

A DICTIONARY  
OF  
APPLIED CHEMISTRY

~~BY~~  
SIR EDWARD THORPE, C.B., LL.D., F.R.S.

EMERITUS PROFESSOR OF GENERAL CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES  
OF THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON, LONDON;  
LATE PRINCIPAL OF THE GOVERNMENT LABORATORY, AND A PAST PRESIDENT OF  
THE CHEMICAL SOCIETY AND OF THE SOCIETY OF CHEMICAL INDUSTRY

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# ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Pharm.</i>	American Journal of Pharmacy.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Anal. Fis. Quim.</i>	Anales de la Sociedad Española Física y Quimica.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Annalen der Chemie (Justus Liebig).
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim.</i>	Annales de Chimie.
<i>Ann. Falsif.</i>	Annales des Falsifications.
<i>Ann. Inst. Pasteur.</i>	Annales de l'Institut Pasteur.
<i>Ann. Physik.</i>	Annalen der Physik.
<i>Ann. Physique</i>	Annales de Physique.
<i>Annali Chim. Appl.</i>	Annali di Chimica Applicata.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Bentl. a. Trim.</i>	Bentley and Trimen. Medicinal Plants.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Bied. Zentr.</i>	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Bio-Chem. J.</i>	The Bio-Chemical Journal.
<i>Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Brewers J.</i>	Brewer's Journal.
<i>Bull. Imp. Inst.</i>	Bulletin of the Imperial Institute.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Chem. Ind.</i>	Chemische Industrie.
<i>Chem. News</i>	Chemical News.
<i>Chem. Soc. Proc.</i>	Journal of the Chemical Society of London. Proceedings.
<i>Chem. Soc. Trans.</i>	Journal of the Chemical Society of London. Transactions.
<i>Chem. Weekblad</i>	Chemisch Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Dingl. poly. J.</i>	Dingler's polytechnisches Journal.
<i>Färber-Zeit.</i>	Färber-Zeitung.
<i>Flück. a. Hanb.</i>	Flückiger and Hanbury. Pharmacographia.
<i>Frdl.</i>	Friedländer's Fortschritte der Teerfarbenfabrikation.
<i>Gazz. chim. ital.</i>	Gazzetta chimica italiana.
<i>Helv. Chim. Acta</i>	Helvetica Chimica Acta.
<i>Jahrb. Min.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Bd. Agric.</i>	Journal of the Board of Agriculture.
<i>J. Franklin Inst.</i>	Journal of the Franklin Institute.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Brewing</i>	Journal of the Institute of Brewing.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Phys. Chem.</i>	Journal of Physical Chemistry.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>J. Soc. Dyers.</i>	Journal of the Society of Dyers and Colourists.
<i>J. Tokyo Chem. Soc.</i>	Journal of the Tokyo Chemical Society.
<i>J. Washington Acad. Sci.</i>	Journal of the Washington Academy of Sciences.
<i>Kolloid Zeitsch.</i>	Kolloid-Zeitschrift.
<i>Met. &amp; Chem. Eng.</i>	Metallurgical and Chemical Engineering.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshäfte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Zeit.</i>	Pharmaceutische Zeitung.

<i>Phil. Mag.</i> . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i> . . .	Philosophical Transactions of the Royal Society.
<i>Phot. J.</i> . . .	Photographic Journal.
<i>Proc. Roy. Soc.</i> . .	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh.
<i>Rec. trav. chim.</i> . . .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Nahr.</i>	
<i>Genussm.</i> . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. öffentl.</i>	
<i>Chem.</i> . . .	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. physikal.</i>	
<i>Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
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- Dr. M. A. WHITELEY, O.B.E., F.I.C., A.R.C.S., *Assistant Professor of Organic Chemistry, Imperial College of Science and Technology, South Kensington.* [CARNINE; CARNITINE; CARNOSINE; CREATINE; CREATININE; CYSTINE; DIALURIC ACID; DILITURIC ACID.]
- Dr. SYDNEY YOUNG, Sc.D., F.R.S., F.I.C., *Professor of Chemistry, Trinity College, Dublin.* [DISTILLATION.]

A

# DICTIONARY

OF

## APPLIED CHEMISTRY.

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**CALAFATITE** *v.* ALUNITE.

**CALCULI** *v.* URINE.

**CALCUSOL.** Trade name for a preparation of acid potassium carbonate and piperidine-*p*-sulphamine benzoate.

**CALLIATURWOOD.** This wood, the botanical origin of which appears to be unknown, is very similar to though somewhat darker in colour than sanderswood. It was imported from the East Indies and is stated to have been chiefly employed on the Continent. According to Franchimont and Sicherer it contains santalin but in larger amount than sanderswood.

**CALICHE.** The term by which the impure native sodium nitrate or Chile saltpetre is known throughout South America. Also applied to a limestone hardpan found in Arizona and elsewhere (*v.* SODIUM).

**CALLISTEPPIN** *v.* ANTHOCYANINS.

**CALLUTANNIC ACID** *v.* TANNINS.

**CALMATAMBIN** *v.* GLUCOSIDES.

**CALMONAL.** Calcium methylbromide.

**CALOMEL.** Mercurous chloride (*v.* MERCURY).

**CALOMELOL.** A colloidal preparation of calomel.

**CALOPHYLLUM INOPHYLLUM** (Linn.). A tree (ord. *Guttifera*), Alexandrian laurel, dilo of Fiji, tamarind of E. Polynesia, and sultana champa (Hind.) of India), the seeds of which yield 60 p.c. of a fragrant green oil, fluid at ordinary temperatures, solidifying when cooled below 10°. The tree bears fragrant white flowers. The oil, the woodel or bitter oil of Indian commerce, used in medicine and for lamp oil, is of a greenish tint, and a very little imparts its colour to a whole cask of coco-nut oil (Pharm. J. [3] 8, 363).

**CALOTYPE** *v.* PHOTOGRAPHY.

**CALUMBA.** *Calumbæ radix*, B.P.; *Calumba*, U.S.P. *Colombo*, *Columbo*. (*Racine de Colombo*, Fr.; *Kalumba* or *Columbowurzel*, Ger.)

The root of the *Jateorrhiza Columba* (Miers), a herbaceous climbing plant, inhabiting the forests of Eastern Africa (Flück. a. Hanb. 23; Benth. a. Trim. 13). The fleshy root is sliced

transversely and dried. It was introduced into Europe in the 17th century as an antidote for poison, and found a place in the London Pharmacopœia of 1788. It possesses mild bitter tonic properties, for which purpose it is now chiefly employed in medicine.

The drug contains 30–35 p.c. of starch, some mucilage, traces of a volatile oil, but no tannin; the root gives 4–7 p.c., the rhizome 12–17 p.c. of ash. There are further present two bitter principles and three alkaloids.

*Columbin*  $C_{28}H_{32}O_9$  (according to Ulrich, Annalen, 1907, 351, 363; but *cp.* Feist, *l.c.*), the best-known bitter principle, occurs to the extent of 0.8 p.c., and is extracted by hot ether and recrystallised from the same solvent. It forms colourless prisms, m.p. 182°, hardly soluble in hot or cold water, little in cold alcohol or ether, readily in hot ether, chloroform, and alcohol. Columbin adds directly 8 bromine atoms. A crystalline diacetyl derivative melts at 218°. Boiling 5 p.c. potassium hydroxide yields columbic acid  $C_{28}H_{32}O_{10}$ , crystals, m.p. 220° (Frey, Annalen, 1907, 351, 372), boiling 15 p.c. hydrochloric acid gives an amorphous yellow substance and yellowish-green fluorescence. A second bitter principle, m.p. 246°, almost insoluble in most solvents, was isolated by Feist (Arch. Pharm. 1907, 245, 586).

The alkaloids were at first mistaken for berberine, to which they are closely related (Gordin, Arch. Pharm. 1902, 240, 146; Günzel, *ibid.* 1906, 244, 257; Gadamer, *ibid.* 1902, 240, 450; and particularly Feist, *ibid.* 1907, 245, 586). All three yield yellow quaternary salts. The aqueous solution of an alcoholic extract of the drug is extracted with ether to remove columbin (*see* above), and concentrated potassium iodide then precipitates the iodides, which are fractionally crystallised from alcohol. *Columbamine iodide*  $C_{21}H_{22}N_2OI$ , yellow needles, m.p. 224°, is the least soluble. *Jateorrhizine iodide*  $C_{20}H_{20}O_5NI \cdot H_2O$  forms orange-yellow needles, m.p. 208°–210°. *palmatine iodide*  $C_{21}H_{22}O_5NI$ , slender yellow needles, m.p. 238°–240°. The first of these contains four methoxy

groups and one hydroxyl group; it is a methyl ether of the second, which contains three methoxy and two hydroxyl groups, for methylcolumbamine and dimethyljateorrhizine are identical. Palmatine iodide contains four methoxyl groups, but no hydroxyl, and hence remains undissolved on treating the mixed iodides with sodium hydroxide. Its exact relationship to the other two is unknown. Reduction of the corresponding nitrates leads in all three cases to colourless tetrahydro derivatives. Methylcolumbamine is oxidised by permanganate to corydaldine (an oxydation product of corydaline, *q.v.*), a trimethoxy-*o*-phthalic acid (gallo-carboxylic acid?), m.p. 200°, and a nitrogenous acid, m.p. 200°–202°. The free bases corresponding to the above salts are unknown, so that it is doubtful whether the alkaloids are ammonium hydroxides or the corresponding anhydrides.

For the identification of columbin and the alkaloids under the microscope, see Tunmann, Pharm. Zentr. H. 1914, 55, 775. G. B.

**CALYCANTHINE**  $C_{11}H_{14}N_2$ , crystals, m.p. 243°–244° (dry), occurs with isocalycanthine, prisms, m.p. 235°–236° (dry), in the seeds of *Calycanthus glaucus* (Wild.), 2 p.c. One nitrogen is secondary, the other tertiary. Toxic (Gordin, J. Amer. Chem. Soc. 1905, 27, 144, 1418; 1909, 31, 1305; 1911, 33, 1626).

**CAMELINE OIL**, *Dodder* oil, or *German Sesame* oil, is prepared from the seeds of *Myagrum sativum* (Crz.), *Camelina sativa* (Linn.), ('gold of pleasure') Several centuries ago the seed was grown all over Germany as a crop, but at present it is only cultivated on a small scale in some part of South Germany, Belgium, Holland, Hungary, the Balkan States, and South Russia. The seed is occasionally expressed in Hull, but, as a rule, the press cakes arrive in this country from Odessa, and are used (in Liverpool) in the manufacture of 'compound cakes.' The average composition of cameline seed is stated as follows:—

Oil	29.4 p.c.
Water	7.5 "
Proteins	25.9 "
Carbohydrates	17.3 "
Crude fibre	10.5 "
Ash	9.2 "

The oil has a golden-yellow colour and a pungent taste and smell. On exposure to the air it dries slowly. It is a semi-drying oil, and therefore yields, on boiling with litharge or manganese, a slowly drying varnish. The low saponification value of the oil points to the presence of erucic acid.

