THE OLEFINE SERIES OF HYDROCARBONS.

The Olefine Series of Hydrocarbons consists of *unsaturated* hydrocarbons having the general formula C_nH_{2n}. *Ethylene*, C_2H_4; *Propylene*, C_3H_6; *Butylene*, C_4H_8; *Amylene*, C_6H_{10}; *Hexylene*, C_6H_{12}; and *Heptylene*, C_7H_{14}, are well known.

Ethylene, Olefiant Gas, or *Heavy Carburetted Hydrogen*, C_2H_4, is the first of this series. It is formed in the destructive distillation of coal, and is the chief illuminating constituent of coal gas. Coal gas consists of 30 to 40 per cent. of methane, 40 to 50 per cent. of hydrogen, and from 5 to 7 per cent. of ethylene and its homologues. Hydrocarbons, normally fluid, but kept in the vaporous condition by the diluents, also contribute materially to the illuminating power of gas. The impurities are nitrogen, air, carbolic acid, bisulphide of carbon, CS_2, and some badly smelling sulphur compounds. Upward of one hundred and fifty distinct chemical substances have been obtained from the solid, liquid, and gaseous products of the destructive distillation of coal.

Preparation.—Ethylene may be prepared by dropping alcohol into a large retort or flask containing 10 ounces of sulphuric acid and 3 ounces of water heated to 160°–165° C. The gas is washed in cold water and a solution of soda, to free it from ether, alcohol, and sulphurous acid:—

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ethylhydrogen sulphate.}}{C_2H_5HSO_4} + \underset{\text{Water.}}{H_2O.}$$

The product, when further heated, yields ethylene,—

$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

If the ethylene be passed into bromine under water until all the bromine disappears, *ethylene dibromide*, $C_2H_4Br_2$, or *dibrom-ethane*, will be formed.

Properties.—A colorless, odorless, condensable gas, burning with a luminous flame.

Ethylene Sulphate, $C_2H_4SO_4$, is probably contained in the *Spiritus Ætheris Compositus*, U. S. P., a solution of 3 parts of *ethereal oil* in 30 of stronger ether and 67 of alcohol. The so-called ethereal oil or heavy oil of wine is obtained by digesting spirit of wine and sulphuric acid together, then distilling, removing any acid from the distillate by washing with lime-water, and exposing the ethereal fluid to the air to facilitate escape of the more volatile fluids. The product is a mixture consisting probably of ethylene sulphate, ethyl sulphate, ether, dissolved ethylene, and other bodies.

Glycols.—The olefines form dihydric alcohols or glycols (named from glycol, the first member of the series), and these give two sets of aldehydes and acids. Thus,—

$$\underset{\text{Glycol.}}{\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}} \qquad \underset{\text{Glycol.}}{\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}} \qquad \underset{\text{Glycolic aldehyde.}}{\begin{array}{c}CH_2OH\\|\\COH\end{array}} \qquad \underset{\text{Glyoxal or Oxalic aldehyde.}}{\begin{array}{c}COH\\|\\COH\end{array}}$$

$$\underset{\text{Hydroxyacetic acid or Glycollic acid.}}{\begin{array}{c}CH_2OH\\|\\COOH\end{array}} \qquad \underset{\text{Oxalic acid.}}{\begin{array}{c}COOH\\|\\COOH\end{array}}$$

Relation of Paraffins to Olefines.

1st. The paraffins may be converted into olefines either by acting on an alcohol of the paraffin series by sulphuric acid, or by acting on a monochloro-paraffin by caustic potash.

$$\underset{\text{Monochlorethane.}}{C_2H_5Cl} + KHO = \underset{\text{Ethylene.}}{C_2H_4} + KCl + H_2O$$

Inversely, the olefines may be converted into paraffins. By combining an olefine with hydrochloric acid a monochloro-paraffin results, which when acted on by nascent hydrogen yields a paraffin.

$$\underset{\text{Ethylene.}}{C_2H_4} + HCl = \underset{\text{Monochlorethane.}}{C_2H_5Cl}$$

$$\underset{\text{Monochlorethane.}}{2C_2H_5Cl} + H_2 = \underset{\text{Ethane.}}{2C_2H_6}$$

2d. The bromine, chlorine, and iodine additive derivatives of the olefines are either identical or isomeric with the substitution-derivatives of the paraffins. Thus, $C_2H_4Cl_2$ is either dichlorethane or ethylene chloride; and the additive derivatives with the acids, such as hydrochloric, produce mono-substitution-derivatives of the paraffins. In the case of the chloride, however, $C_2H_4Cl_2$, it has a different boiling-point and specific gravity according as it is prepared from ethylene and chlorine (*chloride of ethylene*, alpha-dichlorethane, or the old "Dutch liquid"), or from monochlorethane (chloride of ethyl) and chlorine (chloride of monochlorethyl, beta-dichlorethane, or *chloride of ethylidene*). The former may be represented by the formula $CH_2Cl.CH_2Cl$, and the latter as $CH_3.CHCl_2$. It is the former also which yields glycol (by reaction of the chloride with silver acetate, and of the resulting ethylene acetate with an alkaline hydrate), hence the formula of the glycol also must be $CH_2OH.CH_2OH$, and not $CH_3.CH(OH)_2$:—

$$\underset{\text{Chloride of ethylene (Dutch liquid).}}{\begin{array}{c}CH_2Cl\\|\\CH_2Cl\end{array}} \qquad \underset{\text{Hydrate of ethylene (glycol).}}{\begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}}$$

THE ACETYLENE SERIES OF HYDROCARBONS.

The acetylene series, C_nH_{2n-2}, are characterized by forming metallic substitution-derivatives. *Acetylene* itself, C_2H_2, is formed during

TABLE SHOWING THE RELATIONS BETWEEN THE PARAFFINS, OLEFINES, AND ACETYLENES.

