

ARTIFICIAL PERFUMES.

H. S. GROAT.

The tendency of the present day on the part of both, the large perfume manufacturers and pharmacists who make their own perfumes, is decidedly toward the manufacture and perfection of artificial goods. The constant increase in price and consequent unreliability in quality of essential oils, has been a main factor for this change, augmented by the rapid advancement of the science of organic chemistry.

Since the active principle of many drugs is now made synthetically almost the entire world's supply of these now comes from the chemical laboratory. The active odoriferous principles of many, if not most, of the essential oils have been isolated and their identity with synthetic organic compounds firmly established. In fact, so extensively has this field been developed that now one can obtain commercially and at much lower figures, the odoriferous principle of almost every known essential oil; consequently perfumes made from these synthetic compounds are much cheaper than the natural perfumes, and in many of the cases are the equal, if not the superior, of the natural product itself.

"Artificial Perfumes" is a very exhaustive and complex subject and so closely allied with advanced organic chemistry that in this brief treatise, I can mention in a limited way only the more important of these synthetic bodies of which the artificial perfumes of the present day are merely mixtures.

VANILLIN.—Vanillin is identical with the active ingredient or chief constituent of vanilla, and is extensively used in enhancing natural extracts as well as the chief flavoring agent of artificial vanilla flavorings. Vanillin is methyl protocatechuic aldehyde— $C_6H_3(CO H) (OCH_3)_3 (OH)_4$. It occurs in white needles and melts at $81^\circ C$. It has an intensive vanilla odor and is used extensively in confectionery, as well as in perfumery.

COUMARIN.—Coumarin is the active principle of the Tonka Bean, and is used extensively as a substitute for it in the manufacture of flavoring extracts. It is a white crystalline solid, melting at $67^\circ C$. Coumarin is the delta lactone of coumarinic acid— $C_9H_6O_2$. It is used considerably in perfume manufacture as a fixative for other odors, and is the most important synthetic compound of this class. It is the chief ingredient of *Foin Coupe*, or New Mown Hay Bouquet.

HELIOTROPIN.—Heliotropin is a synthetic compound possessing a powerful Heliotrope odor. It is a white, crystalline compound, melting at $37^\circ C$. Heliotropin is the methylene ether of Protocatechuic aldehyde— $C_6H_3(CHO) (O_3) (CH_2O_3)$. An alcoholic solution of it makes a very fine Heliotrope perfume, which can be improved by a little vanillin or coumarin for a fixative and intensifier, blended with a little bergamot, lemon or neroli oils.

AUBEPINE OR HAWTHORNE.—The concentrated odor of Hawthorne or May blossoms is represented by anisic aldehyde— $C_6H_4(OCH_3) (CHO)_4$. When properly diluted this makes a very pleasant perfume, which is greatly augmented by blending with a small quantity of citrus oil—orange or petitgrain.

IONONE.—Ionone is the concentrated violet odor. In the concentrated form it does not in the least resemble violets, but does when greatly diluted. The commercial product is only a 10% alcoholic solution, because of its great intensity of odor. Ten cubic centimeters of this extract when diluted with pure spirits are sufficient to produce a thousand cubic centimeters of triple extract of violets. The perfume is enhanced by the addition of a little orris oil, which acts chiefly as a fixative. The chemical formula of "Ionone" is kept a trade secret, but it is evident that the several commercial brands now on the market vary chemically; according to Tiemann, they vary from alpha, beta and gamma Irone— $C_{13}H_{20}O$ —to the beta, oxime and alpha ketones of same.

