

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*, $C_7H_8(OH)(COOH)_2$, 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 eichorii* 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 $C_8H_{13}O_2.CO.CO.OH$.

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. *Arnica* ($C_{20}H_{30}O_4$), the chief acid and one of

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

the active principles of Arnica (*Arnica Flores*, U. S. P.; *Arnica Rhizoma*, B. P.), is a resin, and probably a glucoside. 3. *Cannabin*, said to be the active principle of *Indian Hemp* or *Indian Cannabis* (*Cannabis Indica*, U. S. P., the flowering tops of the female plant of *Cannabis Sativa*) and American Cannabis (*Cannabis Americana*, U. S. P., the *Cannabis Sativa* plant grown in the United States), was obtained in 1846 by T. and H. Smith, and is a resin. Personne in 1857 isolated a volatile oil, also said to possess much medicinal activity, consisting of *cannabene* ($C_{15}H_{20}$) and a solid crystalline "hydride of *cannabene*" ($C_{15}H_{22}$). Preobraschensky has stated, and since re-asserted, that the active principle is nicotine. Kennedy searched for nicotine by two methods, but found none. Hay found an alkaloid, *tetano-cannabin*. Warden and Waddell, after careful investigations, consider that the active principle of the plant has yet to be isolated. Jahns finds choline present. 4. *Capsicum-fruit* contains a resin (p. 504). 5. *Castorin*, a resinous matter, is the name given to the chief constituent of *Castor* (*Castoreum*, B. P.), the dried preputial follicles and included secretion of the beaver (*Castor Fiber*). 6. *Copal*.—The best copal is the exuded resin of trees of extinct forests, and is found beneath the surface of the ground in the neighborhood of existing trees. It appears to be a mixture of acids, but its character is still obscure. 6a. *Doundaké-bark*, an African febrifuge, from *Sarcocephalus esculentus*, owes its activity to resinoid substances, according to Heckel and Schlagdenhauffen. 7. *Dragon's Blood*, a crimson-red resin found as an exudation on the mature fruits of a Rotang or Rattan Palm (*Calamus draco*). It consists of resins having the probable formula $C_{20}H_{24}O_4$ and $C_{20}H_{21}O_4$ (Johnstone). 8. *Ergotin* is a very active resinoid constituent of *Ergot* (*Ergota*, U. S. P.), or the sclerotium (compact mycelium or spawn) of *Claviceps purpurea*, produced within the pales and replacing the grain of the common rye, *Secale cereale*. Maize or Indian Corn, *Zea mays*, appears to foster a similar parasite, the *Ustilago maydis*, or Corn Smut (*Ustilago*, U. S. P.). According to Wenzell, ergot contains two alkaloids, *ecboline* and *ergotine*, to the former of which, he says, the activity of ergot is due. Blumberg considers these alkaloids to be identical. Tanret states that an unstable alkaloid termed *ergotinine* occurs in ergot to the extent of 1 per 1000, and that it is accompanied by camphor; also *ergosterin*, $C_{26}H_{40}OH_2O$, resembling cholesterol. Dragendorff and Podwissotzki assert that ergot owes most of its activity to *sclerotic* or *sclerotinic acid*, present to the extent of about 4 per cent. Recent investigations seem to show that *cornutine* is an active alkaloid of ergot, associated with ergotinic and sphacelenic acids, picrosclerotine and ergotinine. The activity really seems to be due to a combination of alkaloids and acids, and not to any one constituent, as no principle representing the full activity of ergot has been extracted. The same may be said of a similar therapeutical agent, the root-bark of *Gossypium herbaceum* (*Gossypii Radicis Cortex*, U. S. P.), the activity of which appears to reside in a red resin. Ergot also contains *choline*, which by decomposition may yield trimethylamine. "*Ergotin*" (*Ergotinum*, B. P.) is an alcoholic extract of an aqueous extract of ergot. 9.

