

anything more comes over. The operation is rather slow, but needs little attention and should be done thoroughly. The distillate contains nearly the whole of the nitrous ether and other interfering substances, while in the retort there remains a non-volatile compound of chloride of calcium and methylic alcohol if the latter be present. Now add to the contents of the flask a fluidrachm of water, which decomposes the compound just referred to, and draw over the half-drachm of spirit required for testing. Add it to the usual oxidizing solution composed of 30 grains of red chromate of potassium, 25 minims of strong sulphuric acid, and half an ounce of water; let the mixture stand a quarter of an hour, then distil half a fluidounce. Treat the distillate with a slight excess of carbonate of sodium, boil rapidly down to two fluidrachms, and drop in, cautiously, enough acetic acid to impart a faint acid reaction; pour the liquor into a test-tube about three-quarters of an inch in diameter; add two drops of *diluted* acetic acid, U. S. P., and one grain of nitrate of silver in half a drachm of pure water; apply heat, and boil gently for two minutes. If the spirit is free from methylic alcohol the solution darkens and often assumes transiently a purplish tinge, but continues quite translucent, and the test-tube, after being rinsed out and filled with water, appears clean or nearly so. But if the spirit contains only 1 per cent. of methylic alcohol, the liquid turns first brown, then almost black and opaque, and a film of silver, which is brown by transmitted light, is deposited on the tube. When the sample is methylated to the extent of 3 or 4 per cent., the film is sufficiently thick to form a brilliant mirror. To ensure accuracy, the experiment should be performed by daylight.

#### Ethylic Alcohol.

*Ethyl Alcohol*, or Methyl Carbinol, commonly called simply *Alcohol* ( $C_2H_5OH$  or  $CH_3CH_2OH$ ).—It is a colorless liquid, having a boiling-point of  $173.6^\circ F.$  and sp. gr. 0.7935. Ethyl alcohol may be obtained by passing ethylene into strong sulphuric acid. The product, ethylhydrogen sulphate, when distilled with water yields alcohol:—

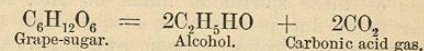


On the large scale alcohol is always formed by fermentation.

*Formation of Alcohol*.—Ferment two or three grains of sugar by dissolving it in a test-tube full of water, adding a little yeast (*Cerevisia Fermentum*, B. P.), or a piece of the so-called German or dried yeast, and setting the whole aside

for several hours in a warm place at a temperature of  $70^\circ$  or  $75^\circ F.$ ; carbonic acid gas is evolved, and, if the tube be inverted in a small dish containing water, may be collected in the upper part of the tube and subsequently tested: the solution contains alcohol. If the experiment be made on larger quantities (four ounces of sugar, one of yeast, and a pint of water), the fermented liquid should be distilled, one-half being collected, shaken with a little lime, soda, or potash to neutralize any acetic acid and decompose ethereal salts, and again distilled till one-half has passed over; the product is dilute spirit of wine. It may be still further concentrated or rectified by repeating this process of *fractional distillation*.

*Fermentation*.—The act of fermentation is commonly the result of, or rather accompaniment of, some vital action. *Alcoholic fermentation* would appear to be always attended by or to attend development of life and free multiplication of cellular structure. It follows the development of the fungus already referred to as constituting the chief active part of yeast, the *Saccharomyces cerevisiae*. In the presence of this fungus, with small quantities of phosphates and albumenoid matter, *glucose* is converted into alcohol and carbonic acid gas, together with small proportions of glycerin, succinic acid, and other substances. Yeast also contains a soluble ferment analogous to diastase, which is capable of converting sucrose into glucose. Therefore if yeast be used, *sucrose* or cane-sugar may be converted into carbonic acid gas and alcohol, the soluble ferment first converting the sucrose into glucose.



Not more than 20 per cent. by weight of alcohol can be obtained in a fermenting fluid, for more than this proportion prevents fermentation.

*Other kinds of fermentation*, arising from the action of special ferments which have not received in all cases distinctive names, are the following: *Viscous* or *Mannitic fermentation*, which occurs when beer or saccharine juices, such as that of beet-root, become "ropy." Gum, mannite, and carbonic acid gas are produced. (For *Lactic* and *Butyric fermentations*, see "Lactic Acid.") *Putrefactive fermentation* occurs when a liquid containing albumenoid matter is exposed to the air. Infusoria appear in the liquid, using up the dissolved oxygen, and the ferments of the genus *Vibrio* are developed. These are protected from oxygen, which is fatal to them, by a thin surface-layer crowded with bacteria—small, rod-like organisms having powers of locomotion. The vibronic action or putrefaction proceeds with evolution of sulphuretted hydrogen, together with other gases having unpleasant odors and of complex chemical constitution. (For *Acetic fermentation*, see "Acetic Acid;" for *Ammoniacal fermentation*, see "Urine.")

