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PERFUMES AND AROMATIC CHEMICALS.

BY ROBERT GLENK.*

(Continued from p. 919, October issue.)

TUBEROSE TYPE.

Tuberose is a member of the lily family with a characteristic fragrant odor. It is native to Brazil and has been introduced into all civilized countries. It is cultivated in southern France on a large scale for the manufacture of enfleurage products and absolutes which are very extensively employed in the perfume industry to develop the fine floral notes in synthetic compositions.

Its cultivation is attended with considerable risk and many times the harvest, which occurs in August and September, is unfavorable and high prices prevail for the natural products.

The synthetic equivalent of the tuberose odor is methyl benzoate or "Niobe oil" of commerce and which has also been detected in the natural flower product. The modifying odor is obtained by the use of methyl anthranilate, methyl salicylate, benzyl alcohol and benzyl acetate.

Jonquil, hyacinth and narcissus are usually considered of the tuberose type of odor although their fragrance is quite characteristic and individual. The flowers are largely cultivated for their natural products in France and harvested in April. The enfleurage and volatile solvent products are both made. Phenylacetic aldehyde is the odor base employed in making perfume reproductions or perfume oils.

VIOLET TYPE.

The violet has been esteemed as a favorite flower from time immemorial. Sweet violets are highly prized for their delightful fragrance everywhere and are largely cultivated in the south of France for the extraction of their fragrant constituents.

The plant flourishes in the South and the variety called Mexican violet bears a profusion of large blossoms which are very fragrant and are quite extensively grown for florists' use.

The perfume is extracted by enfluerage, maceration and by volatile solvents but the yield is so small that these products are unusually expensive, the price of violet absolute having been quoted at \$750.00 per pound.

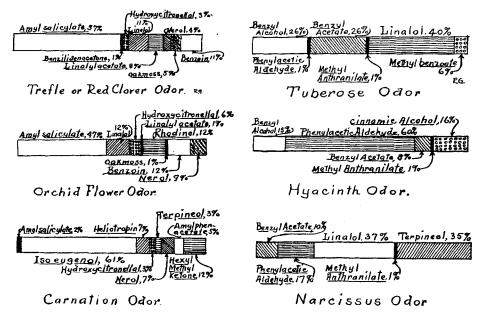
Violet perfume is perhaps the most popular of all the floral essences. This fact is accounted for by the use of the synthetic "Ionone" which was the first perfume synthetic put in the market. It is so powerful that only small quantities are needed to make a very satisfactory product and the price varies according to the flowery finish given to the particular perfume. Only the highest priced perfumes have even a trace of the natural violet product.

Ionone is a condensation product of citral from lemon grass oil and acetone, the preparation of which requires considerable skill and careful purification at the various stages to secure a fine quality of products. Numerous substitution and addition products of Ionone are now on the

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market with every variety and tone of violet odor so that the finished perfume perfectly represents all the different kinds of violets. The most recent and most important of the synthetic violet products are the violet ethers which impart freshness and petal effects to violet preparations, namely, the heptin, octyl and decyl carbonates of methyl, ethyl and amyl. These esters are very high in price, but they are so powerful that only trifling quantities are needed to give the flowery effect. Crude castor oil is the starting point for the synthesis of methyl heptin carbonate, which in its concentrated form is pungent and has a disagreeable odor.

Orris root yields on extraction a concrete oil which has a fine violet odor and which is extensively employed in connection with the Ionone and other violet synthetics for the composition of high class violet essences. Cassie, mimosa, wallflower and mignonette flowers have fragrant odors which are suggestive of violet perfume and come under this classification. All of these flowers are extensively cultivated for the production of natural perfume products and are articles of commerce. They are used in connection with synthetic chemicals for the reproduction of the individual odors and in the composition of fancy bouquets; they are high in price. Ionone imparts the important odor note to all compositions of this class. The alcohol Farnesol has been identified as a constituent of cassie which gives distinction to the flower odor.



The wallflower is one of the commonest and sweetest of the cultivated plants. The odor is faithfully reproduced by the use of geraniol, anisic aldehyde, benzyl alcohol, methyl anthranilate and paracresol methyl ether.

Reseda or mignonette is also one of the old-fashioned flowers of fragrant odor, whose artificial counterpart is indistinguishable from the natural product.