ARTIFICIAL MUSK.—For many years attempts have been made to artificially imitate the odor of musk. Not however, upon the basis of any knowledge of the constitution of the natural perfume. The chemistry of natural musk—the preputial secretion of the musk deer, *Moschus Moschiferus*, is entirely unknown. The artificial musk of modern perfumery is tri-nitro-butyl toluene—a white, crystalline solid, melting at $96^{\circ} C$. The entire commercial supply has been manufactured under the patents of Albert Bauer until recently, when a rival manufacturing chemist successfully marketed a di-nitro-butyl xylene as an artificial musk. The odoriferous constituent of the musk does not appear until the nitrated hydrocarbon radical has been introduced into the compound. The use of musk is extensive for perfumery of a certain kind, where powerful odors are desired. It is used very extensively in the scenting of toilet soaps, the presence of alkali improving its odor as well as acting as a fixative.

ARTIFICIAL NEROLI.—At present there are two artificial neroli substances on the market; one a solid, sold under the name of "Nerolin," the other a liquid called "synthetic Neroli oil." "Nerolin" is beta naphthol Methyl ether, a white crystalline compound, melting at $70^{\circ} C$., first introduced into commerce under the name of "Bromelia." Synthetic neroli oil is a mixture of the alcohol geraniol— $C_{10}H_{16}O$ —and linolol— $C_{10}H_{18}O$ —together with their acetic esters. The characteristic odor, according to Erdmann, is due to the presence of the Methyl ester of anthranillic acid. The artificial neroli oils of commerce are uneven in value, and as their exact composition is a trade secret, the only road open to the practical perfumer is to imitate the natural oil by experimental mixtures of the compounds named.

ARTIFICIAL LILAC.—Terpineol— $C_{10}H_{16}OH$ —in dilute form possesses an odor almost identical to that of natural lilacs, though also suggesting elder flowers and hyacinth. Terpineol is the basis of many floral perfumes of this class. A mixture of 90% terpineol and 10% palmarose oil, yielding perfume indistinguishable from the favorite French perfume, *Muguet*. (The term *Muguet* is merely a French equivalent of Lily of the Valley.) In general, lilac extracts, or "white lilac," may be regarded as solutions of terpineol, which are slightly modified by the addition of other perfumes, generally oils of ylang ylang, geranium, sandalwood or rose, according to taste. For perfuming soaps a straight solution of 1% terpineol does very well.

ARTIFICIAL HYACINTH.—Several of the artificial oils of Hyacinth are on the market which are fairly good imitations of the natural perfume, chief among

them being chlorstyrolene and alpha bromstyrolene. Styryl alcohol— $C_9H_{10}O$ —also known as cinnamyl alcohol, has a powerful odor of hyacinths, while benzyl alcohol— $C_6H_5CH_2OH$ —is an aromatic body of strong hyacinth and bitter almond odor.

ARTIFICIAL LEMON OIL.—There are on the market several preparations which bear the label synthetic oil of lemon, (terpenless), and which possess a strong lemon odor. Analysis by Parry and other authorities shows that citral is the chief compound of these preparations. Citral in a diluted state has been strongly recommended as a substitute for lemon oil by the Schimmel Company, who in one of their late annual reports says, "Normal lemon oil contains, on the average, about $7\frac{1}{2}\%$ of citral. Therefore, 75 grammes of citral would suffice as a substitute for one kilogramme of oil of lemon. As its flavor is somewhat wanting in the degree of freshness characteristic of good lemon oil, this deficiency must be neutralized by an addition of lemon oil." Therefore, citral is now generally used in combination with oil of lemon. The most approved proportion is 100 grammes of citral to 1400 grammes of oil of lemon. This is equivalent in odoriferous strength to three kilogrammes of oil of lemon. We quote farther: "Fifteen grammes of the mixture are sufficient for making one hectoliter of lemon liquor, and this remains clear, even if it contains only 30% alcohol. For making lemon syrup to be used for lemonades, 20 to 25 grammes are sufficient for 100 kilogrammes of syrup. When the use of citral is preferred without the addition of oil of lemon, the following solution deserves the preference: 75 grammes of citral and 925 grammes of alcohol (95%). This equals one kilogramme of oil of lemon in odoriferous power.