Guaiacum-resin is a mixture of substances (see Index). 10. *Jalap-resin* (see Index). 11. *Koussou* or *Kooso* (*Brayera*, U. S. P.) yields yellow crystals of a resinoid body readily soluble in alkaline liquids, *kosin* or *koussin* ($C_{31}H_{38}O_{10}$). It is, perhaps, an anhydride. 12. *Mastic* (*Mastiche*, U. S. P.) is a resinous exudation obtained by incision from the stem of the Mastic or Lentisk tree. Nearly nine-tenths of mastic is *masticic acid* ($C_{20}H_{31}O_2$), a resin soluble in alcohol; the remainder consists of *masticin* ($C_{20}H_{31}O$), a tenacious elastic resin and a terpene having the formula $C_{10}H_{16}$. 13. *Mezereon* (*Mezereum*, U. S. P.), the dried bark of *Daphne mezereum*, Mezereon, and *Daphne laureola*, Spurge Laurel, owes its acidity to a resin. 14. *Pepper* contains resin (see Index). 15. *Burgundy pitch* (*Pix Burgundica*, U. S. P.) is the melted and strained exudation from the stem of the Spruce Fir, *Abies Excelsa*. The term Burgundy is a misnomer, the resin never having been collected at or near Burgundy—Finland, and to a smaller extent Baden and Austria, being the countries whence it is derived. Its constituents closely resemble those of common resin. It is often adulterated and imitated by a mixture of resin with palm oil, water, etc., from which it may be readily distinguished by its duller yellow color, highly aromatic odor, greater solubility in alcohol, and almost complete solubility in twice its weight in glacial acetic acid (Hanbury). 16. *Podophyllum-resin*. In preparing the resin of podophyllum, or May-apple (*Resina Podophylli*, U. S. P.), an alcoholic extract of the rhizome and rootlets of *Podophyllum peltatum* (*Podophyllum*, U. S. P.) is poured into cold water; the resin is then deposited. This resin is the chief active principle of podophyllum-root. According to Guareschi, podophyllin contains a glucoside resembling convolvulin. Podwissotzki has extracted from podophyllum a little crystalline coloring-matter, fat, a bitter crystalline acid, a bitter crystalline neutral principle, and an amorphous acid resin. 17. *Pyrethrin* is the name of the acrid resinous active principle of the root of *Anacyclus pyrethrum* or *Pellitory-root* (*Pyrethrum*, U. S. P.). According to Buckheim, the action of alkalies breaks it up into piperidine and pyrethric acid. The crystalline poisonous principle obtained by Bellesme from *Pyrethrum carneum*, the powder of which (and of *P. roceum*, and especially *P. cinerariae folium*, or Dalmatian Insect Powder) is the well-known "insecticide," has not yet been analyzed. 18. The resins of Rhubarb have already been alluded to in connection with Chrysophanic Acid. 19. *Rottlerin*, $C_{11}H_{10}O_3$ (*mallotoxin*, $C_{11}H_{10}O_3$, Perkin), is the name given by Anderson to a crystalline resin from Kamala (*Kamala*, U. S. P.), the minute glands that cover the capsules of *Rottlera tinctoria*: to this and, apparently, allied resins, Kamala owes its activity as an anthelmintic.

OLEO-RESINS.—1. "*Capsicin*," a term suggestive of a definite chemical substance, is a name somewhat unhappily accorded to an indefinite substance, an oleo-resin, obtained by digesting the alcoholic extract of Capsicum-fruit (*Capsicum*, U. S. P.) in ether and evaporating the clear ethereal fluid to dryness. Besides volatile oil and resin, capsicum-fruits contain much fatty matter which Thresh states is chiefly free palmitic acid. (See also *Capsicine* and

