acetyl derivative at 107° and the methyl derivative at 103°.

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[1]) Report of Schimmel & Co. October **1910**, 147.

[2]) Perfum. and Essent. Oil Record **3** (1912), 37.

[3]) Berl. Berichte **44** (1911), 2885.

[4]) The same substance had previously been found in the oil of *Blumea balsamifera*. Report of Schimmel & Co. April **1909**, 150.

As further constituent of the oil an aldehyde was separated, the semicarbazone of which melted at 210 to 211°. Hence it may be regarded as cuminic aldehyde[1]).

J. Stenhouse[2]) investigated an oil supposed to have been derived from *Xanthoxylum piperitum,* DC. As determined later by Hanbury, it was derived from *X. alatum.* Stenhouse had found a terpene which boiled at 162° and which he named xanthoxylene, and a crystalline substance, $C_{10}H_{12}O_4$, which melted at 80° and which he named xanthoxylin. Both observations agree well with the later ones of Semmler and Schossberger.

392. Oil of Xanthoxylum Aubertia.

Origin and Production. *Xanthoxylum Aubertia,* DC. (*Fagara Aubertia,* DC., *Evodia Aubertia,* Cordem.) is known in Réunion as *Catafaille blanc.* It is highly esteemed for wounds and is also used as diaphoretic and blood purifier.

Two samples of oil have been examined thus far but it is not known from what part of the plant they were distilled. According to Schimmel & Co.[3]), it has the following properties: $d_{15°}$ 0,9052 to 0,9708; α_D — 19° 20′ to — 62° 10′; A. V. 1,1 to 1,3; E. V. 7,3 to 8,7; E. V. after acetylation 33 to 51. In one instance the oil was not completely soluble in 90 p. c. alcohol. Even with 10 vol. only a decidedly turbid solution was obtained. In 95 p. c. alcohol the oil was at first soluble to a clear solution, but upon the addition of more than 2 vol. opalescence was produced due to the separation of paraffin. The second oil formed a clear solution with 90 p. c. alcohol in all proportions. In extreme dilution, however (1:10), slight opalescence was observed. With 10 vol. of 80 p. c. alcohol it did not form a clear solution.

Composition. F. W. Semmler and E. Schossberger[4]) found in the oil an aliphatic terpene related to ocimene or allo-ocimene. It possessed the following properties: $d_{20°}$ 0,8248; α_D + 30°; n_D 1,49775. The higher boiling fractions contained an unknown,

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[1]) See vol. I, p. 422.

[2]) See Japanese pepper oil, p. 626.

[3]) Report of Schimmel & Co. April 1907, 105.

[4]) Berl. Berichte 44 (1911), 2885.

monocyclic sesquiterpene which they named evodene (b. p. 119 to 123° under 9 mm. pressure; $d_{20°}$ 0,8781; α_D — 58°; n_D 1,49900). In addition Semmler and Schossberger proved the presence of 40 to 60 p. c. of methyl eugenol which was characterized by its oxidation product, veratric acid (m. p. 180 to 181°). The highest fractions contained phloracetophenone dimethyl ether, the same substance found in the oil of *Xanthoxylum alatum*[1]).

393. Oil of Xanthoxylum Peckoltianum.

Upon distillation, the leaves of *Xanthoxylum Peckoltianum* (*Fagara Peckoltiana,* Engl.) yield 0,068 to 0,079 p. c. of an oil with a rue-like odor and a sp. gr. of 0,894[2]).

394. Oil of Fagara xanthoxyloides.

1. OIL OF THE FRUITS.

The fruit coatings of *Fagara xanthoxyloides,* Lam. (*Xanthoxylum senegalense,* DC.)[3]), yield upon distillation with water vapor 0,37 to 2,4 p.c. of a volatile oil[4]) which is brownish in color and possesses a faint acid reaction. $d_{15°}$ 0,9229; $[\alpha]_{D15°}$ — 1,20°; A. V. 2,19; E. V. 58,51.

When treated with acid sodium sulphite, methyl-*n*-nonyl ketone (m. p. of oxime 45 to 46°; m. p. of semicarbazone 120 to 121°) was isolated. Presumably it was admixed with decylic aldehyde.

Of acids, the oil was found to contain *n*-caprinic acid (m. p. of amide 98°) which occurs in the free as well as the combined state. The saponification liquid also contained acetic acid and a solid acid that was not investigated.

The following additional constituents were also identified, *viz.,* dipentene (m. p. of tetrabromide 124 to 125°); linalool (m. p. of citryl-β-naphthocinchoninic acid 198 to 199°); a sesquiterpene with the following properties: b. p. 170 to 180° (14 mm.); $d_{14°}$ 0,9214; $[\alpha]_D$ + 4° 16′. A chlorhydrate of this sesquiterpene was not obtained.

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[1]) See this, p. 630.

[2]) Th. Peckolt, Ber. d. deutsch. pharm. Ges. 9 (1899), 340.

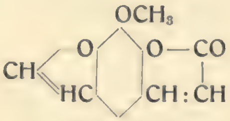
[3]) The root bark, likewise the fruits are used for medicinal purposes by the native Togos.

[4]) H. Priess, Berichte d. deutsch. pharm. Ges. 21 (1911), 227.

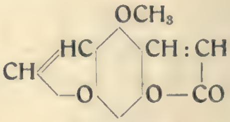
By treating the oil with potassium hydroxide solution, a substance melting at 143 to 144°, the lactone xanthotoxin, was obtained. This substance can be obtained in larger amounts by extracting the carpels with alcohol. The nitro compound of xanthotoxin, $C_{12}H_7O_4NO_2$, melts at 230°, the dibromide, after recrystallization from xylene, at 164°. If to the alcoholic solution of xanthotoxin potassium hydroxide be added, a water-soluble salt is formed, the solution being colored yellow at the same time.

