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ESSENTIAL OILS AND SYNTHETIC PERFUMES.*

BY JOHN GLASSFORD.

We do most things either to avoid pain or to induce pleasure, and, in this paradoxical world of ours, it is through the same five senses that we get what is coming to us or what we go after. Music lovers say that the most sublime heights are reached through music and the sense of hearing, but that is a matter of taste and many of us no doubt would thrill more intensely over a view of the Grand Canyon or Niagara Falls than over the most beautiful symphony ever composed. The

* Address before Baltimore Branch of the AMERICAN PHARMACEUTICAL ASSOCIATION, March 26, 1926.

pleasures of the sense of smell are secondary or auxiliary to those of sight and hearing, enhancing their enjoyment by a subtle charm, unobtrusive yet insistent, like the delicate touch of flavor which the skilful cook adds to the dainty dish and which we do not notice but would miss greatly were it not there. Then, too, the sense of smell is capable of arousing the most poignant memories of persons and places loved and long forgotten.

There have been several theories propounded in explanation of the act of smelling, the electrical, the vibrational and the chemical. It is the last that now is regarded with most favor. The olfactory nerve is situated in an upper chamber of the nasal cavity, out of the direct line of the air currents produced by breathing. It is covered by both an aqueous mucous and a lipoid fat layer, in both of which an odorous substance must be soluble in order to be perceived. The stimulus is probably produced by a chemical reaction between the osmoceptor of the nerve and the osmophore of the odorous material. The osmoceptor may become exhausted, when the nerve can no longer perceive the odor that exhausted it. This fact is useful in the analysis of perfumes. Let us say, the odor of rose has been detected in a mixture. By smelling oil of rose directly, this odor may be removed as it were from the mixture and other constituents more readily perceived. The sense of smell is the most delicate of all the senses. It is said to be capable of detecting 1/460,000,000 of a milligram of mercaptan, 1/120,000 of a grain of oil of rose, or vanillin in a dilution of 1 to 10,000,000.

Odors are variously classified. Beaunis distinguishes between pure scents which affect only the olfactory nerve, pungent odors which irritate the tactile nerves only, and mixed odors which affect both the olfactory and the tactile nerves. Henning's investigations would indicate that there are but six elementary odors, namely: (1) Spicy, as cloves. (2) Flowery, as rose. (3) Fruity, as apple. (4) Resinous, as turpentine. (5) Foul, as hydrogen sulphide. (6) Scorched, as tar. The most elaborate classification is that of Zwaardemaker. This is as follows:

1. Ethereal or Fruity.
2. Aromatic; (*a*) Camphoraceous; (*b*) Spicy; (*c*) Anise-Lavender; (*d*) Lemon-Rose; (*e*) Amygdaline.
3. Fragrant or Balsamic; (*a*) Floral; (*b*) Lily; (*c*) Balsamic.
4. Ambrosial, as musk and amber.
5. Alliaceous; (*a*) Alliaceous; (*b*) Cacodyl-fish; (*c*) Bromine.
6. Empyreumatic or Burnt.
7. Hiroine or Cheesy.
8. Repulsive, as Acanthus and many narcotic plants.
9. Nauseating or Fetid, as products of putrefaction.

I regard Zwaardemaker's classification as unnecessarily complicated and, in places, illogical. For instance, why should rose and lavender be classified as aromatic rather than fragrant? And surely lemon is fruity rather than aromatic. The most practical classification, in my opinion, is that based on Henning's work with the addition of the pungent odors suggested by Beaunis.

It is possible not only to become accustomed to an odor at first disagreeable, but actually to grow to like it. The odor of opium evolved in its digestion in hot water was at first very disagreeable to me but, later, I became very fond of it. A fellow chemist who worked in a red oil and stearic acid plant used to say that he preferred the odor of the foul fats he handled to that of phenyl acetic aldehyde, a most useful synthetic perfume of hyacinth type. Perhaps there is some truth to the story of the poor boy from the slums who complained of the eggs at the fresh air farm because "they didn't have no smell."