Capsaicin, in Index.) 2. *Copaiva* (*Copaiba*, U. S. P.) is a mixture of essential oil ($C_{15}H_{24}$), *copaivaöl*, $C_{20}H_{32}$ (Strauss), with 2 or more per cent. of brown soft resin, and 30 to 60 of a yellow dark crystalline resin consisting mostly of *copaivic acid* ($C_{10}H_{16}O_2$), with *oxy-copaivic acid*, $C_{20}H_{28}O_3$ (Fuhling) and *metacopaivic acid*, $C_{22}H_{34}O_4$ (Strauss). *Copaiva*, containing about equal parts of this acid and of the oil, heated with a fourth of its weight of the official carbonate of magnesium, yields a transparent fluid, owing to the formation of *copaivate* of magnesium and solution of this soap in the essential oil. With an equal weight of the carbonate enough soap is produced to take up the whole of the essential oil and form a mass capable of being rolled into pills. A much smaller quantity of calcined magnesia, as might be expected, effects the same result; but more time, often several days, is required before complete reaction is effected. The *Messa copaiba*, U. S. P., is formed from 6 parts of magnesia and 94 of *copaiva*. Quicklime has a similar effect. Perhaps carbonate reacts more quickly because of its fine state of division and admixture of hydrate—in which case hydrates of calcium and magnesium may be expected to act better than the calcined preparations, and in much smaller quantity than carbonate of magnesium. *Copaiva*, unlike 3, *Wood-oil*, or *Gurjun Balsam* (*Dipterocarpi Balsamum*, P. I.), a similar oleo-resin from the *Dipterocarpus turbinatus* (D. Lævis, P. I.), does not become gelatinous when heated to 270° F. *Copaiva* is often slightly fluorescent; *Gurjun* balsam is highly fluorescent. The stated analogy of *Gurjun* balsam to *copaiva* is borne out by its chemical composition, for by distillation it yields about 40 per cent. of an essential oil identical in composition with oil of *copaiva*, the non-volatile portion being resinous. The adulteration of *copaiva* with fixed oil is best detected by heating 20 or 30 drops in a capsule until all essential oil has evaporated. Turpentine is betrayed by its odor during this evaporation. The residue, *copaiva* resin, is brittle if pure, and more or less sticky or soft if fixed oil is present. The limit of brittleness is stated, by Siebold, to be reached when 1 per cent. of oil has been added to the *copaiva*, that amount preventing the residue being reduced to a fine powder. "The essential oil distilled off from the oleo-resin, when rectified, should not begin to boil below 200° C. (392° F.). On adding 1 drop of *copaiba* to 19 drops of disulphide of carbon and shaking the mixture with 1 drop of a cold mixture of equal parts of sulphuric and nitric acids, it should not acquire a purplish-red or violet color (absence of *Gurjun* balsam)."—U. S. P. *Resina Copaiba*, U. S. P., is the residue left after distilling off the volatile oil from *copaiba*. 4. Oleo-resin of cubebs (*Oleo-Resina Cubebe*, B. P.) is an ethereal extract of cubebs decanted from waxy matter (see *Piperine* and *Oil of Cubebs*). 5. *Elemi* (*Elemi*, B. P.) is an exudation from a tree growing in the Philippine Islands. It consists of volatile oil ($C_{10}H_{16}$), with 80 or more per cent. of two resins, the one ($C_{20}H_{32}O_2$) soluble in cold alcohol, the other, *Amyrin* (C_5H_8) $_2$ H $_2$ O, almost insoluble, associated with *Amyric acid* (C_5H_8) $_2$ O $_4$ (Buri). There is an α and a β amyryn, each having the formula $C_{30}H_{48}OH$ (Vesterberg). It also contains small quantities of two crystalline bodies soluble in water, *Bryoidin*