The constitution of this substance has been determined by H. Thoms[1]). By treating the methyl alcoholic solution of xanthotoxin with methyl iodide, he obtained methyl xanthotoxinic acid (m. p. 114 to 117°) and methyl xanthotoxinic methyl ester (m. p. 44°). Fused with potassium hydroxide it yielded a pyrogallol carboxylic acid thus revealing the xanthotoxin to be a pyrogallol derivative.

In addition to xanthotoxin, the alcoholic extract contains a second lactone, bergaptene[2]) which is isomeric with xanthotoxin and which is derived from phloroglucinol.



Xanthotoxin.



Bergaptene.

Both substances are fish poisons, but the narcotic action of the xanthotoxin is much greater than that of the bergaptene.

From a botanical point of view the occurrence of xanthotoxin and bergaptene in *Fagara xanthoxyloides* and of bergaptene in the fruits of *Citrus Bergamia,* the plant from which the bergamot oil is obtained, is very interesting since both plants belong to sub-families of the same family, *viz.,* the former to the *Rutaceæ-Xanthoxyleæ* and the latter to the *Rutaceæ-Aurantioideæ.*

2. OIL OF THE ROOT BARK.

According to H. Thoms[3]), the oil from the root bark contains a solid constituent, which separates upon standing.

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[1]) Berl. Berichte **44** (1911), 3325; **45** (1912), 3705.

[2]) Comp. Pomeranz, Monatsh. f. Chem. **12** (1891), 379.

[3]) Chem. Ztg. **34** (1910), 1279.

This substance, which H. Thoms and F. Thümen[1]) have likewise isolated from the root bark by extraction with benzene, is fagaramide. It melts at 119 to 120° and has been identified as the *iso*butylamide of piperonyl acrylic acid. They obtained it synthetically by the action of piperonyl acrylic acid chloride on *iso*butylamine in ethereal solution.

395. Oil of Fagara octandra.

The oil[2]) obtained from the wood of *Fagara octandra,* L. (family *Rutaceæ*), a Mexican tree, is light yellow in color and possesses a linalool-like odor. d_{15° 0,922; $\alpha_D + 2°30'$; E. V. 6,09; soluble in 0,5 vol. of 90 p.c. alcohol. The addition of more than 1,5 vol. of alcohol causes turbidity.

396. Philippine Fagara Oil.

According to Bacon[3]) the leaves of an unknown species of *Fagara (Rutaceæ)* which grows in the northern provinces of the Philippines, yields upon distillation a small amount of oil. It contains limonene and presumably a limonene derivative. The latter can also be prepared from limonene by the action of dilute alkaline copper sulphate solution. The constitution of this compound has not yet been determined, but with phenyl hydrazine it yields a crystalline compound[4]).

397. Oil of Evodia simplex.

From the Syndicat du Géranium Bourbon, the firm of Schimmel & Co.[5]), received an oil of *Evodia simplex,* Cordem. (family *Rutaceæ*) which is a native of Réunion. From which part of the plant the oil is obtained is not known. d_{15° 0,9737; $\alpha_D - 13°4'$; A. V. 2,1; E. V. 16,4; E. V. after acetylation 63,3. The oil was soluble in 0,9 vol. of 80 p.c. alcohol with the

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[1]) Berl. Berichte **44** (1911), 3717.

[2]) Report of Schimmel & Co. April **1905**, 82.

[3]) Philippine Journ. of Sc. **4** (1909), A, 93 ff.

[4]) Other *Fagara* species also contain volatile oils, *e.g. Fagara Naranjillo,* (Griseb.) Engl. and *F. nitida,* (St. Hill.) Engl. (the leaves of the latter). Dragendorff, *Die Heilpflanzen.* Stuttgart 1898, p. 350.

[5]) Report of Schimmel & Co. October **1906**, 82.

separation of small amounts of paraffin. In 10 vol. of 70 p.c. alcohol it was not completely soluble. After it had been ascertained that nothing distilled over below 190° under ordinary pressure, the oil was fractionated *in vacuo* (3 mm.), when it distilled between 90 and 140°. A second distillation under 2,5 mm. yielded a fraction between 97 and 100° (d_{15° 1,006; $\alpha_D - 4^\circ$) which consisted of eugenol methyl ether. Oxidation with permanganate yielded veratric acid which crystallized in colorless, thin needles that melted at 177,5°.

From the last fraction of the oil paraffin crystallized that melted at 80 to 81°.

398. Oil of Evodia hortensis.

The *usi* leaves of Samoa are obtained from *Evodia hortensis,* Forst. and their aqueous infusion is used by the natives as a remedy against headache. Upon steam distillation they yield 0,09 p.c. of light brown oil with a quinone-like odor[1]). Its constants are: d_{15° 0,9450; $\alpha_D - 10^\circ$; n_{D20° 1,49685; soluble in 2 vol., or more of 90 p.c. alcohol, insoluble in 20 vol. of 80 p.c. alcohol.

399. Oil of Pelea madagascarica.

From Prof. Heckel, of Marseilles, Schimmel & Co.[2]) obtained a small lot of fruits with an anise-like odor. They were reported as coming from Madagascar and as being probably derived from *Pelea madagascarica,* Baill.[3]) (family *Rutaceæ*). From these seeds 4,05 p.c. of a yellowish oil were obtained. Unlike the odor of the fruits, that of the oil reminded of anisic aldehyde rather than of anethol. This observation was verified, for, even when the oil was subjected to the temperature of a freezing mixture and inoculated with a crystal of anethol, but little anethol crystallized out, whereas the oil reacted strongly with acid sodium sulphite. The aldehyde regenerated from the bisulphite addition product appeared to consist in the main of anisic

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[1]) Report of Schimmel & Co. October **1908**, 137.