HELIOTROPE TYPE.

Several varieties of heliotropes are natives of the South but the fragrant variety is native to Peru and was introduced about 1750. The odor is inclined to be "almondy" and heavy and is extracted by enfluerage and by volatile solvents. The natural floral products are occasionally offered for sale but the reproduced odor is a close approximation of the natural fragrance. The basic odor of synthetic heliotrope is heliotropin, or piperonal, an aldehyde made from safrol on a very large scale. Flowery adjuvants are hydroxycitronellal, geraniol, methyl acetophenone and benzyl acetate.

Mellilotus or sweet clover, honeysuckle and 4 o'clocks or marvel of Peru are familiar flowers which have odors somewhat suggestive of heliotrope but quite distinctive. Coumarin is the basic odor of mellilotus and the new mown hay compositions, while the honeysuckle note is attained by the use of linalol, geraniol, hydroxy citronellal, vanillin, benzylacetate with tuberose essence.

HAWTHORN OR MAYBLOSSOM TYPE.

Many of our commonest and most cherished flowers have anisic aldehyde as the basis of their sweet perfume. This aldehyde, commercially known as aubepine, is a constituent of the natural flower fragrance. To this class belong crabapple, cherry blossom, acacia, locust, linden, loquat, elder, confederate jessamine, nasturtium and oleander flowers. None of these flowers are used commercially for the extraction of natural perfume material at the present day, as the chemical constituents necessary for the perfect reproduction of any of these odors are readily obtainable and comparatively inexpensive.

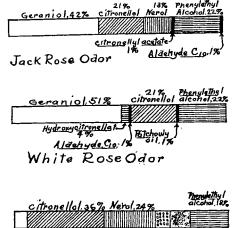
RED CLOVER OR TREFLE TYPE.

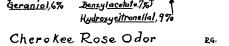
The odor exhaled by the common red crimson clover is of a delightful honey fragrance and has led to the composition of numerous popular perfumes under the names of treffe or orchid. Natural flower products of clover blossoms are not used for these compositions as the basic odor of

the flower is accurately reproduced by amyl or iso-butyl salicylate which are sold under the commercial terms of orchidée and orchidone and which constitute 40 to 60% of such perfumes. Alone, these chemicals do not possess the floral fragrance requisite in a perfume and this note is secured by the use of natural and synthetic rose and jasmin products in greater or lesser amounts according to the price at which they are to be sold. With slight modifications of the formulas the experienced perfumer reproduces the odor bouquet of orchid, lotus, pansy, lupine and wisteria.

SWEET PEA.

The odor of the sweet pea, so largely cultivated in our gardens in spring time for its showy flowers, was one of the difficult odors to imitate by the old-time methods of using natural products. Organic chemistry, however, has solved the problem of accurately reproducing the sweet pea fragrance by the discovery of benzilidene acetone. This chemical product, suitably reinforced





with phenylaceticaldehyde, terpineol and natural absolutes of rose and jasmin, imitates the flower odor to perfection.

LAVENDER TYPES.

The odor of lavender is due to linally acetate which in the French or Barreme oil amounts to as much as 44% while the English or Mitcham lavender is 4 to 7% Lavender is cultivated to a small extent in the United States and the dried flowers are sold as a perfume for the linen closet. The flowering heads with a portion of the leaves are distilled by the peasants in France usually under the supervision of the wholesale dcalers in the oil so as to secure uniformity and quality of product. Lavender has long been a favorite perfume in the form of lavender water.

Among the plants producing essential oils which resemble lavender to a certain extent are rosemary, thyme, marjoram, origanum, sweet basil, mentha citrata and muscatel sage. As these plants are grown under naturally favorable conditions in Spain, France and Italy, and their distillation for essential oils carried on by peasants and with little outlay for equipment, there is no likelihood of diverting this industry to this country at the present time.

MENTHA CITRATA.