*Fermentation by Certain Soluble Albumenoids*.—(For the conver-



sion of starch into sugar by diastase, see "Starch;" of amygdalin into benzoic aldehyde, hydrocyanic acid, and glucose by emulsin, see "Amygdalin;" of salicin into saligenin and glucose, see "Salicin;" of myronate of potassium into sulphocyanide of allyl, etc., by myrosin, see "Mustard;" of cane-sugar into grape-sugar by the soluble ferment in yeast, see the foregoing paragraphs.)

*Alcoholic Fermentation.*—The chief reaction results, as already stated, in the formation of alcohol and carbonic acid gas, though traces of several other substances are simultaneously produced. (*Vide* "Fousel Oil" in Index.) By this reaction are formed the spirits of the various kinds of wine, beer, and liqueurs, such as Orange Wine (*Vinum Aurantii*, B. P.), made "by the fermentation of a saccharine solution, to which the fresh peel of the bitter orange has been added;" Sherry Wine (*Vinum Xericum*, B. P.), the fermented juice of the grape; Whiskey (*Spiritus Frumenti*, U. S. P.), containing from 48 to 56 per cent. of pure alcohol; Bay Rum, or Spirit of Myrcia (*Spiritus Myrciæ*, U. S. P.), prepared by distilling rum with leaves of *Myrcia acris*; and others.

*Alcoholic drinks* vary much in strength. Cider or apple wine, perry or pear wine, and good beer (ale and porter or stout) contain 4 to 6 per cent. of real alcohol; good light wines, both "red" and "white," and natural sherry also, 10 to 12 per cent.; strong sherry and port, which are commonly "fortified"—that is, contain added spirit—16 or 18 per cent.; while "spirits" (gin, rum, brandy, whiskey, etc.) and "liqueurs" (ratafia, almond-flavored; maraschino, cherry-flavored; curaçoa, orange-flavored; chartreuse, a composite flavored liqueur, etc.) are "under-proof" or "over-proof," terms explained in a following paragraph. The well-known effects of these spirituous fluids on the animal system would appear to be due primarily to alcohol, and secondarily to ethereal derivatives of alcohols. Some owe a part of their effect to non-volatile substances, for beer from which all alcohol, etc. has been removed by ebullition still has a powerful influence on the human economy.

The official (U. S. P.) wines are all made with "Stronger White Wine" (*Vinum Album Fortius*, U. S. P.), made by adding 1 part of alcohol to 7 parts of "white wine" (*Vinum Album*, U. S. P.), the latter a kind of natural sherry containing not less than 10 or more than 12 per cent. of absolute alcohol. *Vinum Rubrum*, U. S. P., is of similar strength—a kind of natural port wine.

*Varieties of Alcohol.*—The weak spirit, concentrated by distillation till it contains 84 per cent. by weight of pure alcohol, is an ordinary article of trade; its specific gravity at 60° F. is 0.8382. This is common *Spirit of Wine*, the *Spiritus Rectificatus* of the British Pharmacopœia. The British official *Proof Spirit*\* (*Spiritus*

\* *Proof spirit* is so termed from the fact that in olden times a proof of its strength was supposed to be afforded by moistening a small quantity of gunpowder and setting light to the spirit; if it fired the powder, it was said to be "over-proof;" if not, "under-proof." The weakest spirit that would stand this test was what we should now describe as of sp. gr. 0.920.

*Tenuior*, B. P.) contains 49½ per cent. by weight, 57 by volume, of alcohol, and is made by diluting 100 volumes of "Rectified Spirit" with water until the well-stirred product measures 156 volumes. Sixty volumes of water will be required for this purpose, the liquids occupying less bulk after than before admixture. In the language of the Excise authorities, the rectified spirit of the Pharmacopœia would be described as "56 per cent. over-proof" (56 per cent. O. P.); that is, 100 volumes contain as much alcohol as is present in 156 volumes of proof spirit. Obviously, proof spirit may be made by diluting with water rectified spirit of any other strength than that mentioned above. Thus 100 fluidounces of a spirit of "seventy over-proof" may be diluted to 170, or the same quantity of a spirit of "fifty over-proof" may be diluted to 150, and so on. The specific gravity of proof spirit at 60° F. is 0.920. Spirit 10 per cent. "under-proof" contains as much alcohol as would be present in spirit formed of 90 volumes of proof spirit mixed with sufficient water to form 100 volumes. According to British law, gin is not "adulterated" with water if it is not weaker than 35 degrees under-proof; nor brandy, whiskey, or rum if they are not weaker than 25 degrees under proof.

*Alcohol*, U. S. P., contains 91 per cent. by weight (94 by volume); *Alcohol Dilutum*, U. S. P., 45½ per cent. by weight (53 by volume), of real alcohol, the remainder being water. The former has a sp. gr. of 0.820, the latter 0.928, at 15.6 C., or 0.812 and 0.920 respectively at 25° C. The stronger boils at 78° C.