[2]) *Ibidem* April **1911**, 123.

[3]) Compare E. Heckel, *Sur une plante nouvelle à essence anisée* (Compt. rend. **152** [1911], 565). As the result of a printer's error, the specific gravity is there recorded as 0,953.

aldehyde though the presence of other aldehydes is not excluded. For a positive proof the amount was too small, only a few grams being available. The constants were: d_{15° 0,9553; $\alpha_D + 32^\circ 22'$; n_{D20° 1,51469; soluble in 4 vol. or more of 80 p.c. alcohol.

400. Oil of Rue.

Oleum Rutæ. — Rautenöl. — Essence de Rue.

Origin. The oil of rue of commerce is obtained from several species of the genus *Ruta* (family *Rutaceæ*). According to A. Birckenstock[1]) and to H. Carette[2]), *Ruta graveolens,* L. (Ger. *Gartenraute*) is distilled in France. The yield amounts to about 0,06 p.c. It is not known from which plant the Spanish oil is distilled.

In Algeria two distinct oils of rue are distilled. The one is designated summer oil of rue and is obtained from *Ruta montana,* L.[3]). The other known as winter oil of rue is obtained from *Ruta bracteosa,* L. According to Carette, the *Rue de Corse* is not the *R. corsica* as might be supposed, but *R. bracteosa.*

For commercial purposes the French, Spanish and Algerian oils come into consideration. In Germany oil of rue has been distilled only occasionally. From the dry herb of the *Gartenraute* (*Ruta graveolens,* L.; *R. hortensis,* Mill.) H. Hænsel[4]) obtained 0,135 p.c. of an oil that was not identical with the ordinary oil of rue. Schimmel & Co. distilled dry herb from Smyrna with a yield of 0,7 p.c. The oil obtained congealed between —7 and —8°, hence was rich in methyl heptyl ketone.

Composition. The two characteristic constituents of oil of rue are two ketones, *viz.,* methyl-*n*-nonyl ketone and methyl-

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[1]) Moniteur scientifique Quesneville **1906**, 352. — Birckenstock's opinion that Algerian oil of rue is likewise obtained from *Ruta graveolens* and that the differences in the two oils are due to the different stages of vegetation in which they are distilled, is erroneous. While it is true that the oils are distilled at different periods, the differences in the oils are due to different botanic origin of the respective plants.

[2]) Journ. de Pharm. et Chim. VI. **24** (1906), 58.

[3]) Comp. F. Jadin, Berichte von Roure-Bertrand Fils April **1911**, 11. This article contains complete botanic descriptions, with illustrations, of the several species of *Ruta* subjected to distillation.

[4]) Pharm. Ztg. **51** (1906), 323, 1026.

n-heptyl ketone (See vol. I, p. 434). Of the two the former was first known, its chemical constitution having been ascertained by A. Giesecke[1]) also by E. von Gorup-Besanez and F. Grimm[2]) toward the beginning of the seventies of the past century. Methyl heptyl ketone was discovered by H. Thoms[3]) in a commercial oil probably of French or Spanish origin. The relative amounts of the two vary greatly in individual oils. Whereas the oil examined by Thoms contained about 85 p.c. of the nonyl compound and 5 p.c. of the heptyl compound, H. von Soden and K. Henle[4]) also found about 90 p.c. of ketones in an Algerian oil of which $^2/_3$ were methyl heptyl ketone and $^1/_3$ methyl nonyl ketone. From German (?) oil of rue, J. Houben[5]) isolated 2,4 p.c. of heptyl and 71 p.c. of the nonyl ketone. According to F. B. Power and H. Lees[6]) an oil of unknown origin (presumably Algerian) contained both ketones in approximately the same proportions.

Of those constituents which boil below 190° such small amounts are present in oil of rue that they are overlooked unless very large quantities of oil are subjected to investigation. The following substances were identified by Power and Lees: *l*-α-pinene (m. p. of nitrolpiperide 119 to 120°), cineol (m. p. of iodol compound 114 to 115°) and *l*-limonene (m. p. of tetrabromide 103°). All three together did not constitute one percent of the total oil. The same investigators also found the secondary alcohols corresponding to the two ketones, *viz.,* methyl-*n*-heptyl carbinol and methyl-*n*-nonyl carbinol (See vol. I, p. 351). Their presence in the oil had been suspected by v. Soden and Henle. C. Mannich[7]) as well as Houben[5]) had shown that they can be prepared by reduction of the ketones. Both alcohols are present in the oil to the extent of 10 p.c., partly free, partly as acetic esters[4])[6]). In addition to these Power and Lees demonstrated the presence of a valeric acid ester, probably that of ethyl alcohol. Of the acid constituents of the oil, free fatty acids

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[1]) Zeitschr. f. Chemie **13** (1870), 428.

[2]) Liebigs Annalen **157** (1871), 275.

[3]) Berichte d. deutsch. pharm. Ges. **11** (1901), 3.

[4]) Pharm. Ztg. **46** (1901), 277.

[5]) Berl. Berichte **35** (1902), 3587.

[6]) Journ. chem. Soc. **81** (1902), 1585.

[7]) Berl. Berichte **35** (1902), 2144.

should be mentioned. Among these there is one that boils at 236 to 238° that is probably identical with caprylic acid[1]). Salicylic acid, m. p. 156°, was likewise isolated from the saponification liquid. Presumably it occurs in the original oil as methyl ester[2]).