The 'cold-drawn' oil is used for edible purposes in Russia. The oil expressed in this country, as also the oil expressed by heat in Hungary and the south of Russia, is used for soap making.

It has the following analytical characters: sp.gr. 0.9224–0.9260 at 15°; solidification point, –15°–19°; saponification value, 185–188; iodine value, 133–136; and m.p. of fatty acids, 18°–20°; molecular equivalent of fatty acids, 296. A sample examined by Grimme (Chem. Rev. Fett. Ind. 1912, 19, 102) contained 1.16 p.c. of unsaponifiable matter. According to van Ketel and Antusch (Zeitsch.

angew. Chem. 1896, 581), linseed is liable to be contaminated with cameline seed, and so may yield an oil with a low iodine value. J. L.

**CAMPHOID**. A preparation of one part of guncotton dissolved in 20 parts each of absolute alcohol and camphor.

**CAMPEACHY WOOD** *v.* LOGWOOD.

**CAMPANIC ACID** *v.* LACTONES.

**CAMPHENE, CAMPHINE** *v.* TERPENES.

**CAMPHOL** *v.* CAMPHORS.

**CAMPHOPHORONE** *v.* KETONES.

**CAMPHOR**. The term camphor was applied exclusively, in the sixth century, by Arabian and Chinese writers, to Borneo or Malayan Camphor (Borneol), but in the sixteenth century it included Laurel or Common Camphor, for Garcia d'Orta mentions the latter as well known in Europe in 1563, and points out what indeed is true at the present day, that the much more costly Borneo or Sumatra Camphor is entirely consumed in the East (*cf.* Flick. a. Hanb. 510). The similarity in properties between laurel camphor and the crystalline separations from the volatile oils of plants, led, in the eighteenth century to an extension of the term camphor so as to include these solids. An attempt by Berzelius (Lehrbuch VI. 580) to simplify the nomenclature, by calling all solid portions of volatile oils, 'stearoptenes,' and the liquid portions 'elaeoptens,' has only resulted in the continued use, almost synonymously, of the words stearoptene and camphor. The discovery that laurel camphor contains oxygen has still further amplified the meaning of the word, which in its most comprehensive sense now includes most of the oxygenated products, both liquid and solid, of volatile oils.

Camphors are volatile oxygenated hydrocarbons, usually possessing a peculiar characteristic odour. They are mostly crystalline solids insoluble in water, but soluble in alcohol. Except in the case of a few which are produced artificially they are obtained from plants where they occur associated with hydrocarbons from which they are probably derived. Most plants when distilled in steam yield volatile oils composed of heavier oxidised compounds held in solution more or less by lighter hydrocarbons. The former often separate in crystals during the condensation of the oil or afterwards on standing, or they may be obtained by fractional distillation.

The more important camphors, using the term in its larger signification, may be considered, for convenience, in 4 groups, as isomerides or homologues of: (1) Peppermint camphor, menthol  $C_{10}H_{20}O$ ; (2) Borneo camphor, borneol  $C_{10}H_{18}O$ ; (3) laurel camphor  $C_{10}H_{16}O$ ; and (4) thyme camphor, thymol  $C_{10}H_{14}O$ . For the most part camphors behave like alcohols or phenols, but laurel camphor and menthone are ketones, cineol is an ether and alant camphor a lactone. The majority of camphors belong to saturated or unsaturated cyclic systems, but in 1891 Semmler (Ber. 24, 210) introduced the expression 'olefinic camphors' for certain substances which possess an open chain structure, are closely related to the cyclic camphors, and are responsible for the aroma of many essential oils. The chief members of this group are citronellol  $C_{10}H_{20}O$ , geraniol, nerol and citronellal  $C_{10}H_{18}O$ , and citral  $C_{10}H_{16}O$ . (*See also* PERFUMES.)

**Peppermint camphor.** *Menthol*  $C_{10}H_{18}OH$ . 3-Me-6-isopropyl-1-cyclohexanol. The laevo modification of this camphor is the chief constituent of peppermint oil, the product of distillation of the herbs *Mentha piperita* (Linn.) and *M. arvensis* (Linn.), varieties *piperascens* and *glabrata*. It is also a minor constituent of a few other volatile oils. A menthol of unrecorded rotatory sign predominates in the oil from *Hyptis suaveolens* (Linn.) (Bacon, Philippine J. Sc. 1909, 4, A, 130). The proportion of menthol in normal Japanese oil of peppermint varies between 69 and 91 p.c., whilst English and American oils contain 48 to 68 p.c. A portion, about 10 p.c., of the menthol is present in ester form combined with acetic and isovalerianic acids. The camphor is extracted by freezing oils rich in menthol, whereby the crystals separate and are recovered either by pressure or by centrifugal treatment. The more important papers dealing with menthol in its bearing on oil of peppermint are: Beckett and Wright (Chem. Soc. Trans. 1876, 29, 1), Atkinson and Yoshida (*ibid.* 1882, 41, 50), Moriya (*ibid.* 1881, 39, 77), Power and Kleber (Arch. Pharm. 1894, 232, 639), Power and Fluckiger (Pharm. J. 1880 [3] 11, 220), Andres and Andreef (Ber. 1892, 25, 609), Schindelmeiser (Apoth. Zeit. 1906, 21, 927), and the semi-annual reports of Schimmel and Co., and of Roure Bertrand Fils.

Menthol crystallises in prisms belonging to the hexagonal system, and in appearance resembles magnesium sulphate. It has a strong peppermint odour and taste, and produces a sensation of warmth on the tongue which is replaced by a sensation of cold when air is inhaled. M.p.  $42^{\circ}$ – $43^{\circ}$ ,  $43.5^{\circ}$ – $44.5^{\circ}$  (Gilde-meister and Hoffmann, Die Ätherischen Öle, 1910, i. 405), b.p.  $215.5^{\circ}$  at 758 mm. (P. a. K.), sp.gr. 0.88 at  $20^{\circ}$  (Long, J. Amer. Chem. Soc. 1892, 14, 151),  $[\alpha]_D^{20} = -50.7^{\circ}$  in 10 p.c. alcoholic solution (Beckmann, J. pr. Chem. 1897, [2] 55, 15). Menthol is very slightly soluble in water, but soluble in the usual organic solvents and in concentrated hydrochloric acid. It rotates on the surface of water in a similar manner to laurel camphor. Mixed with chloral, thymol, or laurel camphor, menthol reacts forming a liquid (Kyle, Amer. J. Pharm. 1885, 429; Becker, *ibid.* 1886, 283). When menthol is boiled with sulphuric acid diluted with half its volume of water it acquires an indigo-blue or ultramarine colour, the acid becoming brown (Brit. Pharm. 1914).

Menthol is a saturated secondary alcohol which under the influence of dehydrating agents, e.g. phosphorus pentoxide, zinc chloride, potassium bisulphate, passes into the hydrocarbon menthene,  $C_{10}H_{18}$ . A very large number of esters of menthol are known, of which the acetate  $C_{10}H_{18}OAc$ , b.p.  $227^{\circ}$ – $228^{\circ}$ ,  $[\alpha]_D = -79.26^{\circ}$ , (cf. Kishner, J. Russ. Phys. Chem. Soc. 1895, 27, 480), and isovalerianate,  $C_{10}H_{18}OOCC_4H_9$ , occur in oil of peppermint (P. a. K.). For the identification of *l*-menthol by means of derivatives, the phenylcarbamate  $C_{10}H_{18}OCONHPh$ , m.p.  $111^{\circ}$ – $112^{\circ}$  (Leuckart, Ber. 1887, 20, 115), the hydrogen phthalate  $C_{10}H_{18}OOCC_6H_4O_2$ , m.p.  $122^{\circ}$  (Pickard and Littlebury, Chem. Soc. Trans. 1912, 101, 118), and benzoate  $C_{10}H_{18}OBz$ , m.p.  $55^{\circ}$ – $56^{\circ}$  (P. a. L.) are characteristic.

Two atoms of hydrogen are removed from *l*-menthol by treatment with chromic acid mixture (Beckmann, Annalen, 1889, 250, 325) with formation of *l*-menthone, a liquid ketone which occurs to the extent of about 20 p.c. in oil of peppermint (B. a. W.), and with an isomeride, *d*-isomenthone, forms 50 p.c. of American pennyroyal oil obtained from *Hedeoma pulegoides* (Linn.) (Barrowcliff, Chem. Soc. Trans. 1907, 91, 875). Menthol has been obtained synthetically from menthone and pulegone (Beckmann and Pleissner, Annalen, 1891, 262, 32, Haller and Martine, Compt. rend. 1905, 140, 1298), also from thymol by use of the Sabatier and Senderens method of reduction. By this latter method the four possible menthols corresponding to menthone, namely, *d*- and *l*-menthol and *d*- and *l*-neomenthol, have been prepared (Pickard and Littlebury, Chem. Soc. Trans. 1912, 101, 110). A small proportion of *d*-neomenthol was isolated at the same time from Japanese oil of peppermint.

In its medicinal action menthol resembles phenol. Its chief uses are as a local anæsthetic for relief of superficial pains of various kinds, also dissolved in oil as a spray for influenza, hay fever, &c., and as a local application in certain cutaneous diseases.

**Camphors isomeric with menthol.** *Citronellol*  $C_{10}H_{20}O$ , a liquid isomeride of menthol occurs as *l*-citronellol in rose oil, *Rosa damascena* (Mill.) (Tiemann and Schmidt, Ber. 1896, 29, 922), and as *d*-citronellol in Java citronella oil, *Andropogon Nardus Java* de Jong (Schimmel's Rept. 1902, i. 14), and in the oil from *Barosma pulchella* (Linn.) (*ibid.* 1910, i. 17), whilst both forms occur in geranium oil, *Pelargonium graveolens* (Ait.) (Tiemann and Schmidt, Ber. 1896, 29, 924).

**Borneo and Allied Camphors.** *Malayan, Barus* or *Dryobalanops camphor*; *Borneol*, *camphol*  $C_{10}H_{17}OH$ , 1, 7, 7-trimethyl [1, 2, 2]-bicyclo 2-heptanol. This camphor occurs in nature in the dextro- and levorotatory varieties, esterified chiefly in the levorotatory modification. Common borneol, which is dextrorotatory, is the product of *Dryobalanops aromatica* (Gärtner), a majestic tree indigenous to Sumatra, Borneo, and Labuan. The camphor is deposited in fissures in the old wood, and to obtain it the trees have to be sacrificed. The tree is cut down and the wood is examined by a laborious process of splitting. The collected camphor averages 3 to 11 lbs. from each tree. Owing to the reckless manner in which the trees have been destroyed without the planting of others, the forests of Sumatra now contain few that are worth working (Pharm. J. 1881, [3] 12, 83). The states of Sarawak and Brunei are much richer in trees, and at the present time produce borneol by similar methods (cf. Hanb. and Flück. 516; Kremers, Pharm. Review, 1905, 23, 7; Gilde-meister and Hoffmann, Die ätherischen Öle, 1916, iii. 178). The crude camphor is best purified by sublimation (Pelouze, Annalen, 1841, 40, 326).