	Paraffin, C_nH_{2n+2}.	Olefine, C_nH_{2n}.	Acetylene, C_nH_{2n-2}.
Hydrocarbon . . .	Ethane, C_2H_6, or $CH_3.CH_3$	Ethylene, C_2H_4	Acetylene, C_2H_2.
Alkyl Salts Chloro-derivatives . .	Monochlorethane, or Ethyl Chloride, C_2H_5Cl	Ethylene Chloride, or Dichlorethane, $C_2H_4Cl_2$	Acetylene Chloride, or Tetrachloroethane, $C_2H_2Cl_4$.
Alcohol	Ethylic Alcohol, C_2H_5OH, or CH_3CH_2OH	Ethylene Glycol, $C_2H_4(OH)_2$, or $(CH_2OH)_2$	
Acid	Acetic Acid, $CH_3CO.OH$	Oxalic Acid $(COOH)_2$	
Cyanide	Cyanoethane, CH_3CH_2CN	Ethylenic Cyanide, or Dicyanethane, $C_2H_4(CN)_2$	

the passage of electric sparks between carbon points in the atmosphere of hydrogen; it is the only member which can be formed directly from its elements. Other members of the series are, *Allylene*, C_3H_4; *Crotonylene*, C_4H_6, etc. The hydroxyl derivative of allylene, known as *propargyl alcohol*, has the formula C_3H_3OH.

Preparation.—Acetylene may be obtained by heating ethylene bromide (dibromethane) with caustic potash, and passing the gas into a well-cooled ammoniacal solution of cuprous chloride, with which it combines, forming a red precipitate, probably having the formula $(C_2H_3Cu_2)_2O$ (Berthelot), called cuprous acetylide. Pure acetylene may be obtained from the copper compound by heating with hydrochloric acid. Acetylene is also formed by the incomplete combustion of coal gas, as when an air-gas burner is lighted below. It has an unpleasant odor, well known in every chemical laboratory in which air-gas lamps are used.

QUESTIONS AND EXERCISES.

691. What are the properties of ethylene, and how is it prepared?
692. What alcohols are derived from the olefine series?
693. Mention the relations between the paraffins and olefines.
694. Give three methods of preparing acetylene.

THE TERPENE SERIES OF HYDROCARBONS.

The terpene series have the following general formula: C_nH_{2n-4}. *Valylene*, C_5H_6, is the lowest, and *Terebenthene*, $C_{10}H_{16}$, or pure oil of turpentine, the most common member of the series.

The hydrocarbons, called terpenes, $C_{10}H_{16}$, are very commonly met with in analyzing the volatile oils. Very few of these oils have been artificially produced. Their fragrance appears to be due to the non-terpenoid constituent (Wallach). They differ from one another in the power of deviating a ray of polarized light to the right or left. They may be divided into two classes: (*a*) *Terpenes*, boiling at about 156° C., and found in the ordinary turpentine oils; and (*b*) *Citrenes* (*limonenes*), boiling at about 177° C. and derived from the different species of citrus.

Oil of *Turpentine* (*Oleum Terebinthinæ*, U. S. P.).—Turpentine itself is really an oleo-resin of about the consistence of fresh honey. It flows naturally or by incision from the wood of most coniferous trees; larch (*Larix Europa*) yielding *Venice turpentine*, *Abies balsamea* furnishing *Canadian Turpentine* or *Canada Balsam* (*Terebinthina Canadensis*, U. S. P.), the *bark* of *Pistachia terebinthus* the variety termed *Chian Turpentine* (containing about 1 part of essential oil to 7 of resin), and the *Pinus Australis* (*palustris*), *P. abies*, *P. pinaster*, and *P. tæda* affording the common American Turpentine (*Terebinthina*, U. S. P.). *Pinus maritima* gives the French or Bordeaux Turpentine, and *P. picea* the old fragrant Strasburg Turpentine. By distillation with steam this crude tur-

pentine is separated into colophony, *rosin*, which remains in the still, and *essential oil of turpentine*, often termed simply *turpentine*, *spirit of turpentine*, or "*turps*," which distils over. Mixed with alkali to saturate resinous acids, and redistilled in a current of steam, oil of turpentine furnishes about 80 per cent. of *rectified oil of turpentine*. *Pinus sylvestris* and *P. Ledebourii* furnish Russian Turpentine, which, according to Tilden, consists of two turpenes and cymene, and also (Wallach) a lævogyre limonene. This turpentine is probably a by-product in the preparation of common *wood tar* (*Pix Liquida*, U. S. P.); its odor is very pleasant, quite different from that of ordinary turpentine. The leaves of the *Pinus sylvestris*, or Scotch fir, are in Germany broken down to a woolly condition, producing Pine Wool or Fir Wool, or wadding used in making vermin-repelling blankets; and this substance—or, still better, the fresh leaf—by distillation with water yields *Fir-Wool Oil* (*Oleum Pini Sylvestris*, B. P.), consisting, according to Tilden, of two turpenes, like those of Russian turpentine, and cymene. This oil, diffused through water by aid of magnesia, forms the *Vapor Olei Pini Sylvestris*, B. P. The terpene of Bordeaux turpentine (terebenthene) rotates a ray of polarized light more than, and in the opposite direction to, the terpene of American turpentine.

Turpentine "commences to boil at about 320° F. (160° C.), and almost entirely distils below 356° F. (180° C.), little or no residue remaining," whereas petroleum spirit, with which turpentine might be mixed, covers much wider limits of temperature during its distillation. Petroleum spirit also, when the small round flame of the end of a piece of twine is brought near to some of the spirit in a cup, gives a momentary flash of flame at a much lower temperature than that at which turpentine flashes. Thus tested in the specially arranged flashing apparatus of the Petroleum Act, Mr. Boverton Redwood found that the flashing-point of turpentine was lowered 10 degrees Fahrenheit by 1 per cent. of petroleum spirit. The specific gravity of oil of turpentine is from about 0.855 to 0.870.

