PERFUMES AND AROMATIC CHEMICALS.

BY ROBERT GLENK.*

Investigations and experiments, dealing with aromatic plant materials available in the South which might lend themselves to various industrial uses, and extending over a period of years, have resulted in bringing together much interesting data in this most fascinating field of chemistry.

The work grew out of a desire to secure materials for the exhibit to illustrate the perfume industry, the relative importance of which will be appreciated when it is realized that in twenty-five years it has grown from a business of four millions in annual production to one of nearly one hundred and fifty millions last year.

Human interest in sweet scents and the fragrant odor of flowers is as universal as the love of ornamentation and of the beautiful in art and nature. Both ancient and modern literature teems with allusions to the use of perfumes both as an auxiliary to the mystic rites of religious worship and as a means of enhancing one's personal charms.

The extent of the use of perfumes and spices of a nation was an index of the stage of advancement and refinement of that nation, the most enlightened being always distinguished for highest appreciation of sweet odors. Under the luxurious Greek and Roman civilization, the use of scented waters and oils became a fine art, and a treatise on the use and preparation of perfumes by Rhodius Appolonius gave a clue to the range of the fragrant raw materials employed two thousand years ago, many of which are standard products to-day.

The lure of perfumes is also intimately associated with the incentive for cultural development that delights in and elevates the fine arts, namely, painting, sculpture, poetry, drama and music, and imparts that "esthetic sense of mind and spirit that lifts humanity in the scale of progress." At the present day, the fascination for perfumes and cosmetics has taken such a hold that the nation spends as much on "Aids to Beauty" as it does on education. But we are still behind some of the ancient nations whose extravagance in the use of perfumes led the rich to literally drench themselves from head to foot with scented oils.

Like all other human faculties, the sense of smell is capable of cultivation and enhancement and connoisseurs in essential oils, wines, tea and coffee have their powers trained often to a wonderful degree in their special lines. The skilled perfumer is also capable of making nice discriminations in the recognition and in the blending of odors to produce the artistic results so much admired in the standard French and American perfumes.

As to the physical properties of smell, aside from the fact that the stimulus is always in gaseous form, very little is known. Volatile particles are carried by the act of inspiration into the nostrils where they react on cells found in the mucus membrane giving nerve impulses which are conveyed by the olfactory nerves to the temporal lobes of the brain and there registered in our intelligence. Solubility and volatility are therefore necessary accompaniments of odorous substances, but Backman states that the volatile substances must be soluble in water and in the lipins before they can reach the receptor organs of smell. Undoubtedly, the chemical constitution of an organic substance has much to do with the nature and quantity

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of its odor. The particular organic groups associated with odors have been called aromatophors, as mophors or odoriphors by different investigators.

The odor and aroma of flowers and fruits is generally due to what is termed an essential oil, and these oils are almost without exception very complex compounds or mixtures. The separation and identification of many ingredients of this odor complex is most difficult on account of their sensitiveness to heat and chemical reagents. Many constituents, on the other hand, are so powerful in odor that though an infinitesimal quantity be present, yet it is sufficient to modify the whole combination and give distinction to the floral bouquet.

The extraction of the various flower odors is accomplished in various ways, either by distillation or absorption, depending on the nature of the essential oil present or, in the case of the citrus fruit oils, in a mechanical way by expression. Steam distillation is resorted to when the oil exists in sufficient quantity and is not materially injured by heat or oxidation as in the manufacture of lavender or orange blossom oils. In the case of orange or lemon peel, the distillation process is unsuccessful, the terpenes only coming over. Extraction by volatile solvents, such as petroleum ether, is used when the floral odor exists only in infinitesimal quantities as in violets, jasmin, tuberose, etc.; the volatile solvent method extracts along with the volatile oil, the flower waxes and inert constituents producing the commercial concretes. If these inert substances are removed by further treatment with alcohol still more concentrated products result, commercially sold under the name of hyper-essences, absolutes, etc. These are naturally very costly products.

Another process for obtaining the odor constituents of flowers is called "enfleurage" or absorption with highly purified lard in the cold or by maceration with warm fat. The fat is afterwards washed with alcohol to remove the perfume. The enfleurage essences were for many years the only important perfume materials available in the manufacture of handkerchief extracts.

The flowers which are of primary importance in the manufacture of natural perfumery products of commerce are roses, carnations, mignonette, violets, jasmin, orange blossoms, tuberoses, hyacinths, cassie, heliotrope, mimosa and lavender. These flowers have been grown by the thrifty French gardners and farmers for centuries. They flourish equally well with us and with proper care and selection could be grown to produce natural perfume material abundantly in the South. Skilled workers, however, are necessary in processing the flowers to advantage and in this respect the Grasse District of France is preëminent.