The blue fluorescence of the oil, which is occasionally observed, is traced to the presence of methyl anthranilic acid methyl ester[3]). However, the acid that was isolated had a melting point of 173° instead of 178 to 179°. In addition, Power and Lees isolated from a non-fluorescing oil a base with a quinoline-like odor, that was likewise devoid of fluorescence.

The highest boiling fraction (about 0,5 p.c.) boils between 250 and 320° and is blue[4]).

Properties. Oil of rue is a colorless to yellow liquid which in most instances fluoresces. Its a rue-like odor, pleasant only in great dilution, is intense and persistent. Its properties differ according to its botanical origin, also according to the vegetative condition of the plant at the time of distillation. All oils, however, have in common a low specific gravity, which is lower than that of most volatile oils. The congealing point differs for the several oils. Whereas French and Spanish oils, also some of the Algerian oils, congeal between +6 and +10,5°, other Algerian oils do not solidify at even —15°, for the reasons mentioned above.

FRENCH OIL.

d_{15° 0,8328 to 0,8437; α_D —0°40′ to +2°10′ (the optical rotation is mostly dextrogyrate and independent of the congealing point); n_{D20° 1,430 to 1,434; congealing point +5,8 to 10,8°, mostly above 7°; soluble in 1,5 to 3 vol of 70 p.c. alcohol (in isolated cases the diluted solution reveals opalescence or even turbidity because of the separation of paraffin).

An oil distilled in Guerrevieille (southern France) possessed somewhat different properties: d_{15° 0,8378; $\alpha_D \pm 0°$; n_{D20° 1,43168; soluble in 2,5 vol. or more of 70 p.c. alcohol with a decided

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[1]) Berl. Berichte 35 (1902), 3587.

[2]) Journ. chem. Soc. 81 (1902), 1585.

[3]) Report of Schimmel & Co. October 1901, 47.

[4]) Journ. chem. Soc. 81 (1902), 1585.

separation of paraffin; it did not congeal above —5°, but paraffin crystals were separated at +10°.

ALGERIAN OILS.

1. The oil distilled during the summer from *Ruta montana* with methyl nonyl ketone as principal constituent.

$d_{15°}$ 0,8370 to 0,8381; $\alpha_D \pm 0°$ to $+0°56'$; $n_{D20°}$ 1,43058 to 1,43218; congealing point +7,3 to 10,4°; soluble in 2 to 3 vol. or more of 70 p.c. alcohol, occasionally with opalescence due to the separation of paraffin.

2. The oil distilled during the winter from *Ruta bracteosa* with methyl heptyl ketone as principal constituent.

$d_{15°}$ 0,8373 to 0,8446; α_D —1°14′ to —5°; $n_{D20°}$ about 1,430; the congealing point is very low; some oils not solidifying at —15°; soluble in 2 to 3 vol. of 70 p.c. alcohol, occasionally with turbidity because of its paraffin content.

SPANISH OILS.

$d_{15°}$ 0,834 to 0,847; α_D —1° to +0°30′; congealing point below 0° to +7,5°; soluble in 2 to 4 vol. of 70 p.c. alcohol.

A Syrian oil had the following constants: $d_{15°}$ 0,8408; α_D —0°28′; $n_{D20°}$ 1,43296; congealing point —1,9°; soluble in 2 vol. or more of 70 p.c. alcohol with fluorescence.

Examination. Characteristic for pure oil of rue are its low specific gravity and its solubility in 70 p.c. alcohol.

Petroleum and turpentine oil are recognized by their insolubility in 70 p.c. alcohol. Turpentine oil can be identified by collecting the distillate below 200° and testing it for pinene. The pure oil does not yield more than 5 p.c. below 200°.

The amount of pinene present in pure oil is so small (see under Composition) that the natural pinene can be identified only when large quantities of oil are operated upon. Because of the possibility of preparing a mixture of proper specific gravity and solubility from alcohol and an oil soluble in 70 p.c. alcohol, it is advisable always to examine commercial oils for alcohol.

Most adulterants can be separated by treating the oil with acid sulphite solution and further study of the non-combined portion.

401. Boronia Oil.

Boronia polygalifolia, Sm. (family *Rutaceæ*) is distributed throughout eastern and southern Australia. An oil[1] distilled in Victoria had a sweetish odor reminding of esdragon and somewhat of rue. d 0,839 (!); $\alpha_D + 10°$.

Fractional distillation yielded the following results: from 150 to 170° 31 p.c.; from 170 to 180° 38 p.c.; from 180 to 190° 15 p.c. above 190° 16 p.c.

402. Oil of Buchu Leaves.

Oleum Buccu foliorum. — Buccublätteröl. — Essence de Feuilles de Bucco.

Origin. The genus *Barosma* (family *Rutaceæ*) is represented in southern Africa by about 15 species[2]. The leaves known as *bucco, buccu, buku* or *buchu,* are used by the natives against insects and for medicinal purposes[3].

In commerce a distinction is made between round and long buchu leaves. The former are the leaves of *Barosma betulina,* (Bartl.) and *B. crenulata,* (L.) Hook., the latter those of *B. serratifolia,* Willd. The latter are occasionally adulterated with the leaves of *Empleurum serrulatum,* Ait.[4] (see p. 644). The leaves of the other *Barosma* species are designated false buchu leaves. Moreover, foreign admixtures are not uncommon. Thus Holmes[5] observed the admixture of the leaves of a species of *Psoralea (Leguminosæ),* presumably *P. obliqua,* E. Mey. In a variety of samples of buchu leaves W. Mansfield[6] found up to 17 p. c. of the leaves of *Diosma fragrans* which are known as "clip-buchu".