Absolute or real alcohol,  $C_2H_5(OH)$ , may be prepared from spirit of wine by removing the water which the latter contains. This is accomplished partially by anhydrous carbonate of potassium, and finally and entirely by recently fused chloride of calcium. In operating on, say, one pint, 2 ounces of dried carbonate of potassium are placed in a bottle that can be well closed, and frequently shaken during two days with the spirit. Meanwhile put rather more than a pound of chloride of calcium into a covered crucible, and subject it to a red heat for half an hour; then pour the fused salt on a clean stone slab, cover it quickly with an inverted porcelain dish, and when it has congealed break it up into small fragments and enclose it in a dry stoppered bottle. Put one pound of this fused chloride of calcium into a flask, pour over it the spirit decanted from the carbonate of potassium, and, closing the mouth of the flask with a cork, shake them together and allow them to stand for twenty-four hours with repeated agitation. Then, attaching a dry condenser closely connected with a receiver from which free access of air is excluded, and applying the flame of a lamp to the flask, distil about two fluidounces, which should be returned to the flask, after which the distillation is to be continued until fifteen fluidounces have been recovered. The foregoing details are those of the British Pharmacopœia. The product should be "colorless and free from empyreumatic odor. Specific gravity, from 0.797 to 0.800, and therefore containing 1 or at most 2 per cent. of water. It is entirely volatilized by heat, is not rendered turbid when mixed with water, does not cause anhydrous sulphate of copper to assume



a blue color even after the two have been well shaken together." What little remains may, if necessary, be removed by the cautious addition of a little metallic sodium. If 5 per cent. of sodium be used, solution of ethylate of sodium or caustic alcohol results (*Liquor Sodii Ethylatis*, B. P.) by replacement of the hydrogen in the hydroxyl group of sodium.



The solution contains 19 per cent. of ethylate of sodium.

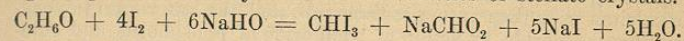
*Spirit of French Wine* (*Spiritus Vini Gallici*, U. S. P.) or *Brandy*, is a colored and flavored variety of alcohol distilled from French wine. Its color is that of light sherry, and is derived from the cask in which it has been kept, but it is commonly deepened by the addition of burnt sugar. Its taste is due to the volatile flavoring constituent of the wine, often increased by the addition of artificial essences. "Brandy has a pale amber color, a distinctive taste and odor, and a sp. gr. not above 0.941 nor below 0.925, corresponding approximately with an alcoholic strength of 39 to 47 per cent. by weight or 46 to 55 per cent. by volume. If 100 c.c. of brandy be slowly evaporated in a weighed capsule on a water-bath, the last portions volatilized should have an agreeable odor, free from harshness (abs. of fusel oil from grain or potato spirit). The residue, dried at 100° C. (212° F.), should weigh not more than 0.250 gm., equivalent to 0.25 per cent. (abs. of an undue amount of solids). This residue should have no sweet or distinctly spicy taste (abs. of added sugar, glycerin, or spices). It should nearly all dissolve in 10 c.c. of cold water, forming a solution which is colored light green by a dilute solution of ferric chloride (traces of oak tannin from casks). 100 c.c. of brandy should be rendered distinctly alkaline to litmus by 3 c.c. of the volumetric solution of soda (abs. of an undue amount of free acid)."—U. S. P.

The foregoing words are also used in describing *Whiskey* (*Spiritus Frumenti*) in the United States Pharmacopoeia, except that the sp. gr. is to be "not above 0.930 nor below 0.917, corresponding approximately with an alcoholic strength of 44 to 50 per cent. by weight, or 50 to 58 per cent. by volume," and that the acidity is not to be greater in 100 c.c. than 2 c.c. of soda solution will neutralize.

*Tests*.—There are no specific tests for alcohol when mixed with complex matters. It is, however, easily isolated and concentrated by fractional distillation, and is then recognizable by conjoint physical and chemical characters. Thus its odor and taste are characteristic; it is lighter than water, volatile, colorless, and, when tolerably strong, inflammable, burning with an almost non-luminous flame; it readily yields aldehyde (see below) and acetic ether (*vide Index*), each of which has a characteristic odor; and, in presence of hot acid, alcohol reduces red chromate of potassium to a green salt of chromium.

According to Lieben, 1 of alcohol in 2000 of water can be detected by adding to some of the warmed liquid a little iodine, a few drops of solution of soda, again warming gently, and setting aside for a time; a yellowish crystalline deposit of *iodoform* ( $\text{CHI}_3$ ) is obtained.

Under the microscope the latter presents the appearance of hexagonal plates or six-rayed and other varieties of stellate crystals.



Other alcohols, aldehydes, gum, turpentine, sugar, and several other substances give a similar reaction.

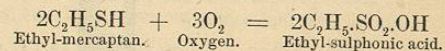
*Tests of Purity*.—Oil or resin is precipitated on diluting spirit of wine with distilled water, giving an opalescent appearance to the mixture. The specific gravity should be 0.838. Fusel oil, aldehyde, and such impurities are detected by nitrate of silver. (*Vide Index*, "Alcohol, test for purity of.") Water in absolute alcohol may be detected by adding to a small quantity a little highly-dried sulphate of copper, which becomes blue ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) if water is present, but retains its yellowish-white anhydrous character ( $\text{CuSO}_4$ ) if water be absent.