The U. S. Department of Agriculture has just issued a press bulletin relative to the work done on *Mentha citrata*, by G. A. Russell near Washington, in connection with research work dealing with essential oil-yielding plants. In *Mentha citrata*, a plant belonging to the mint family, the U. S. Department of Agriculture believes it has introduced a new crop which, under suitable conditions, may bring a financial return per acre equal to that now obtained from other cultivated mints. The crop of the past year was grown on a sufficiently large acreage to give definite indications of its possibilities in Virginia. The yield of oil from the plant when distilled was at the rate of 30 pounds per acre. The oil is very fragrant and contains, on an average, 50 per cent. of linalyl acetate which is more than the French oil of lavender contains. Linalyl acetate is a very important aromatic chemical product and enters into the composition of synthetic oil of bergamot and many kinds of perfumes and flowers oils.

Horsemint is an American plant of the mint family growing wild in many sections of the United States. The oil contains 50% or more of thymol. The synthetic production of thymol from para cymene, a waste product from spruce pulp, will prove to be a chcaper method of obtaining it. In this connection should be mentioned the results of experimental plantings of peppermint near Raceland, Louisiana, on reclaimed land. Owing to the difficulty of keeping down the weeds, the peppermint crop became so contaminated with other odoriferous plants that the essential oil produced brought a very low price on the market and the enterprise failed.

Patchouly is a plant belonging to the mint family which yields an essential oil much used in scenting toilet powders and in oriental types of perfume. It is grown in Indo-China and the dried leaves are largely imported into this country where the oil is distilled under the most favorable conditions.

Vetivert is a tall perennial grass, growing in India and other tropical countries for the fragrant rootlets which are used in the preparation of an essential oil, highly esteemed in perfume compositions and as a fixative. By means of volatile solvents, a resinoid is obtained which takes the place of the oil to some extent. Vetivert is grown commercially to a small extent near Covington and sold as a scent for the linen closet. In California the roots are made into incense sticks and pastilles for fumigation. The odorous constituent of vetivert oil is vetiverol, an alcohol, the esters of which are also used in perfumery.

American Storax had become an article of commerce during the war but is difficult to obtain at the present time. The high cost of labor in collecting the balsam from the sweet gum trees makes competition difficult with the oriental product at one-third of the price. Storax is largely used in perfumery in the form of the volatile oil and colorless products obtained by means of petroleum ether and alcohol, which are valuable fixatives. It is used as a source of cinnamic alcohol and cinnamic esters, which also enter into the manufacture of perfumes of the hyacinth type.

Deer Tongue or Vanilla plant, *Liatris odoratissima*, is native to the southern states. Its leaves develop an aroma when dry, suggestive of vanilla or tonka bean; it is sometimes used for scenting tobacco. Sweet Vernal Grass is an indigenous plant which develops a faint fragrance of coumarin on drying. It is used for making ornamental scented baskets and gives the peculiar fragrance to freshly cut hay fields and to which the new mown hay perfume owes its character. Mellilotus, or sweet clover, likewise develops the tonka bean aroma on drying. The coumarin content in these plants is not large enough to warrant its extraction from the natural material as its synthesis from salicylic aldehyde is a very much cheaper method of making it.

The Illicium or Anise tree is another of our indigenous plants the virtues of which are unrccognized or neglected. The star anise oil of commerce is made from the fruits obtained in oriental countries, mostly China; anethol and anisic aldehyde are prepared from it and used in perfume manufacture. The common fennel is largely grown by local market gardeners as a celery substitute; if allowed to mature, it will produce heads of fragrant fruits or fennel seeds. Fennel oil resembles anise oil both in flavor and composition and could be used as a source of anethol.

Oak moss or Mousse de Chine is a lichen of the Parmelia family abundantly growing on the live and water oaks of the southern states. It has a characteristic odor which is extracted by volatile solvents and possesses remarkable fixative properties. It is in great demand for the composition of oriental bouquets and new mown hay, orchid and trefle perfumes. The resinols and absolutes of oak moss range in price from 5 to 25 dollars a pound. It may be interesting to note that this lichen formed part of the funeral equipment of the early kings, and was an article of commerce 5000 years ago in Egypt, being used as an ingredient in bread making. In colonial days in America, pulverized oak moss was used as a hair powder which imparted both tint and odor to the coiffure of the ladies and wigs of the gentlemen.