(C_5H_8) $_2$ 3H $_2$ O, and *Breidin* (Flückiger). The *Icacin* of Stenhouse and Groves is either identical with amyryn or perhaps has the formula (C_5H_8) $_2$ H $_2$ O. All these bodies are probably hydrous terpenes. 6. *Wood-tar* (*Pix Liquida*, U. S. P.) is a mixture of several resinoid and oily bodies (amongst others Creasote; see Index) obtained by destructive distillation from the wood of *Pinus sylvestris* and other pines. When heated it yields a terebinthinate oil (*Oleum Picis Liquidæ*, U. S. P.) and a residue of pitch. 7. *Turpentine*. These oleo-resins have been mentioned in connection with oil of turpentine, their volatile, and resin, their fixed, constituent. 8. *Common Frankincense* (*Thus Americanum*, B. P.) is the concrete turpentine of *Pinus tæda*. 9. *Canada Balsam* (*Terebinthina Canadensis*, B. P.) is largely gathered in the province of Quebec, and is the turpentine or oleo-resin of the Balm-of-Gilead Fir (*Abies balsamea*). 10. *Sumbul-root*, from *Ferula Sumbul* (*Sumbul*, U. S. P.) contains 9 per cent. of resin, to which probably it owes its stimulating properties. The resin consists of two parts—one soluble in ether and the other in alcohol, together with valerianic, sumbulic, and sumbulic acids. By dry distillation it yields a blue oil. 11. *Oleo-resin of Lupulin* (U. S. P.) is an ethereal extract of the yellow glandular powder (*Lupulinum*, B. P.) attached to the small nuts at the base of the scales which form the aggregate fruit of the *Humulus Lupulus*, or Hop (*Humulus*, U. S. P.). It contains essential oil of hop (valerol, $C_8H_{10}O$), oxidized oil or resin, bitter extract containing the hop-bitter, lupulinic acid ($C_{32}H_{50}O_7$), and tannic acid. It generally contains a good deal of earthy dust, but should not yield more than 15 per cent. of ash and not more than 30 or 40 per cent. of matter insoluble in ether. *Oleo-resina Aspidii*, *Capsici*, *Cubebæ*, *Piperis*, and *Zingiberis* are official in the United States Pharmacopœia. 12. *Pix Canadensis*, U. S. P. (*Canada Pitch* or *Hemlock Pitch*), is the concrete juice of *Abies Canadensis*.

GUM-RESINS.—1. *Ammoniacum* (*Ammoniacum*, U. S. P.) is an exudation from the *Dorema Ammoniacum*. It contains nearly 20 per cent. of gum, a little volatile oil, and about 70 of resin ($C_{40}H_{50}O_9$ —Johnston). 2. *Asafoetida* (*Asafoetida*, U. S. P.), formerly spelled *assafoetida*, is a gum-resin obtained, by incision, from the living root of *Narthex asa-foetida*. It contains from 50 to 70 per cent. of a resin which is partly *ferulaic acid* ($C_{10}H_{10}O_4$), 25 to 30 per cent. of gum (about two-thirds arabin, one-third bassorin, p. 113), a little vanillin, and 3 to 5 per cent. of volatile oil, which is probably a sulphur derivative of allyl, but owing to its overpowering odor it has not yet been examined. 3. *Euphorbium*, an old drug which is an emetic and purgative resin. It contains an amorphous active resin ($C_{20}H_{32}O_4$), crystalline *euphorbon* ($C_{26}H_{44}O_2$), and mucilage (Flückiger). 4. The ordinary or Siam Gamboge (*Cambogia*, U. S. P.) of European trade is obtained from the *Garcinia morella*; the gamboge of India (*Cambogia Indica vel Mysoriensis*, P. I.) from *G. pictoria*. When of best quality it contains about 20 per cent. of a gum, and 80 to 75 per cent. of a yellow resin termed *gambogic acid* ($C_{20}H_{23}O_4$). 5. *Galbanum* (*Galbanum*, U. S. P.) contains from 20 to 25 per cent. of gum, about 65 per cent. of resin ($C_{40}H_{54}O_7$), and 3 or