Upon distillation the leaves of *B. betulina* yield 1,3 to 2,5 p. c. of oil, those of *B. crenulata* 1,7 and those of *B. serratifolia* 0,8 to 1 p.c.

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[1] Umney, Imperial Institute Journal 2 (1896), 302. — Pharmaceutical Journ. 57 (1896), 199.

[2] Engler, *Die natürlichen Pflanzenfamilien,* Vol. III, Section IV, p. 149.

[3] Chemist and Druggist 76 (1910), 358; 77 (1910), 17 and 622.

[4] Flückiger and Hanbury, Pharmacographia. Second Edit. 1879, p. 110.

[5] Pharmaceutical Journ. 85 (1910), 69, 464. See also *ibidem* 73 (1904), 893.

[6] Chemist and Druggist 81 (1912), 546.

Properties. Buchu leaf oil is dark in color and has a strong, sweetish, mint-like unpleasant odor and a bitter, cooling taste.

The oil of *B. betulina* separates crystals of diosphenol even at ordinary temperature. The liquid portion separated from these crystals has the following properties: d_{15° 0,937 to 0,97; α_D — 14 to — 48°[1]); n_{D20° 1,474 to 1,478; soluble in 3 to 5 vol. of 70 p.c. alcohol, but sometimes requiring 8 to 10 vol.; diosphenol content, determined by repeated shaking with 5 p.c. sodium hydroxide solution, 17 to 30 p.c.

An oil distilled from *B. crenulata*[2]) had the following properties: d_{15° 0,9364; α_D — 15°22′; n_{D20° 1,48005; soluble in 2,5 vol. or more of 70 p.c. alcohol with the separation of paraffin. The original oil was colored green by copper. When this was removed the oil was brownish yellow. The odor was mint-like. The diosphenol content was minimal. When exposed to the temperature of a freezing mixture paraffin crystallized out.

But few observations are available concerning the oil of *B. serratifolia*. d_{15° 0,918 to 0,961; α_D — 12 to — 36°. The diosphenol content is so small that no crystals separate upon cooling.

For the purpose of removing the buchu camphor or diosphenol a single shaking with 5 p.c. sodium hydroxide solution does not suffice. In an experiment 15 p.c. were removed by the first shaking and 5 p.c. by the second. Upon the addition of acid to the alkaline phenol solution hydrogen sulphide is given off.

Composition. The separation of a crystalline substance from buchu leaf oil from *B. betulina* was first observed by Flückiger[3]). This diosphenol or buchu camphor was first examined by him, later by P. Spica[4]), Y. Shimoyama[5]), N. Bialobrzeski[6]), J. Kondakow[7]) and N. Bachtschiew[8]). However, its constitution as

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[1]) Kondakow and Bachtschiew, Journ. f. prakt. Chem. II. **63** (1901), 50.

[2]) Report of Schimmel & Co. October **1911**, 23.

[3]) Pharmaceutical Journ. III. **11** (1880), 174 and 219.

[4]) Gazz. chim. ital. **15** (1885), 195; Jahresber. d. Chem. **1885**, 1821.

[5]) Arch. der Pharm. **226** (1888), 403.

[6]) Pharm. Zeitschr. f. Russl. **35** (1896), 417, 433, 449.

[7]) Journ. f. prakt. Chem. II. **54** (1896), 433; Chem. Ztg. **30** (1906), 1090, 1100; **31** (1907), 90.

[8]) Journ. f. prakt. Chem. II. **63** (1901), 49.

cyclic reduced ketophenol was first interpreted by Semmler and Mc. Kenzie[1]) and proved by synthesis. The melting point of the diosphenol, after repeated recrystallization, was found to be 83 to 84°, the boiling point 109 to 110° (10 mm.). It is optically inactive, gradually soluble in caustic alkalis, reduces other substances while it itself is being oxidized. Alcoholic magenta solution, decolorized by sulphurous acid, is colored a rose red. Constitutional formula, synthesis, derivatives and degradation products of diosphenol are described in vol. I, p. 493.

Diosphenol occurs in the oil partly as such, partly as the ester of an acid melting at 94°.

Of terpenes buchu leaf oil contains *d*-limonene[2]) (m. p. of tetrabromide 104°) and a little dipentene (m. p. of tetrabromide 119°).

The constituent boiling above 200° was already observed by Flückiger and was shown by Bialobrzeski to be a ketone. According to Kondakow[2]) it is identical with *l*-menthone. The fraction in question had the following properties: b. p. 86° (10 mm.); α_D — 51°. The menthone yields a liquid oxime, a hydrazone that melts at 80° and two semicarbazones melting at 180 and 123° respectively. From the former, when hydrolyzed with sulphuric acid, a strongly inverted ketone results: b. p. 85,5 to 86° (10 mm.); $d_{19,5^\circ}$ 0,897; $[\alpha]_D$ — 22,3°; n_D 1,45169; mol.-refr. 46,28. According to Kondakow the oil of *B. serratifolia* contains more ketone than does the oil of *B. betulina*.

403. Oil of Barosma pulchella.

Origin. According to E. M. Holmes[3]), the leaves of *Barosma pulchella,* (L.) Bartl. et Wendl., which are occasionally admixed with those of *B. betulina* and with which they are occasionally confounded, differ from the latter by their citronella-like odor and are smaller. They are about 7 to 12 mm. long and 4 mm. wide. The petiole is short, the leaf ovate lanceolate, serrulate, with a blunt tip and broadest at the base. Like the other species of *Barosma* this shrub is a native of Cape Colony.