Sassafras root bark yields an essential oil containing, as chief constituent, safrol from which

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heliotropin is made. It is also largely used as a scent for cheap soaps. Sandal wood oil plays an important part in the manufacture of perfumes especially those of the oriental type. It has marked fixative value and enters into violet, mignonette and cassie bouquets. The wood is also used in incense pastilles. Lemon grass is native to India. Experimental platings were made at Orlando, Florida, by the U. S. Bureau of Plant Industry and oil distilled from the crops. The value of the oil depends upon the high citral content, 65–88%, which is used in the synthesis of violet ketones. The yield of oil is from 0.5 to 2%.

Lemon oil produced as a by-product of the citrus industry of California has, in recent years, become an article of commerce. It is manufactured by an entirely different process from that followed in Europe. The lemons are conveyed in a continuous stream into a convoluted phosphor bronze machine which massages the fruit and finally crushes it, producing a flow of juice which washes down the spray of oil and carries it through a strainer and into a centrifugal separator. This separator gives a perfectly clear, brilliant and highly colored oil, with none of the fragrance impaired, within 15 minutes from the time the fruit enters. Sweet orange oil is made by the same process and the demand is rapidly increasing as the high quality of the product becomes better known.

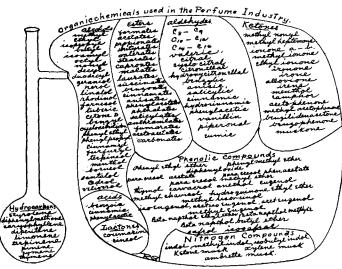
Croton glandulosum is one of our common weeds belonging to the spurge family of which plants yielding croton oil and cascarilla bark are also members. This plant is fragrantly aromatic and yields on distillation with steam a small per cent. of essential oil with a lemon grass odor. It might possibly be used as a source of citral. Pine needles, especially the short leaved varieties, yield essential oils composed largely of pinene with a small percentage of bornyl acetate which gives the peculiar pine aroma or pine woods smell. Commercial pine needles oil is obtained mostly from the Siberian pine which has a high percentage of bornyl acetate and is used as spray perfume for theatres and other public places. Tyropine bouquet is used as a scent for bath salts. Cypress tree branches also yield a fragrant oil on distillation containing a small amount of the peculiar "cypress camphor" which crystallizes from alcoholic solution somewhat like cedar camphor. The oil has been recommended for whooping cough and is an article of commerce. It is also coming into use as a fixative on account of its ambra qualitics.

ANIMAL PRODUCTS.

There are a number of animal products used in perfumery which are practically indispensable for their fixative qualities. These products are ambergris, musk, civet and castoreum and have been used by perfumers since antiquity. In the raw state, these substances have an unpleasant and even nauseating

smell and it is only in extreme dilution that their use is appreciated. Practically every finished perfume on the market contains one or more of these products to give lasting quality to the odor and frequently an excess is used. Ambergris is a pathologic product of the sperm whale. Musk is obtained from the musk deer of Thibet, civet from the domesticated civet cat of Abyssinia, and castoreum from the common beaver.

It is not generally known that the alligator



has two musk glands which contain secretions very similar in odor to the Chinese musk. The quantity is so small, however, that no attention is given to these glands in a commercial way. Ten cc. of secretion were obtained from a 12-foot alligator. On account of the scarcity and

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consequent high price of both musk and ambergris, synthetic musks and ambers have been developed, which, while they have no chemical relationship with the odorous principles of either product, have a very marked similarity in smell and fixative value. Three varieties of synthetic musk are on the market, all white crystalline highly nitrated, tertiary butyl toluenes or xylenes called ketone, xylene and ambrette musk. These musks are not very soluble in alcohol and are nearly always brought into solution by the use of benzyl benzoate, or diethyl phthalate, and constitute the musk oil of commerce.

Ambrinette is a useful ambergris substitute and scatol or methyl indol, and iso-butyl indol are very satisfactory substitutes for civet, which have been developed by American chemists. They are crystalline compounds of a vile odor.

FIXATION OR STABILIZING OF PERFUMES.

In living flowers, the perfume is secreted continuously and given off in infinitesimal quantity and in highest dilution. When this perfume is isolated the flower odor is obtained in a much more concentrated condition and, naturally, it is not nearly as flowery or sweet. Besides many of the constituents, being quite volatile, evaporate more rapidly than others, the various shades of odors become perceptible and the effect is not as pleasing as when smelling a flower. To obviate this fractional evaporation and to obtain a continuously uniform odor note and one which is much more lasting, it is necessary to use fixatives. Fixatives sweeten and blend the odor constituents and retard evaporation so that the fragrance is given off in small quantity and uniform in odor somewhat after nature's method.