4 per cent. of volatile oil. Moistened with alcohol, and then with hydrochloric acid, galbanum yields a purple color, due, probably, to the production and oxidation of resorcin. Galbanum heated for some time to 212° F. with hydrochloric acid, the liquid separated and shaken with ether or chloroform, and the latter evaporated, yields somewhat less than 1 per cent. of colorless acicular crystals of *umbelliferone* ($C_9H_8O_3$). "Umbelliferone is soluble in water; its solution exhibits, especially on addition of an alkali, a brilliant blue fluorescence which is destroyed by an acid. If a small fragment of galbanum is immersed in water, no fluorescence is observed, but it is immediately produced by a drop of ammonia. The same phenomenon takes place with *asafœtida*, and in a slight degree with *ammoniacum*; it is probably due to traces of umbelliferone pre-existing in those drugs. Umbelliferone is also produced from many other aromatic umbelliferous plants, as *Angelica*, *Levisticum*, and *Meum*, when their respective resins are submitted to dry distillation; also from the resin of *Daphne mezereum*. The fluorescence of umbelliferone may be beautifully shown by dipping some bibulous paper into water which has stood for an hour or two on lumps of galbanum, and drying it. A strip of this paper placed in a test-tube of water with a drop of ammonia will give a superb blue solution, instantly losing its color on the addition of a drop of hydrochloric acid" (Flückiger and Hanbury). 6. *Myrrh* (*Myrrha*, U. S. P.), an exudation from the stem of *Balsamodendron myrrha*, contains about half its weight of soluble arabinoid gum, 10 per cent. of insoluble gum (probably bassorin), 2½ of volatile oil, and about 25 per cent. of resin (myrrhic acid). 7. *Olibanum* (P. I.), *Thus masculum* or *Arabian Frankincense* (from various species of *Boswellia*), is about one-third gum and nearly two-thirds resin ($C_{40}H_{30}O_6$), with a little hydrocarbon ($C_{10}H_{16}$) and oxidized hydrocarbon volatile oils. It has always been an important ingredient of *incense*—myrrh, storax, benzoin, and such fragrant combustible resinous substances being other constituents. 8. *Scammony* (see Index).

Gum-resins need only to be finely powdered and rubbed in a mortar with water to yield a medicinal *emulsion*, in which the fine particles of resin are held in suspension by the aqueous solution of gum.

QUESTIONS AND EXERCISES.

695. What are the general chemical characters of volatile oils?
696. How do volatile oils usually differ chemically from fixed oils?
697. Describe the usual process by which volatile oils are obtained.
698. How does natural turpentine differ from turpentine of trade?
699. With what object is commercial turpentine rectified?
700. What is the chemical nature of india-rubber and gutta-percha?
701. How is india-rubber *vulcanized* and converted into *ebonite* or *vulcanite*?

702. Mention the difference in composition between the volatile oils of *Anthemis nobilis* and *Matricaria chamomilla*.
703. Give the systematic name for oil of horseradish.
704. State the general composition of the oils of lemon, lime, bergamot, citron, and cedar.
705. Name the constituents of oil of cloves.
706. In what respect does oil (or otto) of roses differ from volatile oils?
707. To what class of substances do the constituents of oil of rue belong?
708. How is camphor oil related to camphor?
709. In what respects do Borneo or Sumatra camphor and camphor oil differ from the corresponding products of Japan and China?
710. How may borneol be artificially prepared?
711. How do resins occur in nature? Distinguish between resins and camphors. Mention the points of difference of resins, oleo-resins, gum-resins, and balsams.
712. Name the source of the chief constituents of common resin or rosin.
713. Enumerate some official articles of which the active constituents are resins.
714. Give the distinguishing characters of Burgundy pitch.
715. What is the average proportion of oil and of resin in the so-called balsam of copaiva?
716. Explain the effect of carbonate of magnesium, magnesia, and lime on copaiva.
717. Why do ammoniacum, asafœtida, gamboge, galbanum, myrrh, and similar substances give an emulsion by mere trituration with water?

THE BENZENE SERIES OF HYDROCARBONS.