*d*-Borneol is also a constituent of the following volatile oils: Rosemary, *Rosmarinus officinalis* (Linn.) (Gildemeister and Stephan, Arch. Pharm. 1897, 235, 586); Siam Cardamom *Amomum cardamomum* (Linn.) (Schimmel's Rept. 1897, ii. 9); Nutmeg, *Myristica fragrans* (Houtt.) (Power and Salway, Chem. Soc. Trans.



1907, 91, 2037); Lavender, *Lavandula vera* (D.C.) (Bruylants, J. Pharm. Chim. 1879, [4] 30, 139; cf. Charabot, Bull. Soc. Chim. 1897, [3] 17, 380); Spike Lavender, *Lavandula Spica* (Linn.) (Bouchardat, Compt. rend. 1893, 117, 53 and 1094), and Virginian Snake-root, *Aristolochia serpentaria* (Linn.) (Spica, Gazz. chim. ital. 1887, 17, 314). In addition to these natural sources *d*-borneol may be obtained, by the action of reducing agents on laurel camphor when borneol, of the same sign of rotation as the camphor used, is obtained mixed with a small proportion of *isoborneol* of opposite sign (Haller, Compt. rend. 1887, 105, 227; Beckmann, J. pr. Chem. 1897, [2] 55, 31), and in small proportion with *l*-borneol it is found among the products of the distillation of amber with potash (Berthelot and Buignet, Annalen, 1860, 115, 245).

Borneol is harder and less volatile than laurel camphor, and does not sublime in the bottles in which it is kept. It has a peppery camphoraceous odour and burning taste. M.p. 203°–204° (preparations containing *isoborneol* melt 206°–208°); b.p. 212°, sp.gr. 1.011 (Plowman, Pharm. J. 1874, [3] 4, 711). It crystallises in the hexagonal system (Traube, J. pr. Chem. 1894, [2] 49, 3);  $[\alpha]_D +37.7^\circ$  (Beckmann, Annalen, 1889, 250, 353; Haller, Compt. rend. 1891, 112, 143; Pickard and Littlebury, Chem. Soc. Trans. 1907, 91, 1973). Borneol is a saturated secondary alcohol, and on oxidation yields camphor,  $C_{10}H_{16}O$  of the same rotatory sign. Powerful oxidising agents produce camphoric acid  $C_{10}H_{16}O_4$ , and further degradation products (Laurent, Annalen, 1837, 22, 135; Pelouze, *ibid.* 1841, 40, 328; Kachler, *ibid.* 1878, 191, 143). Removal of a molecule of water by phosphoric anhydride gives rise to a solid terpene, camphene,  $C_{10}H_{16}$  (Wallach, *ibid.* 1885, 230, 239); for the mechanism of this change, see Meerwein, *ibid.* 1914, 405, 129). Concentrated hydrochloric acid (Berthelot, *ibid.* 1859, 112, 366), or phosphorus pentachloride (Kachler, *ibid.* 1879, 197, 89) reacts with borneol producing bornyl chloride  $C_{10}H_{17}Cl$ , a product identical with pinene hydrochloride or 'artificial camphor.' For the characterization of borneol the phenylcarbamate,  $C_{10}H_{17}OCONHPh$ , m.p. 138°–139° (Bertram and Walbaum, J. pr. Chem. 1894, [2] 49, 5), the acetate  $C_{10}H_{17}OAc$ , m.p. 29° (B. and W. Arch. Pharm. 1893, 231, 304), and the addition products with bromal, m.p. 105°–108° (Minguin, Compt. rend. 1893, 116, 889), and chloral, m.p. 55°–56° (Haller, *ibid.* 1891, 112, 145), are employed.

*l*-Borneol is a constituent of the following oils: Valerian, *Valeriana officinalis* (Linn.) (Bruylants, Ber. 1878, 11, 452; Oliviero, Bull. Soc. Chim. 1895, [3] 13, 917), Canadian Snake-root, *Asarum canadense* (Linn.) (Power and Lees, Chem. Soc. Trans. 1902, 81, 63); Arbor vitae, *Thuja occidentalis* (Linn.) (Wallach, Annalen, 1907, 353, 213), Citronella, *Andropogon nardus* (Linn.) (Schimmels, Rept. 1912, 1, 43), *Pinus maritima* (Mill.) (Belloni, Chem. Zentr. 1906, i. 1552), Yellow Pine, *Pinus palustris* (Mill.) (Schimmels, Rept. 1910, 1, 106), and Feverfew, *Matricaria Parthenium* (Linn.) (*ibid.* 1894, 1, 71). It is also contained in the fusel oil of the crude spirit obtained by the fermentation of the sugar of madder, and formerly known

as madder camphor (Jeanjean, Annalen, 1857, 101, 95), and in Ngai camphor, the name given to the solid part of the essential oil of *Blumea balsamifera* (D.C.) (Plowman, Pharm. J. 1874, [3] 4, 712; Flückiger, *ibid.* 828; Schimmels, Rept. 1910, 1, 149). From this latter source the *l*-borneol had a higher rotatory power  $[\alpha]_D -39.25^\circ$ , than is usually observed (Schimmels, Rept. 1895, 1, 74). On oxidation with nitric acid *l*-borneol yields levorotatory camphor.

Numerous esters of borneol are known. Those of *l*-borneol, which occur in nature, are bornyl acetate, in oil of valerian (Bruylants), Siberian fir oil, *Abies sibirica*; Ledeb (Hirschsohn, Chem. Zentr. 1892, ii. 793), hemlock spruce oil, *Abies canadensis*; Michx. (Hunkel, Pharm. Review, 1896, 14, 35), and coriander oil, *Coriandrum sativum* (Linn.) (Walbaum and Müller, Wallach Festschrift, 1909, 654), bornyl formate, butyrate and isovalerianate in oil of valerian (Bruylants).

Inactive borneol, the racemic mixture of *d*- and *l*-borneol has been obtained by the distillation of the crude product of the action of sulphuric acid on turpentine (Armstrong and Tilden, Chem. Soc. Trans. 1879, 35, 752); an ester of *i*-borneol is also obtained by treating pinene with oxalic acid (Schindelmeyer, J. Rus. Phys. Chem. Soc. 1902, 34, 954).

*Isoborneol*, a stereoisomeride of borneol and an intermediate product in the manufacture of synthetic camphor, was first obtained by Bertram and Walbaum (J. pr. Chem. 1894, [2] 49, 1) from camphene obtained by the action of sodium acetate and glacial acetic acid on pinene hydrochloride at 200°. Camphene is warmed with glacial acetic acid and a little, 50 p.c., sulphuric acid, and the resulting acetate is decomposed by alcoholic potash. *Isoborneol* can now be prepared from pinene hydrochloride directly, by the action of boiling glacial acetic acid in the presence of a small quantity of a metallic salt such as anhydrous zinc chloride (Weizmann and Clayton Aniline Co., Eng. Pat. 8266, 1906). It is also formed to a small extent in the reduction of laurel camphor (Beckmann, J. pr. Chem. 1897, [2] 55, 35). It differs from borneol, physically, in its greater volatility, its higher m.p. 212° (in sealed tube), and its greater solubility in benzene and light petroleum, chemically in its greater stability towards oxidising agents, and in the ease with which it loses water forming camphene. Its bromal addition compound melts at 71°–72°. The optically active *isoborneols* melt at 214°, and have  $[\alpha]_D \pm 34.3^\circ$  (Pickard and Littlebury, Chem. Soc. Trans. 1907, 91, 1979).

Camphors isomeric with borneol. Cineol, *Cajeputol* or *Eucalyptol*  $C_{10}H_{16}O$ , anhydro 1-Me 4 ( $\alpha$ -Me  $\alpha$ -oxyethyl) 1-oxy-cyclohexane, is a constituent of a great number of volatile oils. It forms the major portion of the volatile oils of *Eucalyptus globulus* (Labill.) (Jahns, Ber. 1884, 17, 2941), Wormseed, *Artemisia maritima* (Linn.) var. *Stechmanni* (Wallach and Brass, Annalen) 1884, 223, 291, Hell and Sturcke, Ber. 1884, 17, 1970); *Cajeput*, *Melaleuca Cajeputi* (Roxb.) (Wallach and Gildemeister, *ibid.* 1888, 246, 276); *M. viridiflora* de Brogn. et Gris (Bertrand, Bull. Soc. Chim. 1893, [3] 9, 432). Cineol melts at 1°–1.5° (Schimmel & Co.); b.p. 176°

(Wallach, *Annalen*, 1888, 245, 195). It has a camphor-like odour and is optically inactive. It is characterised by its addition compounds, with the halogens, with hydrobromic acid, m.p. 56°, which also serves for the isolation of small quantities (Wallach, *Annalen*, 1888, 246, 280), with phosphoric acid (Scammell, D. R. P. 80118), with arsenic acid (U.S. Pat. 705545, Thoms and Molle, *Arch. Pharm.* 1904, 242, 172), with iodole (tetraiodopyrrol), m.p. 112° (Bertram and Walbaum, *Arch. Pharm.* 1897, 235, 178), by means of which very small quantities can be detected (Hirschsohn, *Chem. Zentr.* 1893, i. 503), and with resorcinol (Baeyer and Villiger, *Ber.* 1902, 35, 1209). The compounds with hydrobromic acid, phosphoric acid, arsenic acid, and resorcinol are used for its quantitative estimation (*cf.* Turner and Holmes, *Amer. J. Pharm.* 1915, 87, 101), the question as to their relative efficiency being still a matter of dispute. Dehydrating agents convert cineol into *dipentene*  $C_{10}H_{16}$  (Wallach and Brass; Hell and Sturcke). Oxidation by permanganate gives *cineolic acid*  $C_{10}H_{16}O_5$ , m.p. 197 (Wallach and Gildemeister), but towards reducing agents it is very stable. The oxygen atom in cineol is present as an oxide or ether linking. The artificial production of cineol has been effected by the action of dilute acids on terpineol or terpin hydrate (Wallach, *Annalen*, 1887, 239, 18).

Cineol is used in medicine as a local antiseptic dressing, and for catarrhal conditions of the respiratory mucous membranes.