As there is no universal fixative known, the greatest success is only to be obtained by the structure of the perfume composition itself and that is done by blending ingredients of similar odor and intermediate volatility so that one fixes the other. Here is where the difficulty is encountered in perfume blending as the public demands that perfume shall be lasting and at the same time delicate and flowery, conditions which are very hard to combine. A thorough knowledge of the chemical and physical properties of perfume constituents is absolutely essential to be successful.

DOMESTIC PERFUME FLOWER CULTIVATION.

There is no doubt that soil and climatic requirements are favorable for the production of practically all of the perfume-yielding plants that are now grown in temperate or semi-tropical countries, in many parts of the United States. The tuberose industry which is now flourishing in North Carolina and Texas and produces millions of bulbs for planting purposes, could be made to yield the natural perfume products from the fragrant flowers as a valuable by-product.

Acacia farnesiana which furnishes the Cassie floral products, is at home throughout the South from Florida to California and bears its fragrant flowers in abundance. Our indigenous yellow Jessamine from which Mr. Moulie, of Jacksonville, has prepared a fragrant marketable oil, could readily be propagated and made to yield heavy crops of blossoms and products if the matter of labor could be adjusted.

Orange flowers are utilized to a small extent near Jacksonville for perfumery purposes and lavender, rose geranium, violet and roses are grown in a small way in several sections. It took two centuries to establish the rose industry in Bulgaria and in recent years successful competition has arisen in France and Germany. It may be reasoned that further migration of this industry is to be expected and we may eventually find the center of production in our own country. Already an interest has been aroused in the direction of volatile oil production and the trade may be relied upon to take an active part in any rational attempts at developing such an industry with the usual innovation of new methods and economies so characteristic of American ingenuity and enterprise.

During the past summer, the American manufacturers of toilet articles, as an association, pledged a fund of \$10,000 to be placed at the disposal of Prof. G. A. Russell, biologist, Federal Department of Agriculture, to promote research and coöperation in the cultivation of floral raw materials with the ultimate expectation of creating an important domestic industry. A course in perfume chemistry is also now offered by Columbia University, beginning in 1925. A bibliography or compilation of articles in pamphlet literature or trade journals concerning the newer products of the perfume industry is also urgently needed as none of the modern books on organic chemistry outside of "Parry's Monographs on Essential Oils and Synthetic Perfumes" and Poucher's work on "Perfumes and Cosmetics" afford information on the great numbers of new chemicals on the market. Perhaps this deficiency will soon be remedied by the publication giving chemical and physical constants of essential oils, and odorous materials in general in the forthcoming book which is being prepared by the U.S. Research Council, Washington, D.C., to be called "International Critical Tables of Numerical Data of Chemistry and Technology."

April 25, 1924.

THE DRUG STORE AS AN ADVERTISING POTENTIALITY.*

THE PHARMACIST'S COÖPERATION OR LACK OF IT CONTROLS THE DESTINY OF EVERY Advertising Campaign in His Line.

BY F. H. PECK.

Much can be said and truthfully both in favor of and against advertising as applied to pharmacy. However, whatever our belief, we must admit that advertising has become so potent a factor in our daily life that the business man, in any line, must understand it more intimately than in the past, if he is to succeed.

A few years ago, advertising seemed remote from professional medicine and pharmacy. It was the tool of the charlatan, the vendor of proprietaries and of the large commercial chain stores perhaps, but it was of no interest to the professional man.

Then came the World War with the upsetting of many traditions and precedents. We saw advertising successfully employed to reach the minds and the heartstrings of this great people. We saw our Government call into its service the great advertising minds of America, and launch the most gigantic advertising campaign in history. We witnessed the conflict between the advertising campaigns of two great groups of nations for the moral support of the world; one to succeed the other to ignominiously fail through a failure to understand the psychology of the masses.

Since that struggle we have watched our great banking institutions, our transportation companies, our life insurance organizations, and even our churches

^{*} Section on Commercial Interests, A. Ph. A., Buffalo meeting, 1924.