The Benzene or Aromatic Series, C_nH_{2n-6} .—This series, to which during the last few years most attention has been paid, yields, like other families of hydrocarbons, alcohols, haloid derivatives, aldehydes, acids, etc., obtained, however, as a rule, by special rather than general methods. Just as the consecutive members of the paraffin series of hydrocarbons may be regarded as derived by the displacement of a hydrogen atom of the previous member by the methyl (CH_3) group, or of a hydrogen atom in methane by a paraffin radical, so the consecutive members of the benzene series may for convenience of study be viewed as obtained by the displacement of a hydrogen atom in *benzene* by a paraffin radical; as in the following samples:—

Benzene or Phenylene, C_6H_6 .
 Toluene, Benzene, or Methylphenylene, C_7H_8 or $C_6H_5CH_3$.
 Xylene or Ethylphenylene, C_8H_{10} or $C_6H_4C_2H_5$.
 Mesitylene or Trimethylphenylene, C_9H_{12} or $C_6H_3(CH_3)_3$.
 Cymene or Methylpropylphenylene, $C_{10}H_{14}$ or $C_6H_4CH_3C_3H_7$.

It is perhaps desirable, as suggested by Odling, to designate the first member of this series by the name *phenylene*, rather than *benzene*, as its hydrate is termed *phenol*, and its derivatives *phenyls*—e. g. phenylamine. Toluene (first obtained from balsam of tolu, hence the name) then becomes *benzylene*: from it benzoic acid is derived.

The members of the benzene series are *unsaturated* hydrocarbons. A molecule of benzene itself readily absorbs two, four, or six atoms of chlorine, these, being added on to the benzene, forming what are termed *additive* compounds, as distinguished from the true substitutional compounds, in which the hydrogen atoms in benzene are actually substituted by chlorine, bromine, etc.

Bodies having an aromatic odor are somewhat characteristic of the benzene series; hence the latter is often termed the *aromatic series* of organic compounds.

Benzene or Benzol.

Benzene or Phenylene, C_6H_6 (commercially known as *Benzol*).—Commercially, it is obtained from the portion of coal-tar boiling below $100^\circ C$. It is partially purified by shaking successively with sulphuric acid, water, and caustic soda, and then redistilling, the product still containing large quantities of toluene and other impurities. If pure benzol is required, the liquid must be subjected to a freezing mixture, when the benzol crystallizes out, leaving some impurities in solution; the crystals are then drained. Bromine is then added to the liquid resulting from the melting of the crystals until a permanent coloration results. The liquid is again washed with caustic soda, and distilled. Benzene boils at $81^\circ C$. It may be artificially produced by heating benzoic acid with lime or by passing acetylene through red-hot tubes. It is a colorless, limpid, refractive liquid, having a specific gravity of 0.9. It is a powerful solvent of grease, and under the name of benzine collas was introduced by M. Collas in 1848 for cleansing purposes.

Benzene when acted on by chlorine and bromine in the presence of a little iodine, forms all derivatives from monochloro- and monobromobenzene (C_6H_5Cl and C_6H_5Br) to hexachloro- and hexabromobenzene (C_6Cl_6 and C_6Br_6). It also forms iodine and fluorine derivatives, nitro-derivatives, etc.

Nitrobenzene (nitrobenzol, artificial oil of bitter almonds, or essence of mirbane), $C_6H_5NO_2$, is obtained by mixing fuming nitric acid or a mixture of nitric and sulphuric acids with ben-

* Care must be taken to distinguish between benzene, C_6H_6 , and benzol, petroleum ether, benzolin, etc. (*Petroleum Spirit*, B. P.), which are mixtures of paraffin hydrocarbons of lower boiling-points. *Benzin* (U. S. P.), C_8H_{12} : C_8H_{14} , and other hydrocarbons of the paraffin series having the boiling-point of $122-140^\circ F$, requires six times its bulk of alcohol for solution, whereas benzene, C_6H_6 , dissolves in less than its own bulk. Specific gravity of benzene, about 0.850; of benzin, about 0.700.

zene, the vessel being kept cool by immersion in water. It is a yellow liquid, heavier than water, having a strong odor of oil of bitter almonds, though of very different nature. (*Vide* "Oil of Bitter Almonds" in Index.) When acted on by nascent hydrogen it yields aniline.