Following the above classifications with modifications we may divide essential oils and synthetic perfumes into the following eight classes:

1. Ethereal or fruity oils, as amyl acetate, amyl valerianate, ethyl butyrate, aldehyde C_{14}, etc.
2. Aromatic oils, as cloves, cinnamon, nutmeg, mace, pimento, calamus, Canada snake root, etc.
3. Camphoraceous oils, as oil of camphor, eucalyptus, rosemary, peppermint, thyme, etc.
4. Light flowery oils, as jasmine, rose, ylang-ylang, bay, etc.
5. Heavy flowery oils, as lily, tuberose, narcisse, hyacinth, etc.
6. Balsamic perfume materials, as tolu, balsam of Peru, benzoin, labdanum, etc.
7. Ambrosial, as musk, ambergris, etc.
8. Pungent oils, as oil of mustard.

Essential oils and other perfume materials are obtained either by mechanical expression, distillation, extraction by means of a volatile solvent, absorption by hot fat or by absorption by cold fat.

Only oils occurring abundantly in the oil-bearing tissues can be economically extracted by cold expression. Practically there are only three of them, orange, lemon and bergamot. Oil of limes can also be thus produced but the distilled oil is preferred. These are the citrus oils, all containing terpenes which readily acquire a rank odor on heating in the presence of air. Recently, however, vacuum distillation in the absence of air has been so perfected that citrus oils of very high quality have been distilled.

By far the greater number of volatile oils are produced by distillation with steam. The steam carries over with it a quantity of volatile oil which is proportional to its molecular weight times its partial vapor pressure at the temperature at which distillation occurs. Nitrobenzol, for instance, boils at 204° C. A mixture of nitrobenzol and water, however, boils at 99° C., and the mixed vapors contain about 20% by weight of nitrobenzol.

Extraction with volatile solvents is applicable to a number of flowers formerly extracted by hot or cold fat absorption, such as violets, roses, orange blossoms, jasmine, cassie and mignonette. The volatile solvent employed is usually a highly purified petroleum ether. The residue left after the evaporation of the solvent is called a concrete. It contains undesirable waxes which are removed by treatment of the concrete with alcohol in which the waxes are insoluble, filtering and evaporating off the alcohol from the filtrate. This leaves a highly concentrated floral essence called a "quintessence" or an "absolute."

Hot absorption is of limited application but is used for the manufacture of certain floral "pomades" such as rose, orange blossoms and lily of the valley; the pomades thus produced are inferior to those produced by cold absorption or "enfleurage a froid" next to be described.

The most delicate perfumes are extracted from the flowers in which they occur, with the least injury to their quality, by absorption by a cold mixture of lard and beef tallow which, of course, has been highly purified. Thin layers of the fat on glass plates are exposed to the flowers in frames for from one to three days; the flowers being changed, in some cases, as often as thirty times. The saturated fat is then extracted with alcohol, the alcoholic extract being strongly cooled to separate dissolved fat and evaporated to obtain the "quintessence" or "absolute," as in the case of the extraction by means of volatile solvents.

It is a peculiarity of certain flowers that they continue to produce their perfume during the process of extraction by cold absorption, thus yielding many times as much essence as can be obtained by processes of extraction which kill the active flower cells. Thus Hesse found that ten times as much perfume is extracted from jasmine flowers by cold enfleurage as by extraction with volatile solvents.

The constituents of essential oils are hydrocarbons, terpenes, alcohols, esters, aldehydes, ketones, phenols and phenolic compounds, oxides and lactones, nitrogen compounds, sulphur compounds and free acids.

The hydrocarbons are of very minor importance as perfume materials though they make up the great bulk of many essential oils. Styrolene occurs in styrax. Of the terpenes, $C_{10}H_{16}$, pinene occurs in oil of turpentine, and limonine constitutes 92% of oil of lemon. Otherwise they are very widely distributed, occurring in oils of hyssop, eucalyptus, savin, marjoram, cardamom, orange, bergamot, dill, caraway, origanum, sage, bay, basil, sandalwood, limes, ginger, patchouli, cade, juniper, camphor, cedarwood, cloves, allspice, cinnamon, copaiba, hops and many other essential oils.

The alcohols are a far more odorous class of compounds than the terpenes: Octyl alcohol of rosy character, laurinic alcohol in lily perfumes, alcohols, C_{10} and C_{12} which are useful synthetics, geraniol in oils of rose, geranium, citronella, ginger-grass, nerol in neroli, linalol in oils of linaloe, bergamot, lavender and ylang-ylang, citronellol and rhodinol in oil of rose, benzyl alcohol in jasmine, tuberose, cassie and ylang-ylang, phenyl-ethyl alcohol in rose and neroli oils, cinnamic alcohol in styrax, balsam of Peru and hyacinth, anisic alcohol in Tahiti vanilla, and terpineol, a cheap but very useful synthetic used in enormous quantities, comprise the principal alcohols.