Under the influence of heat and sulphuric acid or other chemical agents pure oil of turpentine ($C_{10}H_{16}$) yields many derivatives of considerable chemical interest. Amongst them are two optically inactive terpene isomers named *terebene* and *colophene*, used for inhalation and as disinfectants and deodorizers. When acted on by gaseous hydrochloric acid, the product is a white crystalline monohydrochloride, $C_{20}H_{16}HCl$. Bromine acts violently on turpentine and terpenes, resulting in dibromides which yield cymene when heated.

$$C_{10}H_{16}Br_2 = C_{10}H_{14} + 2HBr.$$

Volatile Oils.

Most of the *Volatile* or *Essential Oils* contain terpenes, the constitution of which are at present but imperfectly known. The oils exist in various parts of plants—at first, probably, as mere combinations of carbon and hydrogen; but such *hydrocarbons* are prone to

change when in contact with oxygen or moisture; hence these liquids, even when freshly obtained from the plants, and more especially as they occur in pharmacy, are usually mixtures of the liquid hydrocarbons or *elæoptens* (from ἔλαιον, *elaion*, oil, and ὄπτομαι, *optomai*, I see) with oxidized hydrocarbons, which are commonly solid or camphor-like bodies termed *stearoptens* (from στεαρ, *stear*, suet), and which on cooling often crystallize out; or on distilling an oil the stearopten may remain in the retort, being less volatile than the elæopten. Volatile oils should, obviously, be preserved in well-closed bottles. Oxidation also proceeds more slowly in a cold than in a warm temperature. The oils are also often associated with further oxidized bodies termed *resins*. Of the hydrocarbons, those most commonly occurring are identical with, or are isomers of, that from oil of turpentine, and these terpenes are easily converted into their polymers, $C_{15}H_{24}$ and $C_{20}H_{32}$, by the action of heat, strong acids, etc.

The process by which volatile oils are usually obtained from herbs, flowers, fruits, or seeds may be imitated on the small scale by placing the material (bruised cloves or caraways, for instance) in a tubulated retort, adapting the retort to a Liebig's condenser, and passing steam, from a Florence flask, through a glass tube to the bottom of the warmed retort. The steam in its passage through the substance will carry the particles of oil over the neck of the retort into the condenser, and thence, liquefied and cooled, into the receiving vessel, where the oil will be found floating on the water. It may be collected by running off the distillate through a glass funnel having a stopcock in the neck, or by letting the water from the condenser drop into an old test-tube which has a small hole in the bottom, or any similar tube placed in a larger vessel, the water and oil being subsequently run off separately from the tube as from a pipette. Volatile oils, like fixed oils, stain paper; but the stain of the former is not permanent like that of the latter. Oils of lemon and orange are sometimes obtained by mere pressure of the rind of the fruit.

The following official (U. S. P.) waters are made by distributing 2 parts of volatile oil over the large surface afforded by 4 parts of cotton, and percolating with 1000 parts of distilled water: *Aquæ Anisi*, *Cinnamomi*, *Fœniculi*, *Menthæ Piperitæ*, *Menthæ Viridis*. *Aqua Aurantii Florum*, U. S. P., and *Aqua Rosæ*, U. S. P., are obtained by distilling 40 parts of flowers with 200 of water.

The presence of alcohol in an essential oil may be detected and its quantity estimated by shaking with an equal bulk of pure glycerin. The latter dissolves the alcohol, and is augmented in volume according to the amount of alcohol present (Boettger). (For test for alcohol, see Index, "Alcohol.")

A large number of volatile oils are employed in medicine, either

in the pure state, in the form of saturated aqueous solution (medicated water), solution of spirit of wine, 1 in 5 (*Essentia Anisi* and *Essentia Menthæ Piperitæ*, B. P.) and 1 in 50 (*Spiritus Cajuputi*, *Juniperi*, *Lavandulæ*, *Menthæ Piperitæ*, *Myristicæ*, *Rosmarini*—B. P.), or as leading constituents in various barks, roots, leaves, etc. The strength of *Spiritus Anisi*, U. S. P., and *Sp. Cinnamomi*, U. S. P., is 10 of oil to 90 of alcohol. *Sp. Menthæ Piperitæ*, U. S. P., and *Sp. Menth. Viridis*, U. S. P., are of similar strength, but also contain whatever may be extracted by the 100 parts of the spirit from 1 part of the dried herb. *Spiritus Aurantii*, U. S. P., contains 6 of oil and 94 of alcohol; *Sp. Gaultheriæ*, U. S. P., *Sp. Juniperi*, U. S. P., *Sp. Lavandulæ*, U. S. P., and *Sp. Myristicæ*, U. S. P., contain 3 of oil and 97 of alcohol; *Spiritus Limonis*, U. S. P., is made with 6 of oil, 4 of freshly-grated lemon-peel, and alcohol sufficient to produce 100 of filtered product. *Perfumes* ("scents" or "essences," including "Lavender-Water" and "Eau de Cologne," or "Cologne-Water, Perfumed Spirit or *Spiritus Odoratus*," as it is termed in U. S. P.) are for the most part solutions of essential oils in spirit of wine or spirituous infusions of materials containing essential oils. The following oils are, directly or indirectly, official in the Pharmacopœias: 1. Volatile oil of *Bitter Almond* (p. 416). 2. Oil of the fruits of *Ajwain* or *Omum*, *Carum*, *Ajowan*, or *Ptychotis Ajowan* (*Fructus Ptychotis*, P. I.), contains *cymol* or *cymene* ($C_{10}H_{14}$) and a stearopten (*Ajwain-ka-phul*, flowers of ajwain) identical with *thymol*, $C_{10}H_{14}O$. 3. Oil of *Dill* (*Oleum Anethi*, B. P.), a pale, yellow, pungent, acrid liquid distilled from dill-fruit; it contains a hydrocarbon, *anethene* ($C_{10}H_{16}$), and an oxidized oil ($C_{10}H_{14}O$) identical with the carvol of oil of caraway (Gladstone). 4. Oil of *Aniseed* (*Oleum Anisi*, U. S. P.), a colorless or pale-yellow liquid, sp. gr. 0.976 to 0.990, of sweetish warm flavor, distilled in Europe from the Anise-fruit (*Pimpinella anisum*) (*Anisum*, U. S. P.), and in China from the fruit of Star-Anise (*Illicium anisatum*) (*Illicium*, U. S. P.); it is a mixture of a hydrocarbon isomeric with oil of turpentine and *anethol*, a stearopten ($C_{10}H_{12}$) which crystallizes out at low temperatures. 5. Oil of *Chamomile* (*Oleum Anthemidis*, B. P.), a bluish, or, when old, yellow oil, of characteristic odor and taste, distilled from chamomile flower-heads (*Anthemis*, U. S. P.). The official variety (*Anthemis nobilis*) yields about 0.2 per cent. of an oil composed of a hydrocarbon ($C_{10}H_{16}$) and an oxidized portion ($C_{10}H_{16}O_2$), which, heated with potash, gives *angelate of potassium* ($KC_5H_7O_2$), whence is obtained *angelic acid* ($HC_5H_7O_2$). According to Demarcay, Kopp, and Köbig, the oil is a mixture of the angelates of butyl and amyl and similar bodies. The flower-heads of another variety, *Matricaria chamomilla* (*Matricaria*, U. S. P.), contain a stearopten ($C_{10}H_{16}O$) having the composition of laurel-camphor. 6. Oil of *Horseradish-root* (*Armoraciæ Radix*, B. P.) is, according to Hofmann, the sulphocyanate of butyl or tetryl (C_4H_9CNS); it is the chief active ingredient of *Spiritus Armoraciæ Compositus*, B. P. 7. Oil of *Sweet-Orange* peel (*Aurantii Dulcis Cortex*, U. S. P.) and Oil of *Bitter-Orange* rind (*Aurantii Amari Cortex*, B. P.; *Oleum Aurantii Corticis*, U. S. P.), the former the flavoring constituent of the