ARTIFICIAL ROSE OIL.—Although numerous "artificial" and "synthetic" rose oils are listed by various firms, there is nothing which in any way competes with the fine odor of natural otto of roses. The two best defined constituents of oil of rose are the alcohols geraniol— $C_{10}H_{17}OH$ —and citronellol— $C_{10}H_{20}O$ —and these bodies with a trace of their acetic esters will produce as good an "artificial oil of roses" as may be made. A little genuine oil of roses is frequently added to make the substitute a little more passable. A compound patented by Schering, termed di-methyl-heptadinol— $C_9H_{16}O$ —which possesses strong rose odor, has met with commercial success.

NIOBE OIL.—The synthetic perfume sold under this name is merely a methyl benzoate— $C_6H_5COOCH_3$ —. It is a liquid having the specific gravity of 1.102, and a boiling point of $195^\circ C$.

BERGAMOIL.—This body, which is used as a substitute for bergamot oil, and which it resembles very closely, is simply linalyl acetate— $C_{10}H_{17} C_2H_3O_2$.

ARTIFICIAL JASMINE OIL.—The natural jasmine perfume is due to an essential oil, but this is both exceedingly delicate and expensive. The odoriferous principle of jasmine is generally extracted in the form of a pomade. There, however, are several brands of synthetic oil of jasmine on the market, their chemical composition varying greatly. None of them are single compounds, but are mixtures of several odoriferous bodies, which together reproduce very fairly the jasmine perfume.

According to Verley (owner of the French patents for jasmine oil) a mixture

of 10% linalol and 90% phenyl-glyco-methylene-acetal makes an admirable artificial product, as these two chemical compounds are the chief constituents of the natural oil. Other authorities, Hesse and Mueller, deny the existence of phenyl-glyco-methylene-acetal in jasmine oil, or that they even give a jasmine odor. Their conclusion lead us to infer that a fine artificial product results, from a mixture of benzyl acetate, 65%; linalyl acetate 7 to 10%; benzyl alcohol, 6%; linalol 16%. We infer from Parry's experiments that secondary styrolyl acetate— $C_6H_5 \cdot CH(O \cdot COCH_3) \cdot CH_3$ —is in itself a good product. Artificial jasmine oil is made on the basis of these researches, although probably small quantities of some bodies not generally known are added by the manufacturers.

ARTIFICIAL COGNAC OIL.—Cognac oil, which is not an essential oil in the fullest sense, is prepared by distilling wine lees with seven or eight times its weight of water. Commercial "oenanthic ether" serves its purpose fully and is a product of more reliable quality than the genuine oil. It is not used so much in the manufacture of artificial perfumes as in the manufacture of brandies, chiefly for flavoring poor qualities of brandies made from corn.

Any intelligent perfumer can produce most all of the natural perfumes from the synthetic bodies of which we have spoken briefly or otherwise. Very finished products can be perfected by the proper and cautious use of the more common aromatic alcohols and esters for correctives, intensifiers and fixatives.

DETERIORATION OF GALENICALS.

E. KIMMICH, PH. G.

Many of the U. S. P. and N. F. galenical preparations deteriorate after storage for periods varying from a few weeks to several years, and this change in constitution is due to the action of light, changes in temperature, oxygen of the air, the action of living organisms, and the spontaneous breakdown which must take place sooner or later. These changes sometimes alter the physical properties of a preparation to such an extent that it seems like a different product.

Every pharmacist has had his troubles with liquid preparations containing Iron Phosphate and Pyrophosphate; he knows that when such products, (mainly elixirs) are freshly made they are usually of a light amber or pale greenish color; but on aging some turn to a darker green or brown, depending on the solvents or adjuvants used, such as the alkaline citrates, ammonium chloride or acetate, and sodium chloride.

When exposed to light for a much longer period, decomposition and precipitation takes place. While these changes are largely brought about by the action of light and temperature, the solvents and menstrua used have a great deal to do with hastening the process.

Some years ago I made several series of experiments in an effort to determine the principal cause of such changes. These experiments, consisted mostly of the group containing Iron Phosphate Sol., Iron Pyrophosphate Sol., and Tincture