The variability in both quality and cost of perfumery products from natural sources has stimulated the chemists to search for substitute perfume materials which would either replace or augment natural perfumes. Years have been spent in the painstaking study of the constituents of a single flower odor and many of the substances isolated and identified. However, on mixing these substances in the proportions as determined in the laboratory, the odor is not exactly duplicated. Artificial odor substances are not entirely substitutes as yet for natural flower products. The synthetics contribute to their strengthening and have also made it possible to reproduce flower odors not obtainable from the plants themselves like arbutus, sweetpeas, honeysuckle and magnolia. Synthetics likewise make it possible to obtain results more quickly and accurately, besides supplying an infinitely greater variety of substances to choose from in producing new and striking bouquet effects

and in greater concentration. Also, more uniformity in character, quality and odor value is to be attained and they are not subject to the price fluctuations as is the case with natural products grown under varying climatic conditions.

As a great many of the newer synthetic perfume materials are derived from essential oils occurring in plants, it becomes necessary to include these indispensable chemicals in dealing with perfumery products. Thus, the field of inquiry is enormously widened, and becomes well nigh inexhaustible. While the synthetic perfume industry is of much less commercial importance than the aniline dye industry, and of a much later development, it is of great scientific interest, nevertheless. When a new substance is discovered, it requires a chemist trained to the valuation of odors to recognize its worth as a perfume product, as its odor is seldom appreciated unless in a highly purified and much diluted condition. The dye color, on the other hand, is at once visible and recognizable.

In buying natural perfumery materials, experts agree that chemical analysis does not suffice in determining the quality, as flavor and odor value are the characters sought after and not chemical percentages or physical constants. Perfumers have always resorted to the olfactory examination of their essential oils and perfume materials to determine their worth as compounding ingredients. In the olfactory method of examination, the universal custom has been to smell attentively a strip of paper previously dipped into the liquid to be tested. Of late years an instrument, called an evapolfactometer has been invented by a French chemist, Dr. Oddo, which replaces the smelling paper. This instrument does not give to every one, even a skilled analyst, the requisite capacity for detecting the various components of a perfumery product, but it does make their study much easier. The instrument is based upon the following principle:

The vapor tensions or shades of evaporation of odor substances are in most cases distinct and individual and so by heating very slightly and gradually a blend or perfume, the various components evaporate one after the other according to their differing volatilizing powers. Thus a sort of fractionation takes place which has to be made as slowly as possible in order to give sufficient time for the analyst to perceive and recognize the perfumed vapors which are successively evaporating.

In practice, this study of a perfume has to be made in several stages as the sense of smell is subject to more or less rapid fatigue. On beginning the examination, the fraction evaporating up to 30° Centigrade is studied for about 10 minutes. In half an hour the instrument is dipped again and when the temperature reaches 30°, another 10 minutes' study is made up to 40° Centigrade and so on up the entire scale until all the odor is gone. The rise in temperature is produced by an electric current elevating the temperature of a heating unit inside the silver reservoir. In the hands of one who is familiar with natural and synthetic perfume materials, this instrument is very useful and is constantly employed.

The rôle of the perfumer of the past appears comparatively simple in comparison with the art of the perfumer of to-day. Then, only the essential oils, balsams and other odorous products furnished by nature herself were used for perfume compositions. The bases were, therefore, finished perfumes already in existence and it was only necessary to skilfully proportion the compounds so as to obtain harmonious notes. The compositions too were often far from being accurate flower reproductions.

The task of the modern perfume chemist is much more complex, as he has a

wealth of basic odor material to choose from and work with. In fact, it is to this *very complexity* that we owe the impressive progress made in the perfume industry to-day. Many artificial perfumes are wonderfully like the plant originals. Perfumers' efforts are akin to those of the artist. The painter reproduces the flower to the eye while the chemist imitates and preserves the fleeting fragrance of the blossom and combines its charms into a delightful bouquet. Numerous artistic combinations of colors and shades are possible in making up a bouquet of wild flowers; just so it is with the composition of the odor bouquet of these flowers. The perfumer must have an artistic sense to secure complete odor harmony in blending the combination, to obtain original effects.

We have only to think of what harmony means in music to understand what the expression is intended to convey when it is applied to odor. It consists, in music, of the unity, concentration, similarity and agreement of tones so as to produce beautiful effects, sometimes soothing, sometimes exhilarating, always fresh and various, and in perfumes a form of temperamental expression of one's personality, as it were.