official syrup of the *peel* (*Syrupus Aurantii*, U. S. P.), and the oils of various species of *Citrus*—namely, 8, *lemon* (*Oleum Limonis*, U. S. P.), from Lemon Peel (*Limonis Cortex*, U. S. P.); 9, *lime*; 10, *bergamot* (*Oleum Bergamii*, U. S. P.); 11, *citron*, and a variety of citron termed *cedra*—resemble each other in composition, all containing *hesperidene*, a hydrocarbon ($C_{15}H_{24}$), and a small quantity of oxidized hydrocarbons ($C_{10}H_{10}O_5$,$C_{15}H_{10}O$), and (Wright and Piesse) ($C_{20}H_{30}O_3$), etc. Tilden states that lemon oil, distilled from the fresh peel, consists chiefly of a terpene ($C_{10}H_{16}$), boiling at 176° C., with small quantities of a terpene boiling below 160° and a hydrous terpene; the odor of the oil being due to the mixture. Expressed lime-essence also contains a soft resin. 12. *Oleum Aurantii Florum*, U. S. P., Oil of *Neroli*, or *Orange-Flower* (*Aurantii Flores*, U. S. P.), the aqueous solution of which is official in the forms of water (*Aqua Aurantii Florum*, U. S. P.) and syrup (*Syrupus Aurantii Florum*, B. P. and U. S. P.), contains a fragrant hydrocarbon ($C_{10}H_{16}$), colorless when fresh, but becoming red on exposure to light, and an inodorous oxidized hydrocarbon. Strong acids, especially nitric, attack the oil in orange-flower water, coloring the fluid of a rose tint. 13. Oil of *Petit Grain*, distilled from the leaves and shoots of the orange tree, consists chiefly of a hydrocarbon apparently identical with that of oil of neroli. 14. The leaves of *Boldo* (*Peumus Boldus*), a Chilian shrub (tonic and hepatic), yield 2 per cent. of essential oil (and according to Bourgon and Verne, an alkaloid, *boldine*). 15. Oil of *Buchu-leaves* (*Buchu*, U. S. P.) consists chiefly of a fluid oil, $C_{10}H_{18}O$, holding in solution a crystalline stearopten, diosphenol, $C_{14}H_{22}O_3$ (Flückiger; $C_{10}H_{16}O_2$, Spica, Shimoyana also). 16. Oil of *Cannabis indica*, (see page —). 17. Oil of (the lesser) *Cardamoms*, from the seeds of the capsules (*Cardamomum*, U. S. P.), is chiefly a hydrocarbon ($C_{10}H_{16}$) isomeric with oil of turpentine (terpilene and probably limonine) and a camphor resembling turpentine-camphor ($C_{10}H_{16}3H_2O$). 18. Oil of *Cajuput* (*Oleum Cajuputi*, U. S. P.) is a mobile bluish liquid, consisting chiefly of *hydrous cajuputene* or *cajuputol* ($C_{10}H_{16}$,H_2O). The latter, repeatedly distilled from phosphoric anhydride, yields cajuputene itself ($C_{10}H_{16}$), which has the odor of hyacinths. Fresh cajuput-oil has a green hue, which is perhaps transient, for the color of the oil of trade is due to copper (Guibourt and Heisted): certainly the green coloring-matter of pure cajuput-oil is organic, and probably chlorophylloid. 19. Oil of *Caraway*-fruit (*Carum*, U. S. P., *Oleum Carui*, B. P., *Oleum cari*, U. S. P.) is a mixture of *carvene* ($C_{15}H_{24}$) and *carvol* ($C_{10}H_{14}O$). 20. Oil of *Cloves* (*Caryophyllus*, U. S. P., *Oleum caryophylli*, U. S. P.) and of *Pimento* or *Pimenta*, U. S. P. or *Allspice* (*Oleum Pimentæ*, U. S. P.), both heavier than water, contain a liquid hydrocarbon ($C_{15}H_{24}$), *eugenol* ($C_{10}H_{12}O_2$) a solid body, *eugenin*, isomeric with the eugenic acid, a second crystalline substance, *caryophyllin* ($C_{10}H_{16}O$), isomeric with common camphor, and a salicylic compound. 21. Oil of *Cascarilla*-bark (*Cascarilla*, U. S. P.) has not been fully examined. 22. Oil of *Cinnamon*-bark (*Cinnamomum*, U. S. P.) and of *Cassia*-bark is mostly cinnamic aldehyde (C_8H_7COH). Boiled with nitric acid, it furnishes benzoic aldehyde (C_6H_5COH) and benzoic acid (C_6H_5-