The volatile oils of the following contain other isomerides of borneol: Citronella, *Andropogon Nardus* (Linn.) (Semmler, *Ber.* 1893, 26, 2254) and *Eucalyptus citriodora* (Hook.) (Schimmels, *Rept.* 1907, 2, 35) contain d-*Citronellal*, whilst l-*Citronellal* is contained in 'Java lemon oil' (*ibid.* 1903, 1, 21). Linaloe, *Ocotea caudata* (Mez.) (Barbier, *Compt. rend.* 1895, 121, 168), Lavender, *Lavandula vera* (D.C.) (Bertram and Walbaum, *J. pr. Chem.* 1892, [2] 45, 590); Bergamot, *Citrus Aurantium* (Linn.) (Bertram and Walbaum, *ibid.* 602) contain l-*linalol*; whilst d-*linalol* ('*coriandrol*') is contained in oil of coriander, *Coriandrum sativum* (Linn.) (Barbier, *Compt. rend.* 1893, 116, 1460). Geranium, *Pelargonium graveolens* (Ait.) (Bertram and Gildemeister, *J. pr. Chem.* 1894, [2] 49, 191); Citronella, *Andropogon Nardus* (Linn.) (Schimmels, *Rept.* 1893, 2, 12); Lemon grass, *Cymbopogon flexuosus* (Stapf.) (Tiemann and Semmler *Ber.* 1893, 26, 2721), contain geraniol ('*rhodinol*'). Neroli oil from *Citrus Aurantium* (Linn.), subsp. *amara* (Linn.) (Hesse and Zeitschel, *J. pr. Chem.* 1902, [2] 66, 481) contains nerol. d-a-Terpineol, m.p. 37°–38°, is a constituent of oil of sweet orange, *Citrus Aurantium* (var.) *dulce* (Linn.) (Stephan, *J. pr. Chem.* 1900, [2] 62, 523) of neroli and petit-grain oils; 1-a-terpineol of oil of camphor, *Cinnamomum Camphora* (Nees et Eberm.) (Schimmels, *Rept.* 1903, 2, 39); i-Terpineol, m.p. 35°, of cajeput oil, *Melaleuca cajuputi* (Roxb.) (Voiry, *Bull. Soc. Chim.* 1888, [2] 50, 108).

**Common and allied camphors.** *Laurel Camphor*; *Dextro Camphor*. (*Camphre*, Fr.; *Campher*, Ger.)  $C_{10}H_{16}O$  1.7.7-Trimethyl [1.2.2]-bicyclo 2-heptanone. Common camphor is contained in all parts of the camphor laurel, *Cinnamomum*

*Camphora* (Nees et Eberm.), a tree inhabiting Japan, Formosa and Southern China. It occurs also as a constituent of the volatile oils of Spike, *Lavandula spica* (D.C.) (Lallemand, *Annalen*, 1860, 114, 198); Rosemary, *Rosmarinus officinalis* (Linn.) (*ibid.* 197); Sage, *Salvia officinalis* (Linn.) (Muir, *Chem. Soc. Trans.* 1880, 37, 678); Siam Cardamom, *Amomum Cardamomum* (Linn.) (Schimmels, *Rept.* 1897, 2, 9); American Wormseed, *Chenopodium ambrosioides* (Linn.) var. *anthelminticum* (Gray) (*ibid.* 1908, 1, 112), and Sassafras, *Sassafras officinalis* (Nees) (Power and Kleber, *Pharm. Review*, 1896, 14, 101).

Although camphor is at the present time still manufactured artificially, most of the camphor of commerce is obtained from the camphor laurel, the chief industry being confined to Japan, Formosa and China. The experimental plantations which were undertaken for the production of natural camphor in Florida, California, Jamaica, East Africa, Malay States, Algeria and Ceylon have at least in one case, that of Florida, begun to furnish camphor on the commercial scale (Oil, Paint and Drug Rep., March 29, 1915). In Formosa the camphor industry before the China-Japanese war was nominally in the hands of the Chinese, but owing to the savage state of the interior of the island, and the unscrupulous methods of the dealers, it had declined to small and unimportant proportions. Afterwards Japan assumed the control of the industry, and it was made a government monopoly in 1899, and this was extended to Japanese camphor in 1903. Since the establishment of the monopoly the old crude methods of obtaining the camphor (Flück. and Hanb. 513) have been replaced by more modern ones. The camphor wood in the form of chips is steamed in roughly built furnaces, and the camphor which is driven off is condensed in cooled wooden vessels, and freed from most of the oil by draining, crude or 'grade B' camphor being thus obtained. For the production of refined or 'grade A' camphor, the crude material is heated in large iron retorts, through which a current of air is passed. For the first 48 hours only sufficient heat is applied to drive off the water and oil. The retorts are then connected with a condensing chamber, the roof of which is cooled by running water, and are heated to a high temperature in order to volatilise the camphor. It is then formed into blocks in wooden moulds and pressed, first by steam power and finally by a very high hydraulic pressure (Collins, *J. Soc. Chem. Ind.* 1904, 75). The yield of camphor is greater in winter than in summer, while the reverse is true of the oil. In summer a charge of 120 kilos. of wood gives 2.4 kilos., or 2 p.c. of camphor, and 1.8 litres of oil; in winter, 3 kilos., or 2.4 p.c. of camphor and 0.5–0.7 litre of oil.

Crude camphor appears in commerce as a coarse wet powder of a greyish-white colour. Chinese crude camphor is packed in round wooden pots of about 150 lbs. net content, Japanese in lead-lined wooden boxes containing about 130 lbs. net. The principal impurities of crude camphor are water, camphor oil, iron, sand, wood, &c. Light oil of camphor has a sp.gr. of 0.895–0.920; b.p. 170°–180°, and contains pinene, camphene, dipentene, phellandrene and



fenchene. *Heavy oil of camphor*, having a sp.gr. of 0.960-0.970, and b.p. 240°-300°, contains cadinene, safrol, eugenol, cineol, fenchone, terpineol, &c. Besides these compounds, both of the oils contain a large amount of camphor in solution. Before refining crude camphor, the oil and water must be got rid of, as the oil gives the refined camphor a fatty touch, and the water renders it opaque. The elimination of water and oil is often effected by washing in a centrifugal machine with small quantities of water; the liquid draining off contains both oil and water. The separation is also done by hydraulic pressure, or by crystallisation from boiling benzene or light petroleum. Resublimation in Europe is done principally in glass retorts, yielding a round concave cake weighing 6-8 lbs., having an opening in the centre. In America the camphor is sublimed from flat iron pans with iron covers, yielding plates of about 18 inches square and 1 inch thick, weighing from 8 to 10 lbs. The process consists in mixing the camphor with a little lime, charcoal or iron filings, according to the quality, and charging each pan with about 12 lbs. of material; the subliming pans are heated slowly for 2 hours, and then fired rapidly up to 190°, this temperature being kept for from 12 to 16 hours. After cooling, the refined product is removed from the cover by slightly heating, and is then cut into the desired shape (Drobbeg, J. Soc. Chem. Ind. 1907, 381).

Purified camphor comes on to the market in three forms, 'bells,' 'blocks' and 'flowers.' Block camphor consists of colourless translucent masses traversed by numerous cracks. It can be broken but is too tough to admit of being powdered by trituration. This may, however, be readily effected if a little alcohol be added, which escapes again during the operation. Camphor finds very extensive commercial application in the preparation of celluloid, in medicine where it is used externally as a mild rubefacient and to destroy parasites, internally, as a carminative and intestinal disinfectant, and to a minor extent in the manufacture of explosives. Sp.gr. 0.986-0.996; m.p. 175°, 178.75° corr. (Lenz, Arch. Pharm. 1911, 249, 289); b.p. 204°. It sublimes to some extent at ordinary temperatures and condenses in hexagonal crystals (cf. Folger, Y.B. Pharm. 1886, 232);  $[\alpha]_D^{20}$  44.22° in 20 p.c. alcoholic solution (Beckmann, Annalen, 1889, 250, 353). Refraction coefficient (Kanonnikov, J. pr. Chem. 1885, [2] 31, 348). Camphor in common with chloral hydrate and some other substances rotates in a peculiar manner on the surface of water (lowering of surface tension by solution), (Tomlinson, Phil. Mag. 1873, [4] 46, 376; Pharm. J. 1874, [3] 4, 654, 672; Chem. News, 1885, 52, 50). It is very sparingly soluble in water (1:700), readily in 90 p.c. alcohol (1:1), also in chloroform and ether. Mixed with chloral hydrate, it forms an oily liquid  $C_{10}H_{16}O$ ,  $CCl_3CHO.H_2O$ , which has been employed in medicine as an anodyne pigment (Brown, Pharm. J. 1873, [3] 4, 729; Saunders, *ibid.* 1876, [3] 7, 89; Cazeneuve and Imbert, Bull. Soc. Chim. 1880, [2] 34, 209; Zeidler, J. 1878, 645; Albright, Amer. J. Pharm. 1886, 282). Similar combinations take place between camphor and chloral alcoholate (Zeidler), phenol

(Léger, Bull. Soc. Chim. 1890, [3] 4, 725); menthol (Kyle, Amer. J. Pharm. 1885, 429), and thymol (Symes, Pharm. J. 1879, [3] 9, 598).

Camphor is a saturated hydroaromatic ketone, but does not combine with sodium bisulphite. For identification purposes use is made of the *oxime*  $C_{10}H_{16}NOH$ , m.p. 118°-119° (Auwers, Ber. 1889, 22, 605), the *semicarbazone*  $C_{10}H_{16}=N.NHCONH_2$ , m.p. 236°-238° (Tiemann, Ber. 1895, 28, 2191), the *oxymethylene compound*  $C_{10}H_{14}O=CHOH$ , m.p. 80°-81°, and the *benzylidene compound*  $C_{10}H_{14}O=CHC_6H_5$ , m.p. 96°. Of its substitution products, one, *a-bromocamphor*  $C_{10}H_{15}OBr$  has been employed in medicine as a sedative in nervous excitement, and is an article of trade. It is best prepared by treating powdered camphor with bromine at 100°, pouring the liquefied product into water and recrystallising from spirit (Armstrong and Matthews, Chem. News, 1878, 37, 4). It has a weak camphoraceous odour and taste; m.p. 76°; b.p. 274°. It is insoluble in water, but soluble in the common organic solvents, in fixed oils, and in sulphuric acid. By the action of reducing agents camphor is converted into a mixture of borneol and isoborneol, the former predominating (Beckmann, J. pr. Chem. 1897, [2] 55, 35; Haller, Compt. rend. 1887, 105, 227). On oxidation with nitric acid (Kachler, Annalen, 1878, 191, 143) or hot alkaline permanganate (Grosser, Ber. 1881, 14, 2507), camphor yields *camphoric acid*  $C_8H_{14}(COOH)_2$ .