*Note*.—Most ethyl derivatives are formed from alcohol, such as the nitrite of ethyl in spirit of nitrous ether, iodoethane, etc. These have been treated under "Ethane." Aldehyde and acetic acid are obtained from alcohol by oxidation.

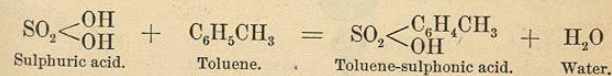
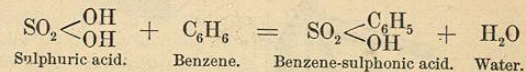
*Alcohols and Ethers*.—Just as such elementary radicals as potassium (K) form hydrates (as KOH) and oxides (as  $\text{K}_2\text{O}$ ), so do such compound radicals as ethyl ( $\text{C}_2\text{H}_5$ ) form hydrates (as common alcohol,  $\text{C}_2\text{H}_5\text{OH}$ , and other alcohols) and oxides (as common ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , and other ethers).

*Sulphur Alcohols*,  $\text{CH}_3\text{SH}$ ,  $\text{C}_2\text{H}_5\text{SH}$ , etc., analogous to sulphhydrates, KHS, etc., are known. They originally were termed *mercaptans* (*mercurius captans*) from the readiness with which they took mercury captive ( $(\text{C}_2\text{H}_5\text{S})_2\text{Hg}$ ). *Sulphur Ethers* also are known,  $(\text{CH}_3)_2\text{S}$ ,  $(\text{C}_2\text{H}_5)_2\text{S}$ , etc. The vapors of such sulphur compounds have an extremely unpleasant smell.

*Sulphonic Acids* are the products of the oxidation of sulphur alcohols. For example,



They also may be formed by acting on hydrocarbons with sulphuric acid. Examples:

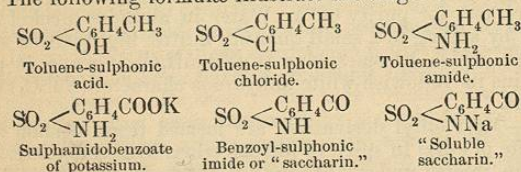


Sulphonic acids are isomeric with acid sulphites. *Orthophenol sulphonic acid*,  $\text{C}_6\text{H}_4\text{OH} \cdot \text{SO}_3\text{OH}$ , *sozolic acid*, or *aseptol*, is a non-poisonous, non-irritating antiseptic.

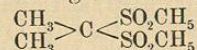
*Saccharin*, which is a harmless, non-alimentary, purely sweetening agent, two or three hundred times as sweet as sugar, is *benzoyl-*



*sulphonic imide.* Fahlberg obtains it by converting the toluene,  $C_6H_5CH_3$ , of coal tar into toluene-sulphonic acid (above); this into a calcium salt, then into a sodium salt, and the latter into toluene-sulphonic chloride by action of trichloride of phosphorus and chlorine; the liquid ortho-chloride into amide by ammonium carbonate; the amide is then oxidized by potassium permanganate to sulphamidobenzoate and water; hydrochloric acid then precipitating benzoyl-sulphonic imide or saccharin with elimination of water. "Soluble saccharin" is saccharin in which hydrogen is displaced by sodium. The following formulæ illustrate the stages of manufacture:



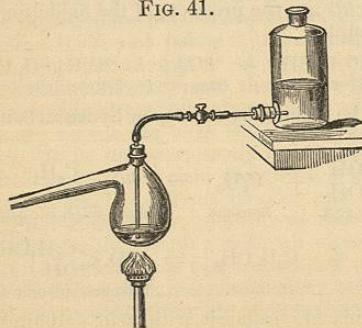
*Sulphonal*, a new hypnotic, is a crystalline, colorless, inodorous, tasteless substance, a product of the action of permanganate solution on mercaptol—a liquid resulting from the reaction of hydrochloric acid, mercaptan, and acetone. Its descriptive name is diethylsulphondimethyl-methane, and the following is its descriptive formula:



### ETHER.

*Experimental Process.*—Into a capacious test-tube put a small quantity of spirit of wine and about half its bulk of sulphuric acid,

FIG. 41.



Preparation of Ether.

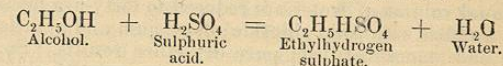
mix, and gently warm; the vapor of ether, recognized by its odor, is evolved. Adapt a cork and long bent tube to the test-tube,

and slowly distil over the ether into another test-tube. Half the original quantity of alcohol now placed in the generating-tube will again give ether; and this operation may be repeated many times.