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[1]) Berl. Berichte **39** (1906), 1158; Chem. Ztg. **30** (1906), 1208.

[2]) Kondakow, Journ. f. prakt. Chem. II. **72** (1905), 186.

[3]) Pharmaceutical Journ. **79** (1907), 598; comp. also Chemist and Druggist **71** (1907), 702.

Properties. The oil has been distilled and examined by Schimmel & Co.[1]). The leaves used contained a small amount of those of *B. pulchella* var. *major* and of *B. latifolia,* (L. f.) Röm. et Schult. Upon distillation they yielded 3 p. c. of a golden-yellow oil with a decided odor of citronella but accompanied by an unpleasant narcotic odor which prevents the use of the oil. d_{15° 0,8830; $\alpha_D + 8^\circ 36'$; n_{D20° 1,45771; A. V. 18,5; E. V. 27,2; E. V. after acetylation 237,0 = 79,3 p. c. of $C_{10}H_{18}O$.

Composition[1]). The unpleasant odor referred to is due to a base which can be extracted from the oil with a 25 p. c. solution of tartaric acid. The base isolated from the tartrate solution by means of soda possessed an unusually strong, narcotic odor. Its boiling point was not constant, varying from 130 to 140° (5 mm.). The solution of its hydrochloride did not yield a crystalline double salt with platinic chloride.

The principal constituent of the oil is *d*-citronellal, which, after regeneration from the bisulphite addition product, has the following properties: b. p. 205 to 208° (atmospheric pressure) 73 to 75° (7 to 8 mm.); d_{15° 0,8560; $\alpha_D + 13^\circ 6'$; n_{D20° 1,44710. The semicarbazone melted at 81 to 82°. From 500 g. of oil about 220 g. of aldehyde were isolated. The lowest fractions contained methyl heptenone (m. p. of semicarbazone 134 to 135°). Another ketone also appears to be present.

In fraction 75 to 82° (5 mm.) which showed an optical rotation of $+ 6^\circ 54'$, the presence of a small amount of *d*-menthone was demonstrated (m. p. of semicarbazone 178 to 181°). *d*-Citronellol is also contained in the oil (b. p. 93 to 95° under 5 to 6 mm. pressure; d_{15° 0,8723; $\alpha_D + 2^\circ 14'$; n_{D20° 1,46288; m. p. of silver salt of acid phthalate 125°).

When acted upon with alkali, the original oil yielded an acid which, in all probability, is identical with citronellic acid, $C_{10}H_{18}O_2$: b. p. 257 to 263° (ordinary pressure); 125 to 131° (5 to 6 mm.); d_{15° 0,9394; $\alpha_D + 5^\circ 2'$; n_{D20° 1,45611. Inasmuch as the amide melted undefinitely at 87 to 88° the amide of citronellic acid was prepared according to the directions of Tiemann[2]) by means of the incomplete saponification of the nitrile of citronellic

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[1]) Report of Schimmel & Co. April **1909**, 94; April **1910**, 20.

[2]) Berl. Berichte **31** (1898), 2902.

acid with alcoholic potassa. The citronellic acid amide[1]) from citronellal, recrystallized from petroleum ether or dilute alcohol, melted at 84 to 85°; the acid amide from the acid of the above-mentioned oil melted at 87 to 88°; a mixture of both derivatives melted at 80 to 82°. So far as appearance is concerned the two cannot be distinguished. It may be that the amide with the undefinite melting point of 87 to 88° is a mixture of the amide of citronellic acid with traces of the amide of another acid (possibly caprinic acid). It was further ascertained that the citronellic acid from citronellal also boils at 257° and its chloride, like that of the acid from the above oil, boiled at 122 to 123° (5 to 6 mm.). Hence they may be regarded as identical.

404. Oil of Barosma venusta.

From the dry leaves of *Barosma venusta*[2]), Eckl. et Zeyh., H. R. Jensen[3]) distilled 1,1 p.c. of a volatile oil with the following properties: $d_{15.5°}^{15.5°}$ 0,8839; $\alpha_{D20°} + 0° 30'$; $n_{D20°}$ 1,4967; A. V. 2,4; S. V. 13,4; S. V. after acetylation 52,8; phenol content 16 p.c.; 4 p.c. of the oil combine with neutral sulphite. Jensen found 35 p.c. of a terpene with the following properties: b. p. about 66,5° (15 to 18 mm.); $d_{15°}$ 0,790; $n_{D20°}$ 1,4778. It did not boil without decomposition at ordinary temperature and when hydrated yielded an alcohol, the acetic ester of which had the odor of linalyl acetate. In contact with the air it resinified very rapidly. All of the properties accord with those of myrcene. Jensen assumes that the following constituents are likewise contained in the oil: methyl chavicol (conversion into anethol), the acetate of myrcenol or an isomer thereof, chavicol (n 1,538; green color with ferric chloride) and possibly an olefinic sesquiterpene. Diosphenol was not present.

405. Oil of Diosma succulenta.

A new kind of false buchu leaves has been described by C. Edward Sage[4]). They are known as "karroo buchu" and

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[1]) Tiemann records 81,5 to 82,5° as melting point.

[2]) Comp. Chemist and Druggist **78** (1911), 854.

[3]) Pharmaceutical Journ. **90** (1913), 60.

[4]) Chemist and Druggist **65** (1904), 506, 737.

are derived from *Diosma succulenta* var. *Bergiana.* The leaves are 3 to 6 mm. long and 1,75 mm. wide, the margin is entire, the blade ovate with a pointed, slightly recurrent apex. The tissue is leathery and studded with oil glands.