*Synthetic Camphor*; *Inactive Camphor*. Camphor can be manufactured from turpentine oil, and has from time to time appeared on the market. It is termed 'synthetic' camphor to distinguish it from the so-called 'artificial camphor,' which consists of pinene hydrochloride, and is unsuitable for the chief purposes to which camphor is applied. Only when the prices of the natural product are abnormally high has synthetic camphor been able to compete with it. During the war, in Germany, owing to the failure of supplies of *d*-camphor, the Schering interests and probably other firms (Houseman, Amer. J. Pharm. 1915, 87, 58) produced synthetic camphor in quantity, whilst the American Camphor Corporation contend that they can supply the requirements of the celluloid trade with synthetic camphor (Oil, Paint and Drug Rep., March 29, 1915). Natural camphor and synthetic camphor only differ in their action on polarised light, the latter being either inactive or showing only a slight activity; in their physiological action they are identical (Joachimoglu, Ber. deut. Pharm. Ges. 1916, 26, 427). By working at low temperatures, however, Darmon (Compt. rend. 1910, 150, 925) has obtained synthetic camphor with the rotation of natural camphor, French oil of turpentine yielding *l*-camphor, whilst turpentine from the Aleppo pine, *Pinus halepensis* (Mill.) yielded *d*-camphor. The various routes taken by patented processes for the manufacture of synthetic camphor are shown by Fig. 1.

The first commercial process consisted essentially in converting oil of turpentine into pinene hydrochloride, which compound by elimination of hydrogen chloride yields camphene. Camphene is then converted into isoborneol, which, like natural borneol, yields camphor on oxidation. For the preparation of pinene

hydrochloride, oil of turpentine, which contains 70-90 p.c. of pinene, depending on its origin, is treated with dry hydrogen chloride, whereby a solid hydrochloride is obtained together with a

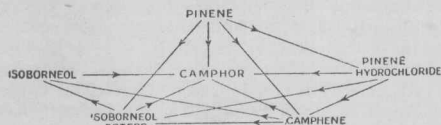


FIG. 1.

liquid hydrochloride which is not suitable for the manufacture of camphene. This liquid hydrochloride contains a considerable proportion of the solid hydrochloride in solution, which may be recovered by oxidising the oily product with dilute nitric acid, or by extraction with petroleum after treatment with sulphuric acid at 40°, which polymerises the oil (Eng. Pat. 7319, 1908). The preparation of camphene by the removal of hydrogen chloride from pinene hydrochloride (Wallach, *Annalen*, 1887, 239, 6; Brühl, *Ber.* 1892, 25, 147; Reyehler, *Bull. Soc. Chim.* 1896, [3] 15, 371) was at first attended with difficulty; the yield was small and the product was liable to contain chloride. During the last two decades the following methods have been patented for the production of camphene in large quantities, many of which are claimed to give almost theoretical yields and a product free from chloride: Heating the hydrochloride with bases of the aliphatic series such as methylamine, or with piperazine or piperidine (U.S. Pat. 707270, 1902), or with tertiary bases of the pyridine and quinoline group (Eng. Pat. 5032, 1906); by heating with alcoholic, aqueous, or gaseous ammonia (U.S. Pat. 707271, 1902), or ammonia in presence of a phenol (D. R. P. 264246, 1912); by heating with aqueous sodium hydroxide or ammonia in presence of a soap (U.S. Pat. 725890, 1903); by heating with lead acetate in glacial acetic acid solution (Fr. Pat. 349896, 1904); by heating with glacial phosphoric acid in glacial acetic acid solution (D. R. P. 207888, 1908); by heating with a metallic salt of a higher fatty acid (Eng. Pat. 19960, 1906; 1948, 1907), or with a mixture of metallic salts of the fatty acids (Eng. Pat. 2488, 1913); by heating with a metal and an oxidising agent, such as zinc and barium peroxide in molecular proportions (Fr. Pat. 361333, 1905); by heating with salts of phenols or naphthols either anhydrous or in presence of water (Eng. Pat. 16429, 1906; 21180, 1906; 5674, 1908); by heating with lime or other similar oxide (Fr. Pat. 375897, 1907; Eng. Pat. 25453, 1907), in the presence of phenol at 180° (Eng. Pat. 22810, 1906), in the presence of polyvalent alcohols or carbohydrates (Eng. Pat. 10784, 1907); by heating with alkali, and alkali or alkaline earth salt of a sulphonic acid of the benzene or naphthalene series (Eng. Pat. 10783, 1907); by heating with alkali or alkaline earth salts of organic sulphamides or with phenolsulphonic acids (D. R. P. 197346, 197805, 1907); by heating with alkali or alkaline earth hydroxides in presence of compounds which combine with water such as alkali or alkaline earth oxides (Fr. Pat. 413282, 1909); by heating with zinc oxide in presence of alkali hydroxide (Eng. Pat. 11029, 1911); by

heating with  $\alpha$ - or  $\beta$ -naphthylamine (D. R. P. 206386, 1907), or with aniline (D. R. P. 205850, 1907); by heating with a meta- or pyro-borate, silicate, phosphate or arsenate in aqueous solution (D. R. P. 205295, 1908); by heating with phenol, cresol or naphthol and the carbonate of an alkali or alkaline earth metal (Eng. Pat. 13902, 1909); by heating under reflux until the hydrochloric acid has gone (U.S. Pat. 923967, 1909); by the Grignard reaction (Hesse, *Ber.* 1906, 39, 1127). According to Eng. Pat. 10227, 1910, pinene vapour when passed over a catalyst at 200°-300° is converted into camphene.

Bertram and Walbaum (*J. pr. Chem.* 1894, [2] 49, 1) made the discovery that camphene is converted into isoborneol by warming with a mixture of acetic acid and a little sulphuric acid, and decomposing the resulting isobornyl acetate by alcoholic potash. This method is employed on the manufacturing scale. A variant of the method is described in Eng. Pat. 19961, 1906, where camphene is heated with oxalic acid in a suitable solvent with a condensing agent such as sulphuric or phosphoric acids with formation of normal and acid esters of isoborneol. Camphene has also been directly converted into isoborneol by boiling in acetone with half its weight of 20 p.c.  $H_2SO_4$  for 10 hours, or in an autoclave at 100° for a shorter time (Fr. Pat. 385341, 1907). The isoborneol purified by crystallisation from light petroleum or benzene is then oxidised to camphor. For this purpose various oxidising agents are employed, many of which have been patented. Amongst these are: potassium permanganate in glacial acetic acid (Ber. 1900, 33, 3430); aqueous solution of permanganate employed with a benzene solution of isoborneol (Fr. Pat. 341513, 1904); potassium permanganate in alkaline solution (D. R. P. Ann. 38311, 1904); chlorine, either gaseous or in solution (Eng. Pat. 28035, 1904; U.S. Pat. 802792, 1905); hypochlorite, either alone (U.S. Pat. 864162, 1907), or in presence of copper and ferric chlorides (Eng. Pat. 20050, 1908); chromic acid or chromates (Eng. Pat. 26779, 1904; 14550, 1907); in acetone solution (Eng. Pat. 21946, 1907); or in presence of an indifferent solvent (Eng. Pat. 5513, 1908; 24779, 1912); nitric acid in which the presence of nitrous acid is essential (Eng. Pat. 9857, 1907); nitric acid in presence of vanadic acid and oxygen (Eng. Pat. 18047, 1908); nitric acid in presence of a halogen (U.S. Pat. 1313661, 1919); oxygen (U.S. Pat. 801485, 1905); oxygen, oxides of heavy metals or peroxides (Fr. Pat. 385352, 1907); basic oxidising substances, e.g.  $CuO$ ,  $HgO$  (Eng. Pat. 3750, 1908); metals or oxides which can liberate hydrogen from isoborneol (Eng. Pat. 26708, 1908); electrolytic methods (U.S. Pat. 875062, 1907; Fr. Pat. 387539, 1907); ozone (U.S. Pat. 801483, 1905); nitrous anhydride (U.S. Pat. 802793, 1905); metallic copper at 300° in absence of air (Eng. Pat. 17573, 1906). According to U.S. Pat. 790601, 1905, and Eng. Pat. 21171, 1906, isobornyl acetate and other isobornyl esters can be directly oxidised to camphor without previous saponification.

Camphene can also be directly oxidised to camphor (Armstrong and Tilden, *Ber.* 1879, 12, 1756), and the following processes have been patented: Treatment with ozone at 80° (Eng. Pat. 21294, 1890); treatment with hot air or

oxygen (Eng. Pat. 3555, 1896); oxidation by potassium permanganate in acetone solution (addition to Fr. Pat. 349896, 1904); treatment of camphene at 180° with an oxidising agent, such as chromic acid, converts it into oxonide  $C_{10}H_{16}O_3$ , which loses oxygen on treatment with water, and is converted into a lactone, camphenolide, which yields camphor on heating in presence of water (Fr. Pat. 361333, 1905); oxidation with a per-salt of potassium and sulphuric acid (Fr. Pat. 389092, 1908).

Another method of obtaining synthetic camphor depends on the formation of bornyl and isobornyl esters by the direct action of various acids on pinene or turpentine oil. The following processes have been patented: Treatment of anhydrous turpentine at 120°–130° with anhydrous oxalic acid (U.S. Pat. 698761, 1902, cf. Pond, J. Soc. Chem. Ind. 1907, 385); by heating pinene with anhydrous oxalic acid in presence of anhydrous chlorides, e.g.  $AlCl_3$  with the addition of a diluent (Eng. Pat. 14408, 1908); by heating turpentine with an alcohol and an acid anhydride, e.g.  $B_2O_3$  at 120°–140° (Eng. Pat. 11248, 1908); by heating pinene with an aromatic polysubstituted acid (Eng. Pat. 18049, 1908); terpenes or oils containing terpenes heated at 160° with propionic or butyric acid (Fr. Pat. 408106, 1909). Similar methods, based on the direct formation of bornyl or isobornyl esters from pinene hydrochloride, have been patented: by heating with an alkaline formate or oxalate in alcohol and water for 10 hours to 120° (Eng. Pat. 5549, 1904); by heating with metallic formates and formic acid (Eng. Pat. 14379, 1907); solid pinene hydrochloride is heated with an alkaline earth oxide in presence of excess of a lower member of the fatty acids (Fr. Pat. 393504, 1908); turpentine treated with dry hydrochloric acid gas is boiled with an alkali, alkaline earth or metallic butyrate or propionate in presence of excess of the corresponding fatty acid (Fr. Pat. 408065, 1909); by heating pinene hydrochloride in acetic acid solution with lead acetate (Fr. Pat. 349896 1904); by heating in acetic acid solution with an acetate and fused  $CaCl_2$  or  $KHSO_4$  (Eng. Pat. 1936, 1908); by heating with acetic acid in presence of zinc chloride (Eng. Pat. 8266, 1906), or some other zinc salt (Eng. Pat. 10798, 1906), and with addition of an alkali or alkaline earth salt of a formate, acetate or butyrate (Eng. Pat. 18280, 1906); by heating with the acetate of an alkaline earth for 20 hours at 180° (Fr. Pat. 375590, 1907); by heating with a fatty acid in presence of metallic zinc (Eng. Pat. 16605, 1907), or by heating with organic acids in presence of zinc (Eng. Pat. 14752, 1908); by heating with fatty acids and zinc chloride in presence of cobaltous chloride or other suitable inorganic salt (Eng. Pat. 22129, 1907); solid pinene hydrochloride is shaken with a salt of acetic or stearic acid or phenol with an excess of either acetic, stearic acid or phenol in presence of a dehydrant (Fr. Pat. 382790, 1906).