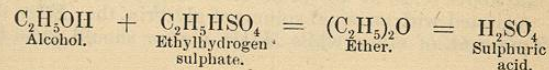
*On the larger scale*, and according to the following official process (*Æther*, B. P.), the addition of alcohol, instead of being intermittent, is continuous, a tube conveying alcohol from a reservoir into the generating-vessel. Mix ten fluidounces of sulphuric acid with twelve fluidounces of rectified spirit in a glass retort or flask capable of containing at least two pints, and, not allowing the mixture to cool, connect the retort or flask, by means of a bent glass tube, with a Liebig's condenser, and distil with a heat sufficient to maintain the liquid in brisk ebullition. (If a thermometer also be inserted in the tubulure of the retort or through the cork of the flask, the temperature may be still more carefully regulated—between  $284^\circ$  and  $290^\circ$  F.) As soon as the ethereal fluid begins to pass over supply fresh spirit in a continuous stream, and in such quantity as to about equal the volume of the fluid which distils. For this purpose use a tube furnished with a stopcock to regulate the supply, as shown in Fig. 49, connecting one end of the tube with a vessel containing the spirit supported above the level of the retort or flask, and passing the other end through the cork of the retort or flask into the liquid. When a total of fifty fluidounces of spirit has been added and forty-two fluidounces of ether have distilled over, the process may be stopped.

To partially purify the liquid, dissolve ten ounces of chloride of calcium in thirteen ounces of water, add half an ounce of lime, and agitate the mixture in a bottle with the impure ether. Leave the mixture at rest for ten minutes, pour off the light supernatant fluid, and distil it, with a gentle heat until a glass bead of specific gravity 0.735 placed in the receiver begins to float. The ether and spirit retained by the chloride of calcium and by the residue of each rectification may be recovered by distillation and used in a subsequent operation.

*Explanation of Process.*—On the addition of sulphuric acid to alcohol in equal volumes, one molecule of each reacts and gives a molecule of ethylhydrogen sulphate and one of water:—



More alcohol then gives ether and sulphuric acid by the reaction of one molecule of the alcohol on one of ethylhydrogen sulphate (sometimes termed ethylsulphuric acid or sulphethylic acid or sulphovinic acid):—



The water of the first reaction and the ether of the second distil over, while the sulphuric acid liberated is attacked by alcohol and reconverted into ethylhydrogen sulphate; so that the sulphuric acid originally employed finally remains in the retort in the form of ethyl-



hydrogen sulphate. The effect, however, of a small quantity of sulphuric acid in thus converting a large quantity of alcohol into ether is limited, secondary reactions occurring to some extent after a time.

**Properties.**—Pure ether is gaseous at temperatures above 95° F.; hence the condensing-tubes employed in its distillation must be kept as cool as possible. At all ordinary temperatures it rapidly volatilizes, absorbing much heat from the surface on which it is placed. A few drops evaporated consecutively from the back of the hand produce great cold, and if blown in the form of spray the cooling effect is so rapid and intense as to produce local anaesthesia. Evaporated by aid of a current of air from the outside of a thin narrow test-tube containing water, the latter is solidified to ice. Its vapor is very heavy, more than twice and a half that of air and nearly forty times that of hydrogen ( $H_2 = 2$ ;  $C_4H_{10}O = 74$ ; or as 1 to 37). In a still atmosphere, therefore, it will flow a considerable distance along a table or floor before complete diffusion occurs; the vapor is also highly inflammable; hence the importance of keeping candle and other flames at a distance during manipulations with ether. Exposed to the action of air and light, ether gives rise to ozone.

**Purification.**—To imitate the process of partial purification above described, add to the small quantity of ether obtained in the foregoing operation a strong solution of chloride of calcium and a little slaked lime; the latter absorbs any sulphurous acid that may have been produced by secondary decompositions, while the former absorbs water; on shaking the mixture and then setting aside for a minute or two, the ether will be found floating on the surface of the solution of chloride of calcium.

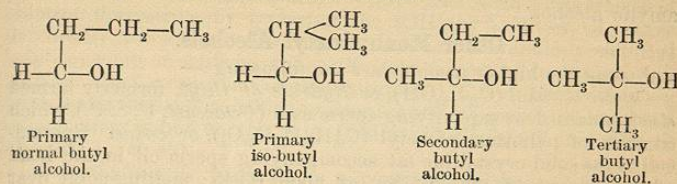
This ether, redistilled until the distillate has a sp. gr. not higher than 0.735, and boiling-point not higher than 105° F., is the ether of the British Pharmacopoeia. It still contains about 8 per cent. of alcohol. The latter may be removed by well shaking the ether with half of its bulk of water, setting aside, separating the floating ether, and again shaking it with water; alcohol is thus washed out. This washed ether containing water (for water and ether are to some extent soluble the one in the other; fifty measures of pure ether agitated with an equal volume of water are reduced to forty-five measures) is placed in a retort with solid chloride of calcium and a little caustic lime, and once more distilled; pure dry ether results. Sp. gr. not exceeding 0.720. *Æther*, U. S. P., contains nearly 74 per cent. of real ether, nearly 26 per cent. of alcohol, and a little water; sp. gr. 0.750 at 15° C. *Æther Fortior*, U. S. P., contains nearly 94 per cent. of real ether, nearly 6 per cent. of alcohol, and a little water; sp. gr. not above 0.725 at 15° C. or 0.716 at 26° C.; boiling-point, 37° C. Agitated with an equal volume of glycerin, the *Æther* should yield 75 per cent. of ether, while *Æther Fortior* should yield 86 per cent.