In order to produce a finished perfume giving the effect of unified and blended odor it is necessary to closely imitate nature. Each of the ingredients used should act to some extent as a fixative for the other ingredients of volatility nearest its own or by the use of substances of intermediate volatility and appropriate odor values.

Owing to the limited significance of odors in our intellectual life, no outstanding scientific work has been done pertaining to the rational classification of odors as in the case of the spectrum for colors and as yet there is no clear basis for accurate comparison of different smells. Rimmel gives a list of related odor types which perfumers recognize as being sufficiently distinctive and this classification is followed in discussing the various perfume materials which we have for consideration. These odor types or related odors are: rose, jasmine, neroli, tuberose, violet, heliotrope, hawthorn, lavender, trefle, mint, vetivert, lemon, vanilla, pine, and animal odors. Nearly all odor substances used in the perfume industry fall within these odor types and they are distinctive enough for practical purposes.

THE ROSE TYPE.

Our available natural products coming under this classification are the Cherokee and the cultivated roses; rose geranium, palma rosa grass and citronella grass. These grasses are the source of Turkish geranium and citronella oil and are produced in large quantity in Oriental countries. The price at which these oils are sold on the market is so low that there is not any likelihood of successful competition even though the grasses flourish in the South.

Rose Geranium. The oils obtained from geranium grown experimentally at Orlando, Florida, were submitted to trade experts and were reported as being equal in odor value to many foreign oils and even surpassing some. Their physical constants were found to fall within the prescribed limits and rhodinol made from these oils was stated to be as fine as any made from foreign oils. The ester content (mainly geranyl tiglinate) was 25 to 28%.

In view of the results thus far obtained by the Bureau of Plant Industry, it is believed that rose geranium can be advantageously grown in the warmer sections of the U. S. and trial plantings are being made in Southern California with the object of establishing the crop on a commercial basis for oil production.

Citronella, palma rosa and geranium oils furnish the terpene alcohols—geraniol and citronellol of commerce, enormous quantities of which are used in scenting cosmetics, soaps and perfumery. They are also used for the manufacture of esters which are highly important perfume constituents. Geraniol and citronellol are constituents of the natural otto of rose and form the bulk of the synthetic rose oils in commerce.

The Cherokee rose fragrance is of the lily rose type, its odor being modified by the aldehyde hydroxy citronellal. The flowers are not sufficiently powerful in odor to warrant any use being made of them commercially. The perfume can be very easily imitated to perfection and at a much less cost than the natural odor could be extracted from the flowers.

The steam-distilled otto of roses does not represent the rose odor nearly as well as the concretes and absolutes produced by volatile solvents from the fact that the phenyl ethyl alcohol which constitutes 50% of the rose absolutes goes into solution in the rose water produced in the distillation of the oil. Otto of roses is so skilfully adulterated that it is said, on good authority, to be impossible of detection either chemically or physically and no pure otto is obtainable at the present time. The constituents are very well known and synthetic oils very largely replace the natural product in the manufacture of perfumes.

For the purposes of comparison diagrammatic formulas are presented showing the varying composition of the primary base of the jack rose, white rose and Cherokee rose artificial perfumes. To make the finished essences it is necessary to round off this basic odor with natural perfume products and appropriate fixatives and to allow the composition time to age.

In the manufacture of perfumes, it is essential that only the finest grade of denatured grain alcohol be employed. Diethyl phthalate is the denaturing substance used in Formulas 39*c* in the proportion of $2^1/_2\%$. Brucine and isopropyl alcohol are also permissible denaturants for perfumers' alcohol. These substances are quite odorless.

Among the important chemical products which simulate the rose odor may be mentioned diphenyl methane, diphenyl oxide, phenyl propyl alcohol, phenyl ethyl propionate, phenyl ethyl phenyl acetate, phenyl acetic acid and decylic acetate.

THE JASMIN BLOSSOM TYPE.

The fragrance of the lilac, lily, magnolia, yellow jessamine, cyclamen and azedarach naturally come within this classification and have benzyl acetate, terpineol, and hydrox citronellal as dominating constituents. Diagrammatic formulas for the primary base of lilac, jasmin and madonna lily are given for comparison.

The perfume of the jasmin blossoms is obtained either by enfleurage or by volatile solvents, and pomades; absolutes and hypercssences are offered. The price of the absolutes fluctuates very greatly, varying with the condition of the harvest which occurs from July to October and depending upon the climate and locality.