The direct conversion of pinene hydrochloride into camphor is claimed in Eng. Pat. 27317, 1913, by heating with nitric acid or its salts in presence of a catalyst, whilst two processes for the conversion of turpentine into camphor have been patented. They are: turpentine is treated with a halogen at a low

temperature,  $-25^\circ$ , until the increase in weight is 25–50 p.c., and the product, still at a low temperature, is mixed with one-eighth to one-fifth its weight of NaOH, when it is converted into camphor (Fr. Pat. 392182, 1907); turpentine in a neutral solvent is treated with nascent oxygen (Fr. Pat. 406005, 1908).

(For analyses and points of difference between natural and commercial synthetic camphor, see Crane and Joyce (J. Soc. Chem. Ind. 1907, 386), Lohmann (Ber. deut. Pharm. Ges. 1909, 19, 222), and Lenz (Arch. Pharm. 1911, 249, 289).)

*Lævo camphor*; *Matricaria camphor*. This camphor occurs naturally in the volatile oils of Feverfew, *Matricaria Parthenium* (Linn.) (Chautard, J. pr. Chem. 1848, 45, 45; Compt. rend. 1853, 37, 166); Tansy, *Tanacetum vulgare* (Linn.) (Schimmels, Rep. 1895, ii. 35); and *Artemisia Nana* (Pursh.) (Whittelsey, Chem. Zentr. 1909, ii. 2160). It is also a constituent of Ngai camphor, the solid portion of the oil of *Blumea balsamifera* (D.C.) (Schimmels Rep. 1910, i. 149). It can be prepared by oxidation of camphene obtained from levorotatory pinene (Riban, Bull. Soc. Chim. 1900, 24, 19; Darrois, Compt. rend. 1910, 150, 925), and by oxidation of *l*-borneol with nitric acid (Pope and Harvey, Chem. Soc. Trans. 1901, 79, 76). It differs from common camphor only in its behaviour towards polarised light.

Inactive camphor is a constituent of the oil of *Chrysanthemum sinense* (var.) *japonicum* (Keimatsu, J. pharm. Soc. Japan, 1909, 236, 1).

The following are the more important isomerides of camphor which occur naturally in volatile oils: *Pulegone*  $C_{10}H_{16}O$ , is only found in oils of the *Labiata*, chiefly in European Pennyroyal, *Mentha pulegium* (Linn.) (Beckmann and Fleissner, Annalen, 1891, 262, 1); *Fenchone* in its *dextro* modification is a constituent of oil of Fennel, *Foeniculum vulgare* (G.) (Wallach, Annalen, 1891, 263, 129), whilst the *lævo* variety is found in oil of Thuja, *Thuja occidentalis* (Linn.) (Wallach, Annalen, 1892, 272, 99); *Thujone* occurs in three forms, as *d*-*α*-*thujone* in Thuja oil (Paolini and Divizia, Atti. R. Accad. dei Lincei, 1912, 21, [1] 570); as *l*-*α*-*thujone* in the same oil (Wallach, Annalen, 1893, 272, 99); and as *d*-*β*-*thujone* in oil of Tansy, *Tanacetum vulgare* (Linn.) (Semmler, Ber. 1892, 25, 3343), and oil of Wormwood *Artemisia Absinthium* (Linn.) (*ibid.*); *Citral* is a frequent constituent of volatile oils and a major ingredient of the oil from *Backhousia citriodora* (F. v. M.) (Bertram, Schimmels, Rep. 1888, ii. 17), and of Lemon-grass oil, *Cymbopogon flexuosus* (Stapf.) (*ibid.*); *Sabinol* is the most important constituent of oil of Savin, *Juniperus Sabina* (Linn.) (Fromm, Ber. 1898, 31, 2025).

The more important homologues of common camphor belong to the sesquiterpene alcohols (see TERPENES). Owing to their capacity for crystallising from volatile oils some of them have long been known.

*Matico camphor*  $C_{15}H_{26}O$ , was formerly a constituent of oil of matico, *Piper angustifolium* (Ruiz et Pavon), but appears to be absent from present day oils. M.p.  $94^\circ$ ,  $[\alpha]_D -28.7^\circ$  (in chloroform). Boiling with 25 p.c. sulphuric acid converts it into a blue sesquiterpene

$C_{15}H_{24}$  (Kügler, Ber. 1883, 16, 2841; Thoms, Arbeit. Pharm. Inst. Berlin, 1905, 2, 125).

*Cedar camphor*, *Cypress camphor*, *Cedrol*  $C_{15}H_{26}O$ , is a frequent constituent of the volatile oil of *Juniperus virginiana* (Linn.), m.p.  $86^{\circ}$ – $87^{\circ}$ ,  $[\alpha]_D$  9.5 (in chloroform). It yields cedrene  $C_{15}H_{24}$  when treated with phosphoric anhydride (Walter, Annalen, 1841, 39, 247, cf. also Semmler and Mayer, Ber. 1912, 45, 1384).

*Cubebs camphor*  $C_{15}H_{26}O$ , is a constituent of the volatile oil of *Piper Cubeba* (Linn.), when it has been exposed to the air for some time. M.p.  $68^{\circ}$ – $70^{\circ}$ , b.p.  $148^{\circ}$ , with loss of water, a change which very readily takes place under various conditions of treatment forming a sesquiterpene (Schmidt, Ber. 1877, 10, 188; Schaer and Wyss, Arch. Pharm. 1875, 206, 316).

*Ledum camphor*  $C_{15}H_{26}O$ , obtained from the volatile oil of Marsh Tea, *Ledum palustre* (Linn.). Needles, m.p.  $104^{\circ}$ – $105^{\circ}$ , b.p.  $282^{\circ}$ – $283^{\circ}$ . The sesquiterpene, *ledene*  $C_{15}H_{24}$ , is readily produced by the action of dehydrating agents (Rizza, Chem. Zentr. 1887, 1257; Hjelt, Ber. 1895, 28, 3087; Lomidse, Chem. Zeit. Repert, 1903, 27, 284).

*Patchouli camphor*, *patchouli alcohol*  $C_{15}H_{26}O$ , crystallises out from patchouli oil, the product of *Pogostemon Patchouli* (Pell.), m.p.  $56^{\circ}$ ,  $[\alpha]_D$   $-97.7^{\circ}$  (in chloroform). It readily loses the elements of water forming *patchoulene*  $C_{15}H_{24}$  (Montgolfier, Compt. rend. 1877, 84, 88; Wallach, Annalen, 1894, 279, 394; Schimmels, Rep. 1905, i, 62).

*Eudesmol*  $C_{15}H_{26}O$ , is a constituent of the oils of various species of *Eucalyptus*, but especially of *E. macrorhyncha* (F. v. M.) (Baker and Smith, J. Linn. Soc. N.S.W. 1899, 33, 86). M.p.  $84^{\circ}$ ,  $[\alpha]_D$   $31.3^{\circ}$  (in chloroform) (Semmler and Tobias; Ber. 1913, 46, 2026; Semmler and Risse, *ibid.* 2303).

**Thyme and allied camphors.** *Thymol*  $C_{10}H_{14}O$ , *Isopropyl m-cresol*.

Thymol is a constituent of the volatile oils of Ajowan, *Carum copiticum* (Benth.) (Haines, Chem. Soc. Trans. 1856, 8, 289; Stenhouse, Annalen, 1855, 93, 269; *ibid.* 1856, 98, 309; Muller, Ber. 1869, 2, 130); Thyme, *Thymus vulgaris* (Linn.) (Doveri, Annalen, 1848, 64, 374; Lallemand, *ibid.* 1857, 102, 119); Wild Thyme, *T. Serpyllum* (Linn.) (Jahns, Ber. 1882, 15, 819, *Ocimum viride* (Willd.) (Goulding and Pelly, Proc. Chem. Soc. 1908, 24, 63); Horsemint, *Monarda punctata* (Linn.) (Arppe, Annalen, 1846, 58, 41); *Satureia Thymbra* (Linn.) (Schimmels, Rep. 1889, ii, 55); *Organum hirtum*, (Link.) (Holmes and Umney, Perf. and Essent. Oil Rec., 1913, 4, 73). On the manufacturing scale it is prepared from Ajowan and Horsemint Oils (cf. Holmes, Perf. and Essent. Oil Rec., 1916, 7, 311; also U.S. Dept. Agric. Bull. 372, 1916), by extraction with caustic soda solution, when the thymol forms a water soluble sodium salt, and is thus separated from the hydrocarbons. The alkaline solution is acidified with hydrochloric acid, which precipitates the crude camphor. It may then be purified by crystallisation from glacial acetic acid or alcohol. Another plan is to submit the oil to fractional distillation and to freeze out the thymol from the heavier portions of the distillate. A possible source for syn-

thetic thymol is cymene (U.S. Pat. 1306512, 1919).

Thymol has the odour of thyme and a warm pungent taste; m.p.  $50.5^{\circ}$ – $51.5^{\circ}$ ; b.p.  $232^{\circ}$  at 752 mm. It is sparingly soluble in water (1 : 1200) and glycerine (1 : 1000), but readily in the usual organic solvents and alkaline solutions. It forms a liquid with menthol (Kyle, Amer. J. Pharm. 1885, 429); camphor (Symes, Pharm. J. 1879, [3] 9, 598); berberine (Lloyd, New Remedies, 1881, 195); but not with chloral hydrate (Symes, cf. Mazzara, Gazz. chim. ital. 1883, 13, 272). If a solution containing thymol be warmed with half its volume of glacial acetic acid, together with more than its volume of sulphuric acid, a deep red-violet colour is developed. This reaction is obtained even in very dilute solutions. For the further identification of thymol use is made of the *phenyl carbamate*  $C_{10}H_{13}OCONHPh$ , m.p.  $107^{\circ}$  (McKenzie and Semmler, Ber. 1906, 39, 1158), and *nitrosothymol*  $C_{10}H_{13}O(NO)$ , m.p.  $160^{\circ}$ – $162^{\circ}$  (Schiff, Ber. 1875, 8, 1500). The *methyl ether of thymol*  $C_{10}H_{13}OMe$  occurs naturally in the essential oil of sea-samphire, *Crithmum maritimum* (Linn.) (Delépine and Belsunce, Bull. Soc. Chim. 1918 [iv.] 23, 24).