*Spiritus Ætheris*, U. S. P., is a mixture of 30 weights of stronger ether with 70 similar weights of alcohol. *Spiritus Ætheris Compositus*, U. S. P., contains 30 of stronger ether, 67 of alcohol, and 3 of ethereal oil. It is the old "Hoffmann's Anodyne."

## ALCOHOLS (continued).

## Propylic and Butylic Alcohols.

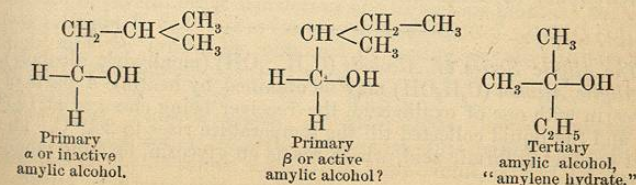
The primary and secondary propyl alcohols ( $C_3H_7CH_2OH$ , and  $CH_3CH_2CHOH$ ) and the four butyl alcohols ( $C_4H_9OH$ ; see below) are of no special pharmaceutical interest.



## Amylic Alcohol.

*Pentyl or Amylic Alcohol (Fousel oil), (Alcohol Amylicum, B. P.)* ( $C_5H_{11}HO$  or  $C_4H_9CH_2OH$ ), is a constant accompaniment of ethylic or common alcohol ( $C_2H_5HO$ ), especially when the latter is prepared from sugar which has been derived from starch; hence the name, from *amylum*, starch. The sugar of potato-starch yields a considerable quantity; hence the alcohol is often called *potato oil*. It is also termed *fousel oil* or *fusel oil* (from *φωσ*, *phuo*, I produce), in allusion to the circumstance that the supposed oil is not simply educed from a substance already containing it, as is usually the case with oils, but is actually produced during the operation. It was described as oil probably because it resembled oil in not readily mixing with water; but it is soluble to some extent in water, and is a true spirit, homologous with the spirit of wine. It often contains variable proportions of propylic, butylic, and caproic alcohols. (See also VALERIANIC ACID.) When used for medicinal purposes "it should be redistilled, and the product, passing over at 262° to 270° F. (or about 128° to 132° C.), be alone collected for use."

Amylic alcohol is "a colorless liquid, with a penetrating and oppressive odor and a burning taste. When pure its specific gravity is .818. Sparingly soluble in water, but soluble in all proportions in alcohol, ether, and the essential oils. Exposed to the air in contact with platinum-black, it is slowly oxidized, yielding valerianic acid" ( $C_5H_9COOH$ ). Two allotropic varieties of amylic alcohol exist—one,  $\alpha$ , having no action on, the other,  $\beta$ , lævo-rotating, a polarized ray. The amylic alcohol of trade probably contains both varieties.





The constitution of the variety of amylic alcohol,  $C_5H_{11}OH$ , known as *tertiary amylic alcohol* or *dimethyl-ethyl-carbinol*, is shown in the above graphic formula. It is used in medicine for hypnotic purposes in place of chloral hydrate, and is known as *amylen hydrate*, for it contains the elements of amylen,  $C_5H_{10}$ , and water,  $H_2O$ .

The pentylic salts of pharmaceutical interest are all derived from amylic alcohol.

#### Other Monhydroxyl Alcohols.

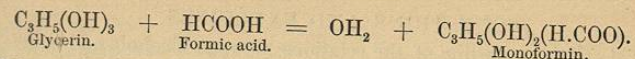
Among the higher alcohols are the following:—

*Cetylic Alcohol* ( $C_{16}H_{33}OH$ ), or *Hydrate of Cetyl*, formerly termed *ethal*, obtained by saponifying spermaceti (*Cetaceum*, U. S. P.), which consists of palmitate of cetyl ( $C_{16}H_{33}C_{16}H_{31}O_2$ ), or *etine*. Spermaceti is the solid crystalline fat accompanying sperm oil in the head of the spermaceti whale. Sp. gr. about 0.945; melting-point near  $50^\circ C$ .

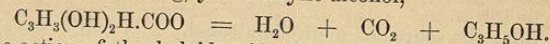
*Cerylic Alcohol* ( $C_{27}H_{55}OH$ ) is obtained in a similar manner from Chinese wax (ceryl-cerolate).

*Melissic Alcohol* ( $C_{30}H_{61}OH$ ) is obtained in a similar manner from melissic palmitate, the portion of beeswax soluble in hot alcohol. *Yellow Wax* (*Cera Flava*, U. S. P.), and the same bleached by exposure to moisture, air, and sunlight, or *White Wax* (*Cera Alba*, U. S. P.), is the prepared honeycomb of the hive-bee. According to Brodie, it is in the main a mixture of the alcohol just named with cerotic acid ( $C_{26}H_{53}COOH$ ) and about 5 per cent. of *ceroleine*, the body to which the color, odor, and tenacity of wax are due. Amongst the possible adulterants of wax are paraffin and *ceresine*. The latter is the purified native *ozokerite* of Galicia, a solid hydrocarbon, largely used as a substitute for beeswax, especially in Russia. Both paraffin and *ceresine* reduce the melting-point of wax, which should not be lower than  $146^\circ F$ . ( $63.3^\circ C$ .) when taken in the manner described in connection with the quantitative determination of temperature (*vide Index*). The amount is obtained by destroying the wax with warm oil of vitriol, and afterward with fuming sulphuric acid, which scarcely affects paraffin and *ceresine*. Pure wax will not yield more than about 3 per cent. to cold rectified spirit, whereas rosin, etc. would be extracted by the spirit. Solution of soda extracts nothing from pure wax, but dissolves fat acids, fats, rosin, Japan wax, etc., and the alkaline fluid then yields a precipitate of acids on the addition of hydrochloric acid. Soap would be dissolved from wax on boiling the sample with water, and the aqueous fluid would yield oily acid on adding hydrochloric acid. Flour or any starch would be detected in the cooled aqueous fluid by iodine.