The oil obtained from a small sample was insufficient for an investigation, but it appeared to be the equal of that from the leaves of *Barosma betulina,* Bartl. The oil obtained by steam distillation is semisolid (even in August) and has a strong, peppermint-like odor. Ferric chloride produces a faint red color.

406. Oil of Empleurum serrulatum.

The leaves of *Empleurum serrulatum,* Ait., which species grows in Cape Colony, are occasionally found admixed with buchu leaves. They yield 0,64 p.c. of a volatile oil¹), the odor of which reminds of rue and which is very different from that of buchu leaves; d 0,9464. It boils between 200 and 235°, mostly between 220 and 230°. With acid sodium sulphite this fraction yields a crystalline derivative, thus indicating the presence of methyl nonyl ketone, the principal constituent of oil of rue.

407. Jaborandi Leaf Oil.

Oleum foliorum Jaborandi. — Jaborandiblätteröl. — Essence de Feuilles de Jaborandi.

Upon distillation the genuine jaborandi leaves²), from *Pilocarpus Jaborandi,* Holmes³) (family *Rutaceæ*) yield 0,2 to 1,1 p.c. of volatile oil⁴) which has a decided odor reminding somewhat of rue and a mild, fruity taste. d_{15° 0,865 to 0,895; $\alpha_D + 0^\circ 50'$ to $+ 3^\circ 25'$. It is soluble in 1½ to 2 parts of 80 p.c. alcohol, forming a clear solution, boils between 180 and 290° and congeals upon cooling.

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¹) Umney, Pharmaceutical Journ. III. **25** (1895), 796.

²) The leaves of *Pilocarpus racemosus,* Vahl, which is a native of the Antilles, are said to possess the same medicinal properties as the genuine jaborandi leaves. They yield a greenish oil with a strong and aromatic odor that becomes liquid at 25° (G. Rocher, Journ. de Pharm. et Chim. VI. **10** [1899], 236. Comp. also E. M. Holmes, Guadeloupe Jaborandi. Pharmaceutical Journ. **71** [1903], 713).

³) Pharmaceutical Journ. **55** (1895), 522, 539; **73** (1904), 891, 970; **84** (1910), 52.

⁴) Schimmel's Bericht April **1888**, 44.

Fractionation yields a hydrocarbon named pilocarpene[1]) which boils at 178° ($d_{18°}$ 0,852; $[\alpha]_D + 1,21°$) and which forms a solid dihydrochloride. This would indicate that pilocarpene is either dipentene or terpinene rendered slightly active by some impurity.

Fractions 260° plus congeal in the cold and contain a solid that melts at 27 to 28°. Apparently it is a hydrocarbon, probably of the olefinic series, since in petroleum ether solution it decolorizes considerable bromine[2]).

Jaborandi bark contains but very little volatile oil.

408. Angostura Bark Oil.

Origin and Production. Genuine angostura bark comes from Venezuela and the upper Orinoco and is derived from *Cusparia trifoliata,* Engl. (*Galipea Cusparia,* St. Hil., *G. officinalis,* Hancock[3]), family *Rutaceæ*). Upon distillation with water vapor it yields 1,0[4]), 1,5[5]) to 1,9[6]) p.c. of volatile oil with an aromatic odor and taste. The light yellow color of the fresh oil becomes dark upon standing. $d_{15°}$ 0,928 to 0,96; α_D —7° 30′ to —50°; $n_{D20°}$ 1,50744; A. V. 1,8; E. V. 5,5; E. V. after acetylation 35,7; with 9 vol. of 90 p.c. alcohol it forms a turbid solution[4]).

Composition. According to the extensive investigations of H. Beckurts and J. Trœger[7]), the aromatic principle of angostura bark oil is a sesquiterpene alcohol galipol, $C_{15}H_{26}O$. It boils between 260 and 270°, has a specific gravity of 0,9270 at 20°, is optically inactive and is present to the extent of about 14 p.c. It is very unstable, giving off water at higher temperatures.

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[1]) Hardy, Bull. Soc. chim. II. **24** (1876), 497; Chem. Zentralbl. **1876**, 70.

[2]) Report of Schimmel & Co. April **1899**, 27.

[3]) Comp. C. Hartwich and M. Gamper, *Beiträge zur Kenntnis der Angosturarinden.* Arch. der Pharm. **238** (1900), 568.

[4]) Report of Schimmel & Co. April **1913**, 26.

[5]) Schimmel's Bericht April **1890**, 47.

[6]) Oberlin and Schlagdenhauffen, Journ. de Pharm. et Chim. IV. **26** (1877), 130; Jahresb. d. Pharm. **1877**, 178.

[7]) Arch. der Pharm. **235** (1897), 518 and 634; **236** (1898), 392. — Comp. also Beckurts and Nehring, *ibidem* **229** (1891), 612 likewise Herzog, *ibidem* **143** (1858), 146.

Another important constituent is cadinene, $C_{15}H_{24}$, to which is due the lævorotation of the oil. It was characterized by its hydrohalogen addition products.

In addition to the lævogyrate cadinene and the inactive alcohol, the oil contains an inactive sesquiterpene, named galipene, which boils at 255 to 260° and has a specific gravity of 0,912 at 19°. With hydrohalogens it forms liquid addition products that are readily decomposed.

Angostura bark oil also contains a small amount of a terpene that appears to be identical with pinene.

409. Oil of Casimiroa edulis.

From the alcoholic extract of the seeds of *Casimiroa edulis,* La Llave *(Rutaceæ)* F. B. Power and T. Callan¹) obtained 0,021 p.c. (computed with reference to the dry seeds) of a volatile oil with the following properties: d_{20° 0,9574; optical rotation in a 25 mm. tube — 2° 25′; boiling temperature mostly below 130° (25 mm.).