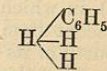
Aniline, or Phenylamine, or Amidobenzene, $C_6H_5NH_2$.—Mix 13 parts of iron filings, 7 or 8 of acetic acid of sp. gr. 1.05, and 13 of nitrobenzene, in a large flask (with an upright condenser) placed in a water-bath, and set the whole aside for some time. After the mixture has digested for several hours, the supernatant liquid is poured off from the deposit of iron filings and distilled in a current of steam. By this method the nitrobenzene yields, first, aniline, distilled over as a yellow oil, and afterward a red oil, which is a mixture of azobenzene, hydrazobenzene, and azoxybenzene.

Aniline, when acted on by arsenic acid or chlorinated lime, produces *roseaniline*, $C_{20}H_{19}N_3$, whose salts and derivatives form most of the well-known aniline colors. Dinitrobenzene is also known.

Constitution of Amines.—Amines are usually viewed as derivatives of ammonia, one, two, or three atoms of hydrogen being replaced by one, two, or three monatomic organic radicals, or equivalents of radicals of higher quantivalence. The products were formerly known as amidogen (NH_2) bases, imidogen (NH) bases, and nitrile (N) bases, but are now termed primary, secondary, and tertiary amines. They are of special interest because alkaloids are included in this class. Thus:—



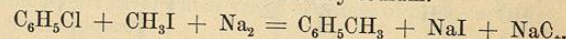
Ammonia.



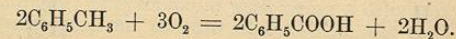
Phenylamine.

(For other examples, *vide* "Alkaloids" in Index.)

Toluene, Benzylene, Methylphenylene, or Methylbenzene, known also as Toluol, $C_6H_5CH_3$, forms the principal portion of coal tar, boiling between $100-120^\circ C$; it may be synthetically made by acting on monochlorobenzene and iodomethane by sodium.



It is also obtained by the dry distillation of tolu balsam. It is an inflammable, refractive liquid, boiling at $111^\circ C$. It may be directly oxidized to benzoic acid.



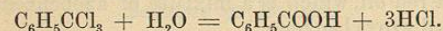
Having both a phenyl (C_6H_5) and a methyl (CH_3) group in its molecule, it forms two sets of isomeric derivatives: one (α) in which,

* Aniline may be obtained from indigo, hence its name, *anil* being Portuguese for indigo.

by acting on toluene in the cold, the atoms of hydrogen are displaced in the phenyl group, and the other (*b*) by acting on boiling toluene, in which the atoms of hydrogen in the methyl group are displaced.*

- a* { Toly chloride, or methylmonochlorobenzene, $C_6H_4Cl.CH_3$.
 Toly dichloride, or methyldichlorobenzene, $C_6H_3Cl_2.CH_3$.
 Toly trichloride, or methyltrichlorobenzene, $C_6H_2Cl_3.CH_3$.
b { Monochloromethylbenzene, or benzyl chloride, $C_6H_5CH_2Cl$.
 Dichloromethylbenzene, or benzyl dichloride, $C_6H_4CHCl_2$.
 Trichloromethylbenzene, or benzyl trichloride, $C_6H_3CCl_3$.

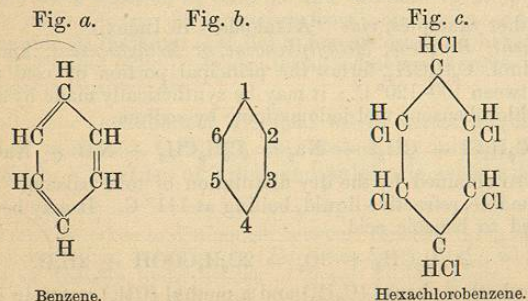
Dichloromethylbenzene, when acted on by glacial acetic acid and zinc chloride and water, produces benzoic aldehyde, C_6H_5COH (Jacobson). By acting on trichloromethylbenzene by water in sealed tubes benzoic acid results.