COOH); with chloride of lime it yields benzoate of calcium ($(C_6H_5COO)_2Ca$; and with caustic potash gives cinnamate of potassium (C_8H_7COOK). The specific gravity of oil of Ceylon cinnamon is about 1.040, and of Chinese cinnamon (oil of cassia) about 1.060. Both are termed *Oleum Cinnamomi* in U. S. P. 23. Oil of *Citronella*, a *grass oil*, from *Andropogon nardus*, is chiefly composed of *citronellol* ($C_{10}H_{16}O$ and $C_{10}H_{18}O$, Wright), probably isomeric with the *absinthol* from the *Artemisæ absinthium* or wormwood (*Absinthium*, U. S. P.) (Gladstone). Kremer also obtains heptoic aldehyde ($C_7H_{14}O$), a terpene ($C_{10}H_{16}$), etc. 24. Oil of *Copaiva* (*Oleum Copaibæ*, U. S. P.) and, 25, of *Cubebs* (*Oleum Cubebæ*, U. S. P.) are hydrocarbons having the formula $C_{15}H_{24}$. This *cubebene* is sometimes associated with a camphor, *hydrous cubebene* ($C_{15}H_{24},H_2O$). Oil of cubebs also contains a small quantity of a terpene ($C_{10}H_{16}$). 26. Oil of *Coriander* (*Coriandrum*, U. S. P.; *Oleum Coriandri*, B. P.) seems to have the composition of hydrous oil of turpentine ($C_{10}H_{16}H_2O$). 27. The fruits of *Cumin* or *Cummin* (*Cuminum cyminum*), an ingredient of many curry-powders, contains about 3 per cent., and those of *Water Hemlock* or *Cowbane* (*Cicuta virosa*) about 1¼ per cent., of an essential oil composed of *cymol* or *cymene* ($C_{10}H_{14}$) and *cumic aldehyde* ($C_9H_{11}COH$). The latter is an aldehyde readily uniting with alkaline bisulphites and by oxidation yielding *cuminic acid* ($C_9H_{11}COOH$). Cymol also occurs in *Garden Thyme* (*Thymus vulgaris*). 27*a*. The fresh flowering herb of *Erigeron canadense*, or Canadian Fleabane, yields an essential oil (*Oleum Erigerontis*, U. S. P.) 28. *Eucalyptus globulus* leaves (*Eucalyptus*, U. S. P.) furnish nearly 1 per cent. of *eucalyptol*, an oil (*Oleum Eucalypti*, U. S. P.) of sp. gr. 0.917, the more volatile and chief portion of which is *cymene*, and a terpene ($C_{10}H_{14} + 2C_{10}H_{16}$), together with an oxidized portion, $C_{10}H_{14}O$ and $C_{10}H_{16}O$, and an oil having the same composition as *cajuputol* and of the chief constituent of *wormseed oil*, $C_{10}H_{18}O$ or $C_{10}H_{16},H_2O$. Different species of eucalyptus may yield oils differing in specific gravity, flavor, and odor. Like the turpentines they are good solvents of resins. Voiry states that eucalyptol is present also in the oil of *Lavandula spica*, oil of *spike* or "foreign" oil of lavender. 29. *Elecampane-root*, *Inula Helenium* (*Inula*, U. S. P.), by distillation with water yields solid volatile *helenin* (C_6H_8O), a camphor oil or *inulol* ($C_{10}H_{16}O$), and *inulic anhydride* ($C_{15}H_{22}O_3$), as well as, according to Marpmann, crystals of *alantic* acid ($C_{15}H_{22}O_5$) and fluid *alantol* ($C_{20}H_{32}O$), each more powerfully antiseptic than helenin. 30. *Oleum Fœniculi*, U. S. P., Oil of *Fennel*-fruit (*Fœniculum*, U. S. P.) differs in odor, but contains the same proximate constituents as oil of anise. 31. Oil of *Geranium*, or *Ginger Grass* oil, from *Andropogon schœnanthus* and various species of *Pelargonium*, contains *geraniol* ($C_{10}H_{18}O$). Oil of *Hedeoma* or American Pennyroyal (*Oleum Hedeomæ*, U. S. P.) has a sp. gr. of about 0.940. It yields *hedeomol* ($C_{10}H_{18}O$), *isoheptoic acid* ($C_7H_{13}O_2$), and other substances (Kremer). 32. *Grains of Paradise* (*Amomum melegueta*), Guinea Grains or Melegueta Pepper, *Semina Cardamomi Majoris*, contain an essential oil ($C_{10}H_{16}$ and $C_{10}H_{16}O$) and a highly pungent resin. 33. Oil of *Juniper* (*Oleum Juniperi*, U. S. P.), the active constituent of Juniper Tops and Berries (*Juniperus*, U. S. P.), contains a hydrocarbon ($C_{10}H_{16}$) which by contact with water yields a white crystalline hydrous compound ($C_{10}H_{16},H_2O$) and a polymeric hydrocarbon ($C_{20}H_{32}$). 34. Oil of *Lavender* (*Oleum Lavandulæ*, U. S. P.), from the flowering tops or whole herb, and *Oleum Lavandulæ Florum*, U. S. P., from the flowers, of *Lavandulæ vera* (*Lavandula*, U. S. P.), have not been satisfactorily examined. 34*a*. Oil of *Myrcia* (*Oleum Myrciæ*, U. S. P.), oil of bay or bayberry oil (sp. gr. about 1.040), is obtained from the leaves of *Myrcia acris*. 35. Oil or butter or camphor of *Orris* (*Iris florentina*) is a soft solid lighter than water. Flückiger and Hanbury found it to be chiefly myristic acid associated with a little essential oil. 36. Oil of *Peppermint* (*Oleum Menthæ Piperitæ*, U. S. P.) consists of a hydrocarbon, *menthene* ($C_{10}H_{18}$), different from that of most volatile oils, and hydrous menthene ($C_{10}H_{18},H_2O$), menthol, a crystalline stearopten. 37. Oil of *Spearmint* (*Oleum Menthæ Viridis*, U. S. P.), the Common Mint of the kitchen-garden, contains a liquid having the formula $C_{10}H_{20}O$ or $C_{10}H_{18},H_2O$; also, according to Gladstone, an oil ($C_{10}H_{14}O$), isomeric with carvol. 38. Oil of *Pennyroyal* (*Mentha pulegium*) contains, according to Kane, $C_{10}H_{16}O$. 38*a*. The leaves and tops of *Melissa officinalis* or *Balm* (*Melissa*, U. S. P.), yield a volatile oil containing a camphor. 39. Oil of *Nutmeg* (*Oleum Myristicæ*, B. P. and U. S. P.), and of the arillus of the nutmeg or mace (*Macis*, U. S. P.), is composed of a hydrocarbon, *myristicene* ($C_{10}H_{16}$) and *myristicol* ($C_{10}H_{16}O$) (Gladstone). 39*a*. Oil of *Origanum*, from *Origanum vulgare*, or *Wild Marjoram* (*Origanum*, U. S. P.), is of a bright yellow, and has an odor somewhat like peppermint; it is a mixture of a liquid hydrocarbon and a camphor which is deposited after long standing. 40. Oil or *Otto* or *Attar* of *Cabbage-Rose Petals* (*Rosæ Centifolia*, U. S. P.; *Oleum Rosæ*, U. S. P.) gives the fragrance to rose-water (*Aqua Rosæ*, B. P.). It resembles most other volatile oils in being composed of a hydrocarbon and an oxidized portion, but differs from all in this respect, that the hydrocarbon is solid and is destitute of odor, while the oxygenated constituent is liquid and the source of the perfume. According to Flückiger, the solid hydrocarbon ($C_{18}H_{16}$) yields succinic acid as the chief product of its oxidarton by nitric acid, and in other respects affords evidence of belonging to the paraffin series of fats. 41. *Rosmarinus*, U. S. P., Oil of *Rosemary-tops* (*Oleum Rosmarini*, U. S. P.), exists in the plant to the extent of from 1½ to 3 parts per 1000. It chiefly consists of a hydrocarbon ($C_{10}H_{16}$) resembling that from Myrtle, *Myrtus communis*, but also contains camphor, borneol, and cyneol ($C_{10}H_{18}O$) in variable proportions. 42. Oil of *Rue* (*Oleum Rutæ*, U. S. P.) contains a small quantity of hydrocarbon ($C_{10}H_{16}$), with some rutic aldehyde ($C_{10}H_{20}O$), but, according to Greville Williams, is chiefly euodic aldehyde ($C_{11}H_{22}O$), some lauric aldehyde ($C_{12}H_{24}O$) also being present, Gorup-Besanez and Grimm have obtained oil of rue ($C_{11}H_{22}O$) artificially as one of the products of the destructive distillation of acetate and caprate of calcium. 43. Oil of *Sage* (*Salvia*, U. S. P.) contains about 40 per cent. of salviol, $C_{10}H_{16}O$; about 20 per cent. of two $C_{10}H_{16}$ hydrocarbons boiling at 156° and 157° C. respectively; about 10 per cent. of a camphor,