For estimation of thymol in essential oils, Kremers and Schreiner (Chem. Zentr. 1897, ii, 147, cf. Messinger and Vortmann, Ber. 1890, 23, 2753) recommend the following process: A known weight of the sample is mixed with an equal volume of light petroleum in a stoppered burette, and agitated with half its volume of aqueous caustic soda till no further diminution of the oily layer takes place, and a drop of the oil dissolved in 20 drops of chloroform, on gently warming with a small piece of sodium hydroxide, does not turn red. The decrease in volume is observed or the alkaline liquor can be titrated with iodine, but it appears the results obtained by titration are about 3 p.c. lower. (For iodometric estimation, see also Messinger (J. pr. Chem. 1900, [2], 61, 247).

(For the estimation of the purity of thymol, see Seidell (Amer. Chem. J. 1912, 47, 508); Elion (J. Amer. Chem. Soc. 1917, 39, 1513); Redman, Weith and Brock (J. Ind. Eng. Chem. 1913, 5, 831).)

Thymol is extensively used in medicine on account of its strong antiseptic properties. In its general behaviour it resembles carbolic acid. It has also been used internally as a vermicide. Of its derivatives a great number have been tried in medicine, but only three have been used to any extent: *Thymol iodide* (Messinger and Vortmann, Ber. 1890, 23, 2754; Carswell, Chem. News, 1893, 68, 181; D.R.P. 49739, 1889) obtained by condensation of two molecules and the introduction of two atoms of iodine is used as a substitute for iodoform; *thymoform*  $[C_{10}H_{13}O]_2CH_2$  (D. R. P. 99610, 1898) used as an antiseptic dusting powder; *thymol carbonate*  $(C_{10}H_{13}O)_2CO$  (Richter, J. pr. Chem. 1883, [2] 27, 505) is used as an anthelmintic.

**Camphors isomeric or homologous with thyme camphor.** *Carvone*, formerly *carvol*  $C_{10}H_{14}O$ , b.p.  $230^{\circ}$ , is a liquid isomeric contained in the following volatile oils: Caraway seed, *Carum carvi* (Linn.) (Wallach, Annalen, 1893, 277, 107), and Dill-fruit *Anethum graveolens* (Linn.) (Gladstone, Chem. Soc. Trans. 1872, 25, 1), both



containing 50 to 60 p.c. d-carvone, whilst l-carvone is contained in the volatile oils of Spearmint, *Mentha viridis* (Linn.) (Gladstone, *ibid.* Flückiger, Ber. 1876, 9, 473); Kuromoji, *Lindera sericea* (Bl.) (Kwasnik, Arch. Pharm. 1892, 230, 265). i-Carvone has been found in Ginger-grass oil, *Cymbopogon Martini* (Stapf.) (var.) *Sofia* (Walbaum and Hüthig, Schimmels, Rep. 1905, i. 34). For the isolation of carvone, its power of combining with sulphuretted hydrogen to form a crystalline hydrosulphide ( $C_{10}H_{14}O_2H_2S$ , m.p.  $210^{\circ}$ – $211^{\circ}$ , is employed (Flückiger, Ber. 1875, 9, 468; Wallach, Annalen, 1899, 305, 224); but a simpler process is to form the water soluble compound with neutral sodium bisulphite (cf. Sadtler, J. Soc. Chem. Ind. 1904, 23, 303). On reduction carvone yields dihydrocarveol  $C_{10}H_{18}O$ , a constituent of Caraway Oil (Schimmels, Rep. 1905, i. 50).

Carvacrol, cymophenol  $C_{10}H_{14}O$ , Isopropyl o-cresol is a thick oil, solidifying at  $0^{\circ}$ , b.p.  $236^{\circ}$ – $237^{\circ}$ , closely related to thymol. It is formed by distilling carvone in presence of sulphuric acid, phosphoric acid, or caustic potash, and occurs mainly in various thyme, origanum and monarda oils. It may also be obtained by chemical means from Spruce Turpentine (U.S. Pat. 1265800, 1918; cf. also J. Ind. Eng. Chem. 1918, 10, 982). For its identification the phenylcarbamate  $C_{10}H_{13}OCO-NHPh$ , m.p.  $140^{\circ}$  (Gildemeister, Arch. Pharm. 1895, 233, 188) and its nitroso-derivative  $C_{10}H_{13}O(NO)$ , m.p.  $153^{\circ}$  (Klages, Ber. 1899, 32, 1518), are especially suitable.

Irone  $C_{13}H_{20}O$  is a constituent of oil of orris, the product of distillation of *Iris germanica* (Linn.), *I. pallida* (Lam.), and *I. florentina* (Linn.) (Tiemann and Krüger, Ber. 1893, 26, 2675). In the diluted state it has an odour of violets. B.p.  $111^{\circ}$ – $112^{\circ}$  at 2 mm.,  $144^{\circ}$  at 16 mm. It has been synthesized from acetone and  $\Delta_4$ -cyclocitral (Merling and Welde, Annalen, 1909, 366, 119), see PERFUMES.

Santalol  $C_{15}H_{24}O$  is a liquid camphor obtained from the volatile oil of sandalwood, *Santalum album* (Linn.). The commercial product known under various trade names is prepared by steam distillation of the finely divided sandalwood. The bulk of the world's supply comes from Mysore, where it was being distilled locally (Perf. and Essent. Oil Rec. 1917, 8, 359). The physiological action of the oil is attributed to its alcoholic constituent, santalol, which is present to the extent of about 90 p.c., and has been separated into a-santalol, a thick colourless liquid with a faint odour of sandalwood, b.p.  $301^{\circ}$ – $302^{\circ}$ ,  $[\alpha]_D^{20} +1^{\circ} 13'$ , and  $\beta$ -santalol, b.p.  $158^{\circ}$  at 5 mm.,  $[\alpha]_D^{20} -41^{\circ} 47'$  (von Soden, Arch. Pharm. 1900, 238, 353, Schimmels, Rep. 1910, ii. 107).

The oxygen content of the foregoing camphors is one atom. The following contain two atoms of oxygen: Diosphenol, *Buchu camphor*  $C_{10}H_{16}O_2$ , a crystalline separation from oil of Buchu leaves, *Barosma betulina* (Bartl.), *B. crenulata* (Hook.), *B. serratifolia* (Willd.) (Flückiger, Pharm. J. 1880, [3] 11, 174, 219), is closely related to thymol and carvacrol, into which it passes quantitatively by the action of concentrated hydrochloric acid at  $150^{\circ}$ – $180^{\circ}$ . M.p.  $83^{\circ}$ – $84^{\circ}$ , b.p.  $109^{\circ}$ – $110^{\circ}$  at 10 mm. It is

characterised by its reduction of ammoniacal silver solution and Fehling's solution (Semmler and McKenzie, Ber. 1906, 39, 1158; Kondakoff and Bachtscheef, J. pr. Chem. 1901, [2] 63, 61).

*Insula* or *Alant camphor*, alantolactone  $C_{15}H_{20}O_2$  is the chief constituent of oil of Elecampane, *Insula Helenium* (Linn.) (Kallen, Dissert. Rostock, 1895). M.p.  $76^{\circ}$ , b.p.  $275^{\circ}$ , with partial decomposition (Bredt. and Posth, Annalen, 1895, 285, 349). It dissolves in alkalis with formation of the corresponding hydroxy acid, which melts at  $94^{\circ}$ . The lactone has been used in medicine, under the name 'helenin,' as an antiseptic for internal use. (See also Sprinz, Arch. Pharm. 1901, 239, 201.)

H. K.

**CAMPHORAL.** Trade name for the camphoric acid ester of santalol.

**CAMPHOSAN.** A solution of camphoric acid methyl ester in santalol.

**CAMWOOD.** Camwood or 'cambe wood,' stated to be derived from a variety of *Baphia nitida* (cf. barwood), is very similar in general properties to the other 'insoluble red' dye-woods. It is, however, more expensive, yields deeper shades on dyeing, and its colouring matter is said to be more soluble than that present in the other woods.

It has been examined by O'Neill and Perkin (Chem. Soc. Trans. 1918, 113, 126), who employed for this purpose similar methods to those found serviceable with sanderswood (l.c.).

*Iso-santalin*, the main colouring matter, forms a chocolate-coloured powder, which on grinding becomes redder in appearance, and is readily soluble in boiling methylated spirit. When heated, it shows no sign of melting, darkens at  $280^{\circ}$ , and is fully decomposed at  $290^{\circ}$ – $300^{\circ}$ , being then a carbonaceous powder. It possesses the formula  $C_{22}H_{16}O_6(OCH_3)_2$ , gives with alcoholic potassium acetate the salt  $C_{96}H_{83}O_{32}K$  or  $C_{72}H_{65}O_{24}K$ , shows evidence of the formation of soluble oxonium salts, and in general properties closely resembles its isomer santalin. The colour reactions and also the dyeing properties of the two compounds indicate, however, that they are distinct substances:—

	Santalin.	Iso-santalin.
Alcoholic hydro-bromic acid . . .	Crimson.	Reddish-violet
Dilute sodium hydroxide . . .	Dull red.	Dull violet.
Alcoholic ferric chloride . . .	Violet.	Bluish-violet.

For dyeing the colouring matter in alcoholic solution was added to the water in the dye-bath and the dyeings were carried out (a) employing wool alone, (b) employing wool alone and subsequently saddening with bichrome, (c) employing wool mordanted with bichrome and cream of tartar, and (d) employing wool mordanted with bichrome and sulphuric acid.

	(a)	(b)
Santalin . . .	Pale dull red.	Dull reddish-brown.
	(c)	(d)
Santalin . . .	Pale reddish-pink.	Pale red-pink.

	(a)	(b)
<i>Iso-santalin</i>	Pale violet-red.	Dull violet-maroon.
	(c)	(d)
<i>Iso-santalin</i>	Violet-red.	Violet-red weaker than (c).

*Acetyl-iso-santalin*  $C_{24}H_{18}O_8(C_2H_3O)_4$ , consists of a deep salmon-coloured powder, and does not possess a definite melting-point, being gradually decomposed without fusion between  $250^{\circ}$ – $280^{\circ}$ . A molecular weight determination employing naphthalene gave the high figure 2344, a result very similar to that given in these circumstances by acetyl-santalin itself, and which may possibly be due to the production of a colloidal solution.