The esters are mainly compounds of the foregoing alcohols with formic, acetic, butyric, benzoic, cinnamic and anthranilic acids. Methyl anthranilate occurs in oils of neroli, tuberose, ylang-ylang, jasmine and gardenia. Geranyl acetate has an exceedingly sweet odor. It is found in palma-rosa oil, lemon-grass oil, sassafras leaf oil, geranium, petit-grain, neroli, coriander, lavender and numerous other oils. Linalyl acetate is a very important perfume material. It is the essential constituent of oil of bergamot and a very important one of oil of lavender. It also occurs in oils of ylang-ylang, petit-grain, neroli, jasmine, gardenia and many others. Benzyl acetate is an important constituent of oil of jasmine; benzyl benzoate occurs in balsam of Peru and oil of ylang-ylang; menthyl acetate with the alcohol, menthol, composes the bulk of peppermint oil. While not occurring naturally, amyl salicylate is a most important synthetic, useful in the production of perfumes of the orchid and red clover type.

In point of odor value the aldehydes are the most important of all perfume constituents or materials. Though occurring in only minute proportions they nevertheless, usually, give the characteristic note to the oil in which they occur, as is the case of citral in oil of lemon, in which it is present to the extent of only four per cent. The synthetic production of aldehydes in a state of purity has revolutionized the art of perfumery and the manufacture of artificial flavors. Natural flower and fruit oils can now be reproduced with remarkable fidelity with the aid of aldehydes. This was impossible only a few years ago. The most important aldehydes are the aliphatic aldehydes, C_8, C_9, C_{10}, C_{11}, all of rosy or neroli-like

characteristics; C_{12}, having the odor of violet leaves; C_{14}, the peach aldehyde; C_{18}, the strawberry aldehyde; C_{20}, the raspberry aldehyde; anisic aldehyde, of hawthorne character; citral in oil of lemon; benzaldehyde in oil of bitter almonds; cinnamic aldehyde, the principal constituent of oil of cinnamon; phenyl acetic aldehyde, giving the key-note to the odor of hyacinth; vanillin or methyl protocatechuic aldehyde, one of the most important constituents of vanilla beans now manufactured synthetically on a very large scale; and heliotropine or piperinol, a synthetic possessing a powerful odor of heliotrope.

The ketones of importance, although few in number, include the ionones, those very remarkable compounds of violet character resulting from the long and patient research of Tiemann and Kruger. These are among the most important of all synthetic perfumes, and are derivatives of condensation products of citral and acetone or its homologues. Another ketone of great commercial importance, though it is not a perfume material, is camphor, $C_{10}H_{16}O$. Among ketones of lesser importance are carvone, occurring in oil of caraway, and jasmine, an important constituent of jasmine and neroli oils.

Among the phenols are found thymol, occurring in oil of thymone; anethol, in anise oil; eugenol in oil of cloves; safrol in oil of sassafras; and para-cresol methyl ether occurring in oil of ylang-ylang, and also a very important synthetic.

Among the oxides and lactones are coumarin, occurring in the tonka bean, deer's tongue and many grasses, also manufactured synthetically on a very large scale; and eucalyptol in oil of eucalyptus.

The nitrogenous perfume materials include the three artificial musks; musk xylol, tri-nitro-iso-butyl-xylol; musk ambrette, dinitro-butyl-meta-cresol methyl ether; and musk ketone, butyl-xylyl-propyl ketone. Indol, occurring in jasmine oil and skatol, its β-methyl derivative, also come under this classification.

Among sulphur compounds there is worthy of mention diallyl disulphide which comprises 60% of oil of garlic, and allyl iso-thiocyanate or oil of mustard.

Merely for the sake of completeness, benzoic, valerianic, phenylacetic and cinnamic acids are noted; as perfume materials they are of very minor importance.

The various perfume materials that we have considered are like the notes on the various instruments, at the disposal of a composer. They must be properly combined to make a finished perfume. A perfume is like a musical symphony. The various odors of which it is composed are like the instruments of the orchestra. If the instruments are well blended, there is music. If not, there is only a noise. If the odors are well combined, there is a perfume. If not, there is only a smell.