$C_{10}H_{16}O$; and about 10 per cent. of cedrene, $C_{15}H_{24}$ (Muir). 44. Oil of *Savin* (*Oleum Sabinæ*, U. S. P.), obtained from the tops of *Juniperus Sabina* or *Savine* (*Sabina*, U. S. P.), contains several hydrocarbons, but none isomeric with oil of turpentine (Tilden). 45. Oil of *Elder-flowers* (*Sambucus*, U. S. P.) occurs in very small quantity; it has a butyraceous consistence; it contains a hydrocarbon, *sambucene* ($C_{10}H_{16}$), and probably a camphor. 46. Oil of *Sandal-wood* (*Oleum Santali*, U. S. P.), or oil of *santal*, is composed (Chapoteaut) of two bodies; mostly of a substance having the formula $C_{15}H_{24}O$ (boiling at 572° F.), and a small quantity of a substance having the formula $C_{15}H_{26}O$ (boiling at 600° F.). It occurs to the extent of about 1 per cent. in the fragrant white or yellow sandal-wood of India, *Santalum album*, a small tree of the natural order Santalaceæ, and not to be confounded with the *Pterocarpus Santalinus*, a tree of the natural order Leguminosæ, and furnishing the inodorous Red Sandal-wood or Red Sanders Wood of the dyer. 47. Oil of *Sassafras-root* (*Oleum Sassafras*, U. S. P.) (*Sassafras*, U. S. P.), sp. gr. 1.094, contains nine-tenths of its weight of *Safrol* or *Sassafrol*, $C_{10}H_{10}O_2$, also a small quantity of a terpene. Sassafras camphor, $C_{10}H_{10}O_2$, is deposited when the oil is exposed to low temperature. 48. Oil of *Mustard* (*Oleum Sinapis Volatile*, U. S. P.) is sulphocyanate of allyl (see Index). If contaminated with alcohol its sp. gr. is below 1.015. 49. Oil of *Sweet Flag* (*Acorus calamus*) contains the hydrocarbon ($C_{10}H_{16}$). The rhizome (*Calamus*, U. S. P.) also contains *Acorin*, $C_{36}H_{60}O_6$, a bitter glucoside, and an alkaloid, *calamine*. 50. The tops and leaves of *Thuja occidentalis*, or *Arbor vitæ* (*Thuja*, U. S. P.), yields two oxygenated oils, also a bitter principle (*penipicrin*). 51. Oil of common garden *Thyme* (*Thymus vulgaris*, *Oleum Thymi*, U. S. P.) is composed of *cymene* or *cymol* ($C_{10}H_{14}$), *thymene* ($C_{10}H_{16}$), and *thymol* ($C_{10}H_{14}O$) (*Thymol*, U. S. P.). Thymol crystallizes out when oil of thyme or of ptychotis, etc. is kept at a low temperature for a day or two. It may also be obtained by shaking the oils with caustic alkali, and treating the separated alkaline liquid with an acid. It may be purified by distillation or by crystallization from alcohol. It would seem that as an antiseptic thymol is far stronger than carbolic acid. Thymol is also contained in oil of *Horsemint* (*Monarda*). 52. Oil of *Turmeric* (*Curcuma longa*) is said by Jackson and Menke to be chiefly an alcohol having the formula $C_{19}H_{27}OH$. They name it *turmerol*. It is a light-yellow volatile oil, having the sp. gr. 0.902. It is to this oil that turmeric (hence curry powder, partly) owes its flavor and odor. 53. Oil of *Valerian-root* (*Valeriana*, U. S. P., *Oleum Valerianæ*, U. S. P.) is a mixture of a hydrocarbon, *valerene* or *borneene* ($C_{10}H_{16}$), and *valerol* ($C_6H_{10}O$). Valerol slowly oxidizes to valerianic acid, known by its smell. A similar change occurs at once if oil of valerian be allowed to fall drop by drop on heated caustic potash: $C_6H_{10}O + 3KHO + H_2O = K_2CO_3 + C_4H_9COOK + 3H_2$. By the action of sulphuric acid on the valerianate of potassium thus produced valerianic acid is obtained. 54. Oil of *Verbena*, *Lemon Grass* Oil, or *Indian Melissa* Oil, is obtained from *Andropogon citratus* (*Oleum Andropogi Citrati*, P. I.). 55. Oil of *Ginger* (*Zingiber*, B. P.) is, according to Thresh, a complex mixture of hydrocarbons and their oxidation-products. Cymene ($C_{10}H_{14}$) is present, a terpene, aldehydes, and ethereal salts. (For an analysis of ginger, by Thresh, and for papers on "Soluble Essence of Ginger," see the *Pharmaceutical Journals* for August 30 and September 6, 1879, and March 4, 1882.) 56. American Wormseed (*Chenopodium*, U. S. P.) contains a volatile oil (*Oleum Chenopodii*, U. S. P.).