*Deoxy-iso-santalin*  $C_{24}H_{18}O_2(OCH_3)_2$ , corresponding to the deoxysantalin of sanderswood, is a scarlet amorphous powder which has not yet been obtained in a definitely crystalline condition. When heated, it did not show a distinct melting-point, but decomposed at  $160^{\circ}$ – $165^{\circ}$  with evolution of gas. A solution of this substance in absolute alcohol gives no immediate precipitate with potassium acetate, as happens in the case of iso-santalin, and only when excess of the reagent is employed is a gelatinous deposit formed.

A comparison of the colour reactions and dyeing properties of deoxy-iso-santalin (a) and deoxy-santalin (b) is given in the following table:—

	(a)	(b)
Alcoholic solution	Orange.	Orange-brown.
Alcoholic hydrobromic acid	Bright crimson.	Scarlet.
Dilute sodium hydroxide	Crimson-scarlet.	Scarlet.
Alcoholic ferric chloride	Violet.	Maroon.

The dyeing experiments were carried out by the same methods as those described above.

	(a)	(b)
Deoxy-iso-santalin	Pale red-violet.	Red puce.
	(c)	(d)
Deoxy-iso-santalin	Dull red-violet.	Pale dull red-violet.
	(a)	(b)
Deoxy-santalin	Red.	Dull bluish-red.
	(c)	(d)
Deoxy-santalin	Dull crimson	Red.

*Acetyl-deoxy-iso-santalin*  $C_{24}H_{20}O_7(C_2H_3O)_4$ , when heated, fused and decomposed at  $170^{\circ}$ – $175^{\circ}$ . It consists of an almost colourless powder differing considerably in appearance from acetyl-iso-santalin. A molecular weight determination, employing naphthalene as solvent, gave the figure 1324, which is approximately half that found in the same circumstances for acetyl-iso-santalin.

By exhaustion with alcohol the sample of camwood employed by these authors gave 16 p.c. of extract.

Camwood does not appear to contain either ptero-carpin or homoptero-carpin. A. G. P.

**CANADA BALSAM** *v.* BALSAMS; and OLEO-RESINS.

**CANADA PITCH** or **HEMLOCK SPRUCE RESIN** *v.* RESINS.

**CANADINE**. A member of the isoquinoline group of alkaloids, occurring together with hydrastine and berberine in *Hydrastis Canadensis*. See under HYDRASTINE.

**CANADIUM**. A term formerly applied to a supposed new element; now used to denote an alloy of 1 part palladium, 2 parts of platinum, and 6 parts of nickel, used as a substitute for platinum. It has similar resisting powers, and melts at about  $1570^{\circ}$ . Its cost is about half that of platinum (Heath, Met. and Chem. Eng. 1917, 17, 666).

**CANADOL**. Petroleum ether or ligroin. That portion of refined petroleum which boils at about  $60^{\circ}$  and has sp.gr. of 0.65 to 0.70; consists mainly of normal hexane (*v.* PARAFFIN; and PETROLEUM).

**CANANGA OIL** *v.* OILS, ESSENTIAL.

**CANARIN**. A yellow colouring matter obtained by the action of bromine or a mixture of potassium chlorate and hydrochloric acid or ammonium persulphate upon potassium or ammonium thiocyanate; it probably consists of  $C_8H_6ON_3S_7$  (Goldberg, J. pr. Chem. 1901, ii, 63, 465; 64, 439; cf. H. Schmid, Dingl. poly. J. 251, 41). (For details of mode of preparation, *v. ibid.* 253, 130; also J. Soc. Chem. Ind. 3, 476). Cloth dyed with canarin resists light and soap. Neither concentrated acids nor alkalis destroy it or dissolve it out of the fibre. Bleaching powder has no action upon it. Acts as a mordant for basic aniline dyes.

**CANDELILLA WAX**. Candelilla wax occurs as a deposit on the surface of the candelilla plant (probably *Euphorbia antisiphilitica*), which grows wild in Mexico and Texas. Originally the wax was separated by boiling the parts of the plant with water, but of recent years a method of extraction with chloroform has been introduced, some of the works being capable of dealing with 5 tons a day. From 2.5 to 6 p.c. of crude wax is obtained, and is purified by straining and melting in water containing 0.5 to 1 p.c. of sulphuric acid. The crude grey product contains up to 6.5 p.c. of water, 3 to 15 p.c. of dirt, and 0.5 to 1.5 p.c. of mineral matter. The purer red or brown variety is probably obtained by the extraction method (Berg, Chem. Zeit. 1914, 38, 1162).

Several methods of extraction have been patented. In Sharp's process (U.S. Pat. 1018589, 1912) the wax plant is boiled with petroleum spirit in the presence of fuller's earth, the extract clarified, and the solvent evaporated. In Watson's patent the plants are heated to  $149^{\circ}$ , and subjected to the action of a downward current of steam (U.S. Pats. 1042992, 1912, and 1058648, 1913). A special form of extractor devised by Thatcher (U.S. Pat. 1056378, 1913) comprises a digesting compartment, reservoir for the solvent, and vaporisers to evaporate the solvent.

The crude greenish-grey wax melts at  $67^{\circ}$ – $68^{\circ}$ , and has sp.gr. at  $15^{\circ}$ , 0.9825–0.9850; acid value 12.4–14.39; saponification value,



46.1-64.9; iodine value, 16.6-36.8; unsaponifiable matter, 77-91.2 p.c., largely consisting of hydrocarbons. The constituents identified include hentriacontane, dotriacontane (m.p. 71°), myricyl alcohol, two cholesterol, an oxylactone (m.p. 88°), and resinous constituents giving the Liebermann-Storch reaction (Fraps and Rather, *J. Ind. Eng. Chem.* 1910, 2, 454; Hare and Bjerregaard, *ibid.* 1910, 2, 203; Sanders, *Chem. Soc. Proc.* 1911, 250; Meyer and Soyka, *Monatsh. Chem.* 1913, 34, 1159; Berg, *l.c.*).

A difficulty attending the use of the pure brown or red wax, is that it can only be bleached after the addition of a considerable quantity of paraffin wax, and is therefore only suitable for the manufacture of inferior kinds of varnish, for insulating telephone wires, and especially for boot polishes, for which its low m.p. is an advantage. For other purposes, such as candle-making, it is inferior to carnauba wax (m.p. 83-91°) (*v. WAXES*).

C. A. M.

**CANDLES.** Candles represent some of the most ancient and most useful forms of illuminants. The excellence of a candle depends on the nature of the wick and of the combustible matter, and on the manner and extent in which these are apportioned. The prototype of the candle was undoubtedly the torch, which must be regarded as a huge wick with the minimum amount of combustible matter, this proportion being gradually altered until the ratio used at present, viz. about 1 part wick to 50 parts of combustible matter, is reached.

*The following table shows the stages in the development of candles.*

**Torch.** Pine branches or slips (Lat. *tæda*), saturated, naturally or artificially, with resinous or fatty matter.

**Link.** Rope-strands steeped in rosin, tar, or pitch; in olden times, doubtless, in asphalt or bitumen.

**Flambeau.** A core of hemp, soaked in rosin and coated with crude beeswax. Later, the outer coat was made of bleached wax.

**Dips.** Wicks of rush-pith (rush-lights), crude flax or cotton, and subsequently of twisted cotton yarn, coated with beeswax or tallow by repeated dippings.

**Moulds.** (Introduced about the 15th century by the Sieur de Brez.) Hard tallow, spermaceti, stearine, or paraffin wax, cast round the wick in a mould.

In addition to these varieties may be mentioned *rolled, poured, and drawn* candles.

**Dips**, the cheapest, as well as the oldest form of candle, were made until comparatively lately of tallow or household grease. Beeswax candles were usually poured, drawn, or rolled. The great advantage of the 'dip' lies in the ease with which it can be made. The thrifty house-keeper was wont to set aside the superfluous kitchen fat for melting day, when part went to make soap, whilst the harder portions were formed into candles. The fat was thrown into boiling water and boiled three or four times with a little salt to 'render' it. The dirt and impurities being removed by subsidence, the clean liquid fat was run through a strainer into the candle pan. Some skill and experience were required to regulate the temperature of the melted fat. If too hot, the liquid fat would run

off the wicks; if too cold, the material would congeal too quickly and adhere to the wicks irregularly and in lumps. In households these would be rushes, divested of their peel with the exception of a thin strip which was left to give strength to the pith. These were usually tied in bunches of four, so that one wick could be held between each pair of fingers, and thus be immersed in the liquid fat. A short time was allowed for each dipping to cool the last coat. Four dippings mostly sufficed, when the finished candles were hung up in an airy loft to harden and whiten.

In dips as manufactured on a large scale, the wicks are of twisted cotton, and are strung on rods, each rod holding eight. The workman, holding an end of the rod in either hand, first immerses the wicks in very hot tallow, in order that their fibres may be thoroughly saturated, and then, as each rod is ready, it is slid on to a cross frame to cool; the wicks are then re-dipped in tallow at a temperature little above its solidifying point, till the desired weight is obtained. As a rule four 'dippings' are required.

Many devices exist for reducing labour and ensuring uniformity of result in manufacturing dips. Of these contrivances, the 'Edinburgh wheel' is the best known. It consists of a long pole, pivoted vertically, and having mortises cut about its centre through which pass long wooden bars, each pivoted at its centre on an iron pin. These bars carry frames at their extremities, each of which, in its turn, holds about eight wick-rods. The post revolves, and as each bar with its frame passes over the melting pan, it is pulled down, so as to immerse the wicks. The opposite frame restores equilibrium, and the rotating and dipping are continued until the proper weight is obtained, which is signalled by some contrivance on the post, itself the object of much inventive ingenuity. The most perfect apparatus of this kind was patented by Price's Candle Company and worked at the Inventions Exhibition in London in 1885.

**Rolled, poured, and drawn candles.** Rolled candles are now almost obsolete. Formerly, the larger sizes of church candles were made by 'rolling' a cake of warm wax, kneaded until it was plastic, round a wick, and imparting the necessary smoothness and uniformity by means of a rolling-pin. This process has now been entirely superseded by that of 'pouring.' 'Drawing' is resorted to only in the case of 'cables' of small sizes, and tapers.

In *pouring*, an apparatus similar to that used in dipping is employed, but instead of the wicks being dipped, the melted beeswax is poured over them while the frame is kept in rotation (Fig. 1). In the larger sizes, the wicks have to be reversed from time to time to ensure a uniform thickness. The workman ascertains the correct dimensions by measuring with a piece of tape. After every two or three pourings, according to the weather, the hoops are hung in a current of air to cool. When the candles are of the requisite thickness, they are severed from the frame and placed on a smooth marble slab. The operator then rolls them to and fro under a board, on which he leans with his full weight. By this process, which requires much skill and practice, the irregularities are smoothed away,