Natural jasmin is largely utilized in the manufacture of perfumes to which it imparts fresh flower effects. It is, however, largely replaced by synthetic flower oils as the price of the floral absolute is between seven and eight hundred dollars per pound, and can only be used in the highest priced perfumes. The chief odor constituents of the natural oil are: benzylacetate, linalol, linalyl acetate, indol and methyl anthranilate. To these are added such flowery adjuvants as methyl nonyl acetaldehyde, phenyl ethylalcohol, benzyl alcohol, geranyl acetate, phenyl ethylacetate, styrolyl alcohol, etc., and as fixatives: octylic and decylic acetate and farnesol. The jasmin flower is employed by the Hindus in their religious rites and is known as Kudda Mulla. In China the flowers are used for scenting tea.

Lilac is one of the ornamental shrubs of the gardens and grown almost anywhere. It produces a profusion of vari-colored flowers in dense clusters in early spring, which are very fragrant. The natural odor has not been satisfactorily extracted but its synthetic counter part has been prepared very perfectly with terpineol as the base and jasmin natural to strike the flowery note. The blossoms of the umbrella or china berry tree have an odor resembling that of the lilac.

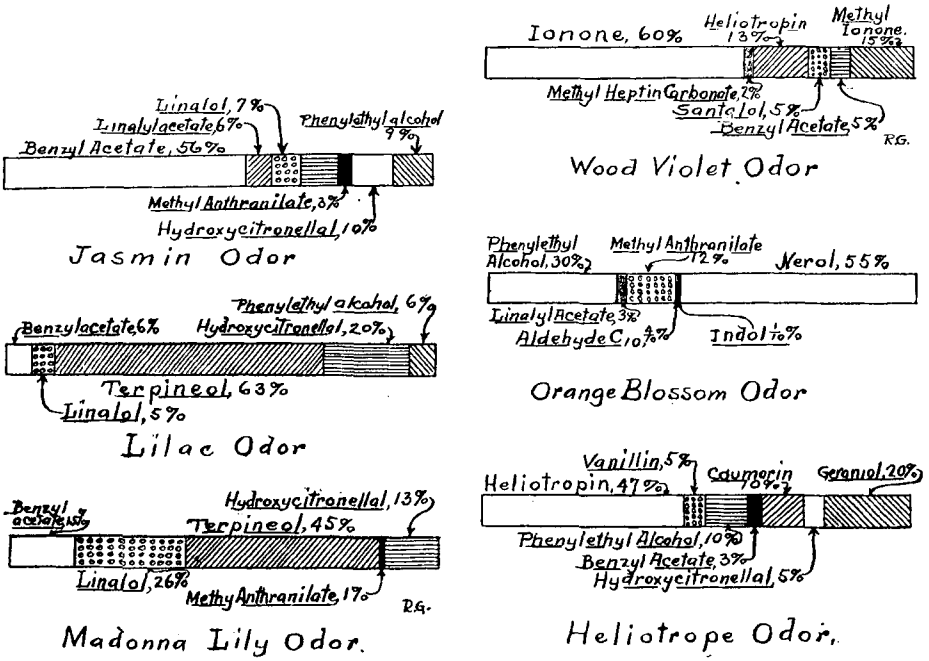
The madonna lily is one of the most delightful of the flowering plants for this section and produces an abundance of highly fragrant blossoms all summer. It is unlikely that it will ever become of importance as a perfume-yielding crop, as the odor is readily and perfectly imitated with synthetics.

The magnolia blossom is interesting in that it has been named the state flower of Louisiana and and Mississippi by acts of the respective legislatures of Louisiana and Mississippi. It is the largest, showiest flower of all the forest trees and has a peculiar fragrance in which the odor of borneol is prominent. The swamp magnolia shrub of the eastern states, however, bears blossoms which have a very fine odor, suggestive of lily and rose. No commercial use is made of the flowers and the magnolia perfume is always compounded of other flower oils and synthetics in which jasmin and

rose predominate. Ethyl acetate is one of the constituents of our sweet shrub or *magnolia fuscata* blossoms.

Lily of the Valley. On account of its exquisite fragrance this is one of the most popular flowers cultivated for bouquets by florists. It is a native of Europe and is known by the name of Muguet. The natural perfume is extracted by petroleum ether and comes on the market in the form of concrete and absolute. The synthetic flower oil is composed of a base of hydroxycitronellal, with linalol, terpineol, nerol, and methyl acetophenone and the flowery note brought out by jasmine natural. The imitation is a very accurate facsimile of the natural floral fragrance.