Caoutchouc, or India-rubber, and Gutta-Percha.

Caoutchouc is the hardened juice of *Dichopsis Gutta*, *Hevea* (*Siphonia*) *Brasiliensis*, *Castilloa elastica*, *Urceola elastica*, *Ficus elastica*, and other plants. Heated moderately with sulphur, it takes up 2 or 3 per cent., and forms *vulcanized india-rubber;* at a higher temperature a hard, horny product termed *ebonite* or *vulcanite* results. *Gutta-Percha* (*Gutta-Percha*, U. S. P.) is the concrete drop or juice of the *percha* (Malay) tree, the *Isonandra gutta*, and of other Sapotaceous plants. White gutta-percha is obtained by precipitating a solution of ordinary gutta-percha in chloroform (*Liquor Gutta-percha*, U. S. P.) by alcohol, washing the precipitate with alcohol, and finally boiling in water and moulding into the desired form while still hot. The British solution of gutta-percha (*Liquor Gutta-Percha*, B. P.) is made by digesting *thin* slices of gutta-percha in 12 parts by weight of chloroform, and then "fining" by shaking with one part of carbonate of lead and setting aside till the fluid is clear.

These two elastic substances, in the pure state, are hydrocarbons (xC_5H_4), usually slightly oxidized. When caoutchouc is distilled, a terpene, $C_{10}H_{16}$, called caoutchin, is obtained.

Camphors.

In addition to the stearoptens or camphors already mentioned as being contained in or formed from volatile oils, there is one that is a common article of trade. It is obtained from the wood of *Cinnamomum camphora* or Camphor-laurel, in Japan (termed, in Europe, "Dutch camphor," because imported by the Dutch) and in China (known as Formosa camphor) by a rough process of distillation with water, and is purified by resublimation (*Camphora*, U. S. P.). The formula of laurel-camphor is $C_{10}H_{16}O$. Sp. gr. 0.990 to 0.995; melting-point, 175° C.; boiling-point, 205° C. Bromine heated with camphor gives *monobrom-camphor* ($C_{10}H_{15}BrO$) and hydrobromic acid. Monobrom-camphor is camphor in each molecule of which an atom of hydrogen has been displaced by one of bromine. Recrystallized, it occurs in white prisms. The essential oil, from which doubtless camphor is derived by oxidation, is easily obtained from the wood, and is occasionally met with in commerce under the name of *liquid camphor* or *camphor-oil*. It contains hydrocarbons resembling terebinthene and citrene, and camphor hydrate, $C_{10}H_{16}O,H_2O$, as well as camphor. By exposure to air it becomes oxidized and deposits common camphor, $2C_{20}H_{32}O + O_2 = 4C_{10}H_{16}O$. Camphor distilled with phosphoric anhydride yields cymol, $C_{19}H_{14}$. There is another kind

of camphor, *borneol*, in European markets, less common than laurel-camphor, but highly esteemed by the Chinese: it is obtained from the *Dryobalanops aromatica*, and denominated Sumatra or Borneo camphor. It differs slightly from laurel-camphor in containing more hydrogen, its formula being $C_{10}H_{18}O$. It may be obtained by acting on camphor with hydrogen, the camphor being dissolved in some inert liquid such as toluene, and sodium added: the sodium forms a compound, $C_{10}H_{15}ONa$, while the hydrogen thus liberated acts on another portion of the camphor, forming borneol, $C_{10}H_{17}(OH)$—a better result being obtained if absolute alcohol is used instead of toluene (Jackson and Menke). It is accompanied in the tree by a volatile oil ($C_{10}H_{16}$) isomeric with oil of turpentine. This oil, *borneene*, is also occasionally met with in trade under the name of *liquid camphor* or *camphor oil*, but differs from laurel-camphor oil in not depositing crystals on exposure to air.