Finished perfumes may be classified as follows:

Colognes and toilet waters of light floral character containing only a small amount of essential oil and designed to be used liberally. Examples of these are Florida Water and German and other colognes which have long been popular.

Perfumes proper are more concentrated solutions in alcohol of perfume oils containing from 8 to 12 ounces of oil per gallon. These may be divided into bouquets and simple odors. The simple odors are named for and consist essentially of the essential oil of one flower, such as rose. This is supplemented and enhanced by traces of other odors. Such a perfume we might liken to a musical solo in which the principal part is taken by some instrument and supplemented by the accompaniment of an orchestra which may be made up of many pieces. The simile is apt in that the ingredients of a finished perfume are often quite as numerous as the number of pieces in a very large orchestra. This is particularly true of the other class of finished perfumes which are called "bouquets" and in which no particular flower predominates. A perfume of this kind is

more difficult to compose than one modifying a simple flower. In the case of the flower, it must not be imagined that the ultimate constituents of the perfume are simple. The only difference is that nature is the perfumer. Oil of ylang-ylang, for instance, contains something like 25 or 30 perfume ingredients which nature has most wonderfully combined to make what the Filipinos have named "The flower of flowers." However, some very beautiful odors have been produced by skilful perfumers, and they deservedly enjoy wide popularity.

I might mention that bouquets might be sub-divided into French bouquets and Oriental bouquets. The French bouquets are of a more flowery character; not necessarily of light flowery character; they may contain heavy floral odors, such as lily, but they are flowery rather than aromatic. Oriental bouquets, on the other hand, contain many perfume notes of an aromatic or ambrosial character, such as sandalwood, amber and musk, amber being, probably, the most prominent.

Perfume materials are used very largely for soap; not the highest quality perfume materials, but a very great bulk, probably a greater bulk than for all other purposes. There is no soap that is not more or less perfumed. Even laundry soaps are perfumed with oil of citronella. For toilet preparations, such as creams and powders, special perfumes are required. In the perfuming of a powder, care must be taken not to use materials which will either oxidize or otherwise deteriorate in odor on exposure to the oxygen of the air on the enormous surface exposed by the particles of powder. Materials which discolor must also be avoided, such as methyl anthranilate, which turns yellow in powder, and indol, one of the constituents of jasmine, which turns red in preparations in which it is used.

Nearly all perfumes require fixatives, or non-volatile materials, to hold the more volatile oils and to prevent their evaporating too fast when the perfume is used. The principal fixative is synthetic amber, which is really an oleoresin of labdanum. Many other resinous bodies are used, however, such as benzoin, tolu, orris, musk, castor, civet, etc.

Time will not permit the discussion of individual oils, but I might say a word or two about the most famous of all perfume materials—otto of rose.

It is said that the otto was first distilled in 1612 in Persia and is first mentioned in the history of the Moguls. At the marriage of Princess Nour-Djihan and Djihan-Guhr, the mother of Nour-Djihan presented the prince with "Essence of Rose Water." The prince called the perfume "Perfume of Djihanguhr" and presented the princess with a 30,000 rupee necklace. Another version of the story is that at the wedding, a rose water canal was constructed in the garden and oil of rose noticed floating on the surface. This was collected and recognized as a most wonderful perfume. Like the oil of ylang-ylang that I have previously mentioned, oil of rose also contains a great many constituents. Among them, I might mention geraniol, citronellol, rhodinol, a paraffin $C_{16}H_{34}$, phenyl-ethyl alcohol, nerol, farnesol, a sesquiterpene alcohol, $C_{15}H_{26}O_1$, eugenol, linalol and nonylic aldehyde. A ton of rose petals yields two-thirds of a pound of otto of rose.

CHARLES E. DOHME LECTURES.

The Charles E. Dohme lectures of this year were delivered by Dr. Walter Ernest Dixon, formerly professor of materia medica and pharmacology at King's College, University of London, and now reader in pharmacology and assistant to the regius professor of physics at the Cambridge University. As is quite generally known the lectureship was founded in memory of the late **Charles E. Dohme,** who was President of the AMERICAN PHARMACEUTICAL ASSOCIATION, 1898–1899. Few, if any, of the A. PH. A. presidents were held in higher esteem by pharmacists.

PHYSICIANS' HOMES.

The American Medical Association has endorsed a campaign for the establishment of three homes for "old and financially insecure" physicians of this country. These will be established in the North, South and Middle West.