Carnation. The carnation or pink has been a favorite flower for centuries and through cultivation and selection has been bred up to yield a delightfully fragrant odor of a spicy nature. Theophrastus, 4th century B. C., stated that the carnation is without smell; fifty or more species are known many of which possess no smell, others are quite odorous. The odor base of the pink is isoeugenol modified by esters of eugenol and isoeugenol, nerol, heliotropin, terpineol and hydroxycitronellal, and the flowery note is brought out by Ylang oil. The natural flower products are pomade extracts and occasionally concretes, but these are high priced and scarce.



ORANGE BLOSSOM ODOR.

The orange is a native of India and China, but it was introduced into Europe more than 600 years ago and has been cultivated for a long time. The golden apples of Hesperides are supposed to have been the fruit of the orange tree. The fragrant oil obtained from the blossoms received the name of nerol from the fact that the wife of the Prince of Neroli used the essence for scenting gloves. In southern France, the tree is cultivated almost entirely for its flowers which yield their fragrance by either distillation with steam, or absorption by means of volatile solvents. Both the sweet and bitter orange flowers are used but the bitter orange or citrus bigaradia are the finest in fragrance and are the most esteemed. The harvest is in May and June. Four kinds of fragrant products are commercially made, namely, the flower oil or Neroli oil and orange flower water; orange flower absolute, petit grain oil from the twigs and buds and orange peel oil made by expression from the rind of the fruit

Present-day prices for these products are as follows:

Neroli oil $87.00 per pound, petit grain oil $8.50 per pound, sweet orange peel oil $3.50, and orange absolute $185.00 per pound. Most of the petit grain oil of trade comes from Paraguay.

The oil of orange peel is an entirely different product from the flower oil, which on analysis is found to contain linalol, nerol, linalyl acetate, phenyl ethyl alcohol, indol and methyl anthranilate. The characteristic odor of the flower is due to this latter constituent which is present to the extent of only 1%. It also gives the fluorescent appearance to the oil. The basic odor of orange peel oil is due to decylicalcohol of which only about 2% is present.

Synthetic neroli replaces the natural product for most purposes at one-fifth the price. No natural products of the orange flower are produced in the U. S. but California is turning out a fine quality of orange peel oil cold pressed. An experiment was made with orange peel to test the quality of the product obtained by steam distillation but the results were disappointing. A series of products were made from sweet orange, grape fruit, mandarin, kumquat and lemon peel by means of a volatile solvent which produced very fine flavored oils. Dextro limonene, which constitutes the greater portion of citrus oils, is also prepared commercially, and is also sold as an adulterant of the pure oils. Beta naphthol ethyl ether or nerolin is a synthetic chemical which is used as a substitute for orange flower products in soap flavor and has about the same odor value. The methyl ether is also used extensively and in trade is known as Yarayara.

Gardenia or cape jessamine introduced from South Africa is one of our most fragrant flowers produced in great abundance during the summer. The perfume is intensely diffusive and even objectionable to some persons. The flower is not used to prepare perfume compositions. The basic odor materials are benzyl, styrolyl and linalyl acetates with methyl anthranilate and terpineol.

Sweet olive is another one of our highly fragrant flowers which blossoms during the winter and spring. The flowers are quite insignificant but exhale an intensely diffusive fragrance, especially during the night. They are native to China and India where they are used to flavor tea. No natural flower products are employed in reproductions of the odor. The odor base is identical with that of the orange blossom but modified by the addition of traces of aldehydes C_{10} and C_{12} and their esters.

(To be continued.)

THE PURPOSE OF COÖPERATIVE WHOLESALE DRUG COMPANIES, AND WHAT THEY ARE ACCOMPLISHING.*

BY R. E. LEE WILLIAMSON.

A profound and widespread interest has, for several years, been shown in the plans and progress of the coöperative wholesale drug business. This has largely been caused by the great volume of business which has flown through the coöperative companies, and the natural interest of the trade in a new and unusual method of merchandising.

At the commencement of this method of wholesaling, the influencing reason that prompted the effort was largely, if not entirely, due to the status of the retail drug business in most of the large metropolitan cities which made it almost impossible for the retailer to secure a gross profit that would allow him to make more than a living. There was no such thing as the average retailer getting ahead and accumulating a surplus. In fact, the great majority of the retail pharmacists in the large cities were reaching a condition in which they were conducting their stores practically without profit, eking out a bare existence. This was a crushing and disheartening situation, which was having a ruinous effect upon pharmacy, blasting the lives of those in the profession, and lowering the standard of pharmacy in regard to the class of men entering the schools of pharmacy. Something had to be done; some help had to be secured. Pharmacists, in their extremity, turned in many

* Presented to and read before the Section on Commercial Interests, A. Ph. A., Asheville meeting, 1923.