*The Allylic Series of Alcohols* ( $C_nH_{2n-1}OH$ ) (monhydric alcohols).—*Allylic Alcohol* ( $C_3H_5OH$ ) may be obtained by heating 4 parts of glycerin with one of oxalic acid, the receiver being changed at  $195^\circ C$ ., and the liquid collected till the temperature rises to  $260^\circ C$ . The first product is formic acid, which reacts on glycerin, forming monoformin:—

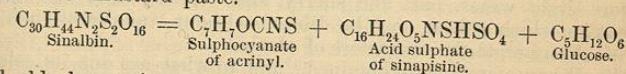


This, on further heating, yields allylic alcohol,



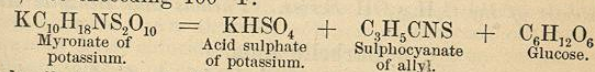
By the action of the haloid acids it produces iodine, bromine, and chlorine derivatives, by replacing the (OH) by I, Br, or Cl; these derivatives, when digested with potassium sulphocyanate, yield allyl sulphocyanate or artificial *Oil of Mustard* (identical in composition with the chief constituent of the natural oil), the sulphocyanate of allyl being the body to which mustard owes its power of inducing inflammatory action on the skin ("Mustard Poultice" and *Charta Sinapis*, U. S. P.).

*Mustard* (*Sinapis*, U. S. P.) is a powdered mixture of black or, rather, reddish-brown mustard-seeds from the *Brassica nigra*, and white mustard-seeds from the *Brassica Alba*. The white mustard-seed contains *sinalbin* ( $C_{30}H_{44}N_2S_2O_{16}$ ), a glucoside which, in contact with the myrosin in an aqueous extract of mustard, yields the sulphocyanate of the radical *acrinyl*, a body which forms part of the essential oil of mustard paste.



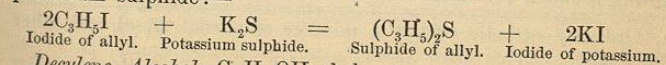
The black contains the albumenoid ferment, *myrosin*, resembling the *emulsin* of almonds, and also myronate of potassium, or *sinigrin*. The latter is the body which, under the influence of the former, yields the chief part of the pungent oil of mustard paste. The amount of myrosin in black mustard is scarcely sufficient to decompose the whole of the sinigrin, while in white mustard the amount is more than sufficient to decompose sinalbin. Hence the most effective mustard is a mixture of white and black.

The ferments act most effectively, and therefore the maximum amount of pungency is produced in mustard paste at low temperatures, not exceeding  $100^\circ F$ .



Crude oil of mustard often contains *cyanide of allyl*,  $C_3H_5CN$ .

In the Pharmacopoeia of India the seed of *Sinapis juncea*, *Rai*, or *Indian Mustard Plant*, is official in addition to that of *S. alba* and *S. nigra*. It is the common mustard of warm countries. It does not differ chemically from other mustard. Allyl compounds are also met with in several other cruciferous and liliaceous plants. *Oil of garlic* (*Allium*, U. S. P.) owes its odor to a sulphide of allyl ( $C_3H_5$ )<sub>2</sub>S, which may be artificially obtained by acting on allyl iodide by potassium sulphide:—



*Decylene Alcohol*,  $C_{10}H_{19}OH$ , belongs to this series. *Menthol* (*Menthol*, B. P.), obtained from oil of peppermint, is said by some to consist wholly of this alcohol.



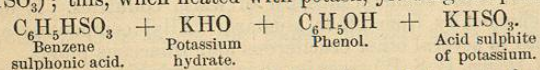
## QUESTIONS AND EXERCISES.