The constitution of camphor is still doubtful. Camphor is soluble to a slight extent in water (40 grains per gallon, Pooley). The official Camphor-Water (*Aqua Camphoræ*, U. S. P.) is such a solution.

Common camphor, and many others of the camphors, oily hydrocarbons, and oxidized hydrocarbons, yield *camphoric acid*, $C_8H_{14}(COOH)_2$, and camphoronic acid, $C_7H_9(OH)(COOH)_2$, when attacked by oxidizing agents. Such reactions indicate natural relationships. Camphoric acid is a good antiseptic.

Cantharidin ($C_{10}H_{12}O_4$), the active blistering principle of cantharides (*Cantharis*, U. S. P.) and other vesicating insects (such as *Mylatris cichorii* or *Telini Fly*, P. I., common in India), has most of the properties of a camphor or a stearopten. It slowly crystallizes from an alcoholic tincture of the beetles in fusible, volatile, micaceous plates. The following process for the extraction of cantharidin is by Fumouze: Powdered cantharides are macerated with chloroform for twenty-four hours; and this treatment is repeated twice with fresh quantities of solvent, the residue having been well squeezed each time. The collected solutions are then distilled, and the dark-green residue treated with bisulphide of carbon, which dissolves fatty, resinous, and other matters, and precipitates the cantharidin. The precipitate is placed on a filter, washed with bisulphide of carbon, and recrystallized from chloroform. The same process, omitting the final recrystallization, may be used for the quantitative estimation of cantharidin in cantharides. The average quantity found is from four to five, or occasionally ten or even twelve, parts in one thousand. Cantharidin is readily soluble in warm glacial acetic acid (Tichborne), and still more readily in acetic ether or chloroform. Cantharides from which the fat has been removed by petroleum ether yield their cantharidin with great facility.

Massing and Dragendorff consider cantharidin to be an anhydride, and that with the elements of water it forms *cantharidic acid* ($H_2C_{10}H_{12}O_5$). Piccard gives the vapor density of cantharidin as about 6.5, and its formula $C_{10}H_{12}O_4$. Homolka assigns to it the formula $C_8H_{13}O_2.CO.COOH$.

Resins, Oleo-Resins, Gum-Resins.

Resins seem to be the oxidized products of terpenes and the allied hydrocarbons; they occur in plants, generally in association with volatile oils. They closely resemble camphors and stearoptens, but are not volatile, and differ from oils and fats mainly in being solid and brittle. For convenience they are classified as resins, oleo-resins, and gum-resins, the distinctions being founded as much on physical as on chemical properties.

Oleo-resins are mixtures of a resin and a volatile oil.

Gum-resins are mixtures of a resin or oleo-resin and gum.

Balsams are commonly described as resins or oleo-resins which yield benzoic and cinnamic acids; they are Benzoin (*Benzoinum*, U. S. P.), Balsam of Peru (*Balsamum Peruvianum*, U. S. P.), Balsam of Tolu (*Balsamum Tolutanum*, U. S. P.), and Storax, and are treated of under the respective acids.

Some oleo-resins, containing neither of the above acids, are often termed balsams (*e. g.* Balsam of Copaiva and Canada Balsam); these will be treated under the head of Oleo-resins.

A physico-chemical method for the identification of the chief resins, gum-resins, and balsams will be found in the *Pharmaceutical Journal* for November 17, 1877.

Resins appear to be somewhat antiseptic. Beer is said never to turn sour in casks lined with Burgundy pitch. The resin of hops has perhaps a similar effect in retarding oxidation of alcohol.

RESINS.*—1. *Resin*, *rosin*, or *colophony* (*Resina*, U. S. P.) is the type of this class. Its source is the oleo-resin or true turpentine of the conifers, a body which by distillation yields spirit of turpentine and a residuum of rosin. "Brown" and "White" rosin are met with in trade. The former is the residue of American, the latter of Bordeaux, turpentine (from *Pinus Abies*, etc. and *Pinus Maritima* respectively). The chief constituents of brown resin are *pinic acid* ($HC_{20}H_{29}O_2$) and *sylvic acid*, identical in composition, but differing in properties (*vide* Isomerism), the former being soluble and the latter insoluble in cold spirit of wine. White resin or "galipot" is chiefly *primaric acid*, also isomeric with pinic acid. Pinic acid cautiously heated yields *colophonic* or *colopholic acid*. Rosin, by destructive distillation, yields *resin oil*, the first portion being "pale," the next "blue," and the third "green resin oil." Mixed with other oils, they are used for lubricating purposes and in the manufacture of printing ink. Among the products of the destructive distillation of resin Tichborne has found "*colophonic hydrate*" ($C_{10}H_{22}O_3,H_2O$), a white inodorous crystalline substance, and by depriving this of water has obtained white crystalline *colophonine* ($C_{10}H_{22}O_3$). Resin is soluble in oil of turpentine. Contact with sulphuric acid immediately colors it strongly red. It is a constituent of eight of the fourteen plasters (*Emplastra*) of the British Pharmacopœia. 2. *Arnicin* ($C_{20}H_{30}O_4$), the chief acrid and one of

* The student is not expected to remember, but to understand, all that follows respecting the resins. (See page ix of Preface.)