Cymene, $C_{10}H_{14}$.—Propylmethylbenzene, $C_6H_4(CH_3)(C_3H_7)$ occurs in several volatile oils, and is readily obtained by the removal of hydrogen from the terpenes ($C_{10}H_{16}$) of those oils. Many of the members of the benzene series have an aromatic odor, hence the synonym *aromatic series*.

CONSTITUTION OF THE BENZENE SERIES.

The fact that benzene forms three additive derivatives with chlorine, C_6H_5Cl , $C_6H_4Cl_2$, and $C_6H_3Cl_3$, 1 molecule uniting with not more than 6 atoms of chlorine, and that it affords no isomeric mono-substitution-derivatives, led Kékulé to represent benzene by the following figure (*a*), in which each atom of carbon is assumed to be linked to an adjacent atom of carbon by three-fourths of its affinity, the remaining fourth of its attraction being exerted toward the equivalent attraction of another atom, thus (Fig. *a*):—



* "Benzyl" is the name given to the derivatives of benzene when substitution takes place in the methane nucleus, "tolyl," when in the phenylene nucleus.

In a mono-substitution-derivative such as chlorobenzene, C_6H_5Cl , no matter where the atom of chlorine be placed, it bears the same relation to the other atoms of hydrogen; but in dichlorobenzene, $C_6H_4Cl_2$, the atoms of chlorine may (representing, for the moment, benzene by a hexagonal figure (*b*), and assuming that the carbon atoms are at the angles) be either placed at 1 and 2, 1 and 3, or 1 and 4, the chlorine atoms being either near to each other, separated by one carbon atom or by two carbon atoms; and in trichlorobenzene, $C_6H_3Cl_3$, the atoms of chlorine may be placed at 1, 2, and 3; 1, 2, and 4; or 1, 3, and 5; 1, 2, and 4 being the same as 1, 3, and 4; 1, 2, 3 the same as 1, 6, and 5, etc., that is to say, the chlorine atoms must all three be near to each other, or two near to each other, and one be separated, or all three be separated as far from each other as possible in the molecule. Hence, theoretically, there can only be three isomeric di- and trichlorobenzenes; which has been verified by experiment. (For other illustrations see page 457.) In the additive compounds a second quarter of the affinity of the carbon atoms for each other is freed, so to say, for exertion toward the added chlorine atoms (Fig. *c*).

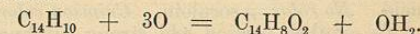
OTHER SERIES OF HYDROCARBONS.

The Naphthalene Series, C_nH_{2n-12} .

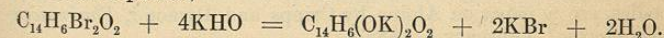
Naphthalene, $C_{10}H_8$, is the only important member of this series. It is a white crystalline body, existing in the higher fractions of coal tar. By oxidation it yields phthalic acid, the anhydride of which, when fused with phenol, forms phenol-phthalein, used as an indicator in alkalimetry. Crude naphthalene is employed for increasing the luminosity of ordinary coal gas.

The Anthracene Series, C_nH_{2n-18} .

Anthracene, $C_{14}H_{10}$, is the only noteworthy member of this series, its importance being due to the fact that *artificial madder*, or *alizarin*, is formed from it by the following reactions: Anthracene is first oxidized to anthraquinone by the influence of the nascent oxygen of nitric acid.



By acting on anthraquinone by bromine, it is easily converted into a dibromo-derivative, which yields alizarate of potassium when fused with caustic potash,



Chrysophanic acid ($CH_3C_{14}H_5(OH)_2O_2$) and the *aloins* are related to anthraquinone; chrysophanic acid being a dihydroxy-derivative of methylanthraquinone, and the aloins ($C_{16}H_{18}O_7$) yielding on oxidation aloxanthin or tetrahydroxy-methylanthraquinone.

Aloins.

Aloins.—The aloes (*Aloe*, U. S. P., and *Aloe Socotrina*, B. P.) is an evaporated juice, doubtless much altered by the temperature to