724. Give an outline of the relations between alcohols and acids.  
 725. Give a general method of preparing the primary alcohols of the ethylic series.  
 726. Name the source of methylic alcohol.  
 727. What is "methylated spirit"?  
 728. Describe the method by which methylated spirit is detected in a tincture.  
 729. How can artificial ethylic alcohol be prepared?  
 730. Write a few sentences on the formation, purification, and concentration of alcohol, and explain the difference between rectified spirit, proof spirit, and absolute alcohol.  
 731. What quantity of water must be added to one gallon of spirit of wine 56 degrees over-proof to convert it into proof spirit?  
 732. To what volume must 5 pints of spirit of wine of 53 degrees over-proof be diluted before it becomes proof spirit?  
*Ans.* 7 pints 13 ounces.  
 733. State the specific gravity of proof spirit.  
 734. State the proportion of alcohol commonly present in malt liquors, light wines, port and sherry, and "spirits," and state the extent to which spirits may be diluted without "adulteration."  
 735. Enumerate the characters of alcohol.  
 736. Whence is brandy obtained? and to what are due its color and flavor?  
 737. Describe the official process for the preparation of ether, giving equations.  
 738. Offer a physical explanation of the mode of producing local anaesthesia.  
 739. How is commercial ether purified?  
 740. Is "amylic alcohol" a simple or complex body?  
 741. How is allylic alcohol prepared? In what relation does allylic alcohol stand to oil of mustard and oil of garlic?

*Alcohols of the  $C_nH_{2n-1}OH$  Series. Phenols and Benzylic Alcohols.*

## Carbolic Acid.

*Phenol, Phenic Alcohol, Phenic Acid, or Carbolic Acid\** ( $C_6H_5OH$ ) may be artificially obtained by heating benzene with sulphuric acid, which forms benzene (page 446) sulphonic acid ( $C_6H_5HSO_3$ ); this, when heated with potash, yielding the phenol:—



Commercially, carbolic acid is obtained from that part of coal tar boiling between  $180^\circ$  and  $190^\circ$  C. When purified it is a colorless†

\* Ordinary carbolic acid is a mixture of phenol, cresol, and other homologues.

† Phenol soon assumes a pink color, probably owing to the formation of aurin ( $C_{19}H_{14}O_3$ ) or rosolic acid ( $C_{20}H_{16}O_3$ ) by absorption of carbonic acid and oxygen.

crystalline body (*Acidum Carbolicum*, U. S. P.). A crystalline, so-called hydrous acid ( $C_6H_5OH.H_2O$ ) may also be obtained.

At temperatures above  $95^\circ$  F. ordinary carbolic acid is an oily liquid. It is only slightly soluble in water, but readily dissolved by alcohol, ether, and glycerin (*Glycerinum Acidi Carbolici*, B. P.). In odor, taste, and solubility (and in appearance when liquefied by heat or by the addition of 5 to 10 per cent. of water) it resembles creasote, a wood-tar product for which carbolic acid has been substituted. Besides phenol ( $C_6H_5OH$ ), coal-tar oil contains *cresol*, cresylic acid ( $C_7H_7OH$ ), or ( $C_6H_4CH_3OH$ ), the alcohol of toluene, while wood-tar oil furnishes *guaiacol* ( $C_7H_7O_2$ ), boiling-point  $200^\circ$  C.—also a product of the destructive distillation of guaiacum resin—and *creasol* ( $C_8H_{10}O_2$ ) or creasote. Certain coloring-matters may be obtained by the oxidation of carbolic acid; ammonia or, still better, phenyl-ammonia (aniline or phenylamine) mixed with it, and then a small quantity of solution of a hypochlorite, gives a blue liquid. No very satisfactory chemical method can be found for distinguishing creasote from carbolic acid, as creasote contains phenol, the chief difference consisting in the fact that the former boils only at  $370^\circ$  F., while the latter readily dries up at  $212^\circ$ . Some other physical differences exist: thus, carbolic acid does not affect a ray of polarized light; creasote twists it slightly to the right. Carbolic acid is either solid or may be solidified by cooling; creasote is not solidified by the cold produced by a mixture of hydrochloric acid and sulphate of sodium. Creasote from coal (impure or crude carbolic acid) gives a jelly when shaken with albumen or with collodion; creasote from wood (*Creasotum*, U. S. P.) is scarcely affected, especially if quite free from even all natural traces of carbolic acid. Coal creasote is soluble in solution of potash and in the strongest solution of ammonia (Read), wood creasote scarcely soluble. The coal product is soluble in twenty volumes of water, and a neutral solution of ferric chloride strikes a more or less permanent green or blue color with the liquid; wood creasote is less soluble (*Aqua Creasoti*, U. S. P., is said to contain 1 in 129), and not permanently colored blue by ferric chloride. An alcoholic solution of the coal oil is colored brown by ferric chloride; a similar solution of true creasote green. A dilute solution of creasote, such as creasote-water, is not affected by agitation with spirit of nitrous ether, while a similar solution of phenol becomes red. A few drops of the spirit of nitrous ether are placed in a test-tube, then about a drachm of the aqueous fluid and an equal volume of sulphuric acid are poured down the sides of the tube. A pink or red color results if phenol be present, especially after standing aside a short time (Eykmán; MacEwan). A solution of carbolic acid gives with excess of bromine-water an insoluble white precipitate of tribromo-phenol,  $C_6H_2Br_3OH$ . This reaction is useful in quantitative estimations of carbolic acid. According to Mr. Thomas Morson, pure creasote is unaffected when mixed with an equal volume of commercial glycerin, while carbolic acid is miscible in all proportions, and will carry into solution even a considerable quantity of creasote.

Carbolic acid and alkalis yield *carbulates* or *phenylates*, as