410. Toddalia Oil.

Toddalia aculeata, Pers. *(T. asiatica,* L. [Kurz], family *Rutaceæ)* is a shrub that grows wild in the Nilgiri country (India), where it is known as "wild orange tree". All parts of the plant have a pungent, aromatic taste. The root, which was known as early as the 17th century as *Radix Indica Lopeziania*²), is known as *Malakarunnay* by the natives and is used by them as a remedy in stomach troubles. The root bark contains a volatile oil the odor of which is described by Schnitzer³) as cinnamon- and balm-like.

The ripe berries are used as spice in India, in place of black pepper. Bark and leaves are also reported to possess medicinal value.

The oil from the leaves has been distilled by D. Hooper⁴). It is limpid and has a pleasant odor reminding of both verbena

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¹) Journ. chem. Soc. 99 (1911), 1996.

²) Flückiger and Hanbury, Pharmacographia, p. 111.

³) Wittstein's Vierteljahrsschrift f. prakt. Pharmacie 11 (1862), 1.

⁴) Report of Schimmel & Co. April 1893, 73.

and basil. It contains considerable amounts of citronellal and an alcoholic constituent which boils above 200°.

Upon the distillation of the leaves, Brooks[1]) obtained an oil with the following constants: $d_{30°}^{30°}$ 0,9059; $n_{D30°}$ 1,4620. When cooled, 18 p.c. of a substance separated which had an odor reminding of camphor, was very decomposable and when recrystallized from petroleum ether melted at 96,5 to 97°. Fractions 195 to 200° contained linalool which was characterized by its oxidation to citral.

411. Oil of Acronychia laurifolia.

198 kg. of leaves of *Acronychia laurifolia,* Bl., a rutaceous plant known as *Kisarira,* when distilled at Buitenzorg[2]), yielded 133 cc. of oil of the following properties: $d_{26°}$ 0,915; $\alpha_D + 1° 52'$; S. V. 11; E. V. after acetylation 50,9. The oil contained no aldehydes.

412. Oil of Hortia arborea.

From the fresh bark of *Hortia arborea,* Engl., Th. Peckolt[3]) obtained 0,054 p.c. of volatile oil. $d_{18°}$ 1,069.

413. Oil of Clausena Anisum-olens.

According to Bacon[4]), the leaves of *Clausena Anisum-olens,* (Blanco) Merrill, which have an odor of anise, are used in the preparation of liqueurs as is also their alcoholic extract. From the leaves of this rutaceous plant Brooks[5]) obtained 1,16 p.c. of a colorless volatile oil with the following properties: $d_{30°}^{30°}$ 0,963; $\alpha \pm 0°$; $n_{D30°}$ 1,5235; S. V. 3,6. From 90 to 95 p.c. of the oil consist of methylchavicol which was characterized by its oxidation to homoanisic acid (m. p. 84 to 86°).

As Brooks states certain Philippine cigarettes are perfumed with the leaves of *Clausena Anisum-olens.*

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[1]) Philippine Journ. of Sc. **6** (1911), A, 344.

[2]) Jaarb. dep. landb. in Ned.-Indië, Batavia **1910**, 49; Report of Schimmel & Co. April **1912**, 23.

[3]) Berichte d. deutsch. pharm. Ges. **9** (1899), 352.

[4]) Philippine Journ. of Sc. **4** (1909), A, 130.

[5]) *Ibidem* **6** (1911), A, 344.

414. Oil of Clausena Willdenowii.

A sample of oil[1]) from *Clausena Willdenowii,* obtained from French India, was a reddish, difficultly mobile liquid of a peculiar odor. It contained 11 p.c. of ester (computed as $C_{10}H_{17}OCOCH_3$) and 6,2 p.c. alcohol ($C_{10}H_{18}O$).

415. Oil of Murraya Kœnigii.

The fruits of *Murray Kœnigii,* Spr., which grows in India, yield upon distillation, 0,76 p.c. of an oil[2]) with a neroli-like odor and a pepper-like taste, but leaves an agreeable sensation of coolness on the tongue. $d_{13°}$ 0,872; $\alpha_D - 27° 24'$; n_D 1,487; boiling point about 173 to 174°.

416. Oil of Aegle Marmelos.

According to a communication by Ritsema[3]), the leaves of the *modjo* tree, *Aegle Marmelos,* Corr. (family *Rutaceæ*) are used by the natives of the island of Madura as a remedy against the hoof-and-mouth-disease. The leaves yielded upon distillation about 0,6 p.c. of an oil with a light yellow color, $d_{25°}$ 0,856; $\alpha_{D26°} + 10,71°$; S. V. 10,6. Distillation resulted in the following fractions: I. up to 100°, 5 g.; II. from 100 to 130°, 5,1 g.; III. 130 to 160°, 1 g.; IV. residue 1,5 g.

Fraction II contained *d*-limonene which was characterized by its b. p. (175°) and its tetrabromide (m. p. 104 to 105°). Aldehydes could not be detected. Noteworthy is the fact that when the oil is exposed to the air it looses about 8 p.c. within a quarter of an hour. At the same time it becomes decidedly turbid. Upon prolonged standing the oil becomes clear again, at the same time viscid and resinous. A similar viscid product was also obtained upon the distillation of the dried leaves.

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[1]) Berichte von Roure-Bertrand Fils April **1903**, 35.

[2]) *Ibidem* April **1900**, 74.

[3]) Jaarb. dep. landb. in Ned.-Indië, Batavia **1908**, 52; Report of Schimmel & Co. April **1910**, 15.

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