zations in lending or soliciting support for the industry. The Research Institute for Fragrance Materials (RIFM), while very independent in its testing functions, is a supporting arm to the EOA. In recent years the International Fragrance Association (IFRA), of which the EOA is a member, has become a strong and dedicated international organization. IFRA is supported by various essential oil trade organizations in countries throughout the free world. As the same problems confront our industry regardless of national origin, such a world organization becomes more necessary with each passing year. The EOA and the RIFM, which has been recognized as the testing body of IFRA, lend very active support to this international body. The interrelationships of EOA, RIFM, and IFRA concern the very heart of our industry; namely, monitoring responsibly the safety of our products on an international scale. This is but one example of how complex and far-flung the activities of the EOA have become.

The development of new and interesting products is ongoing, and the desire to better serve our customers is our constant goal. With this philosophy, the growth of our industry during the next 50 years can only exceed that which we have enjoyed to date.

Historical and recent developments of essential oils and aroma chemicals

Kurt Kulka, PhD, Chemist

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The history of essential oils begins in ancient times. Long ago it must have been realized that the odors and tastes of plant materials were seasonal. Plants bloom only at certain times of the year. When cut, flowers deteriorate and their aroma is lost. To preserve the delicate smell of flowers, several methods were developed. In ancient countries of the Orient and the Mediterranean, flowers and other parts of plants were placed in fatty oils that were exposed to sunlight. The odorous constituents were taken up by the oil. This procedure was the first "enfleurage." In later years this process was modified and refined. In certain instances it is still used.

Water extractions of plant materials were developed by the ancients to obtain medicinal teas intended to cure all kinds of ills. Distilled waters, for example rose water, were produced in the eighth and ninth centuries in Persia and used as a remedy for eye ailments. In ancient Rome a broth made from Allium cepa (an onion) was the household remedy for the common cold. Tea of pennyroyal and other herbs such as sage, cubeb berries, etc., were among the remedies used in colonial America. At that time the aromas of such hot concoctions, which are based on the release of essential oil content, were appreciated. Such primitive but practical approaches were precursors of steam distillation,

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an important procedure to liberate essential oils from botanicals.

Other procedures were also used to obtain the odorous components of botanicals. Oil of turpentine was obtained by a rather crude distillation technique from pine rosin at about 900 A.D. When certain woods and other plant materials were burned, pleasant odors were emitted. This phenomenon was observed and employed in the "destructive disstillation" of plant products practiced in the 16th and 17th centuries.

Essential oils

Sources

Two main groups of materials are produced by today's essential oils aroma chemical industry.

- Those derived from natural plant and animal sources—essential oils, extracts such as oleoresins, concentrated fruit juices
- Synthetic organic materials

Essential oils represent the volatile components of leaves, twigs, roots, buds, stems, whereas oleoresins comprise the total amounts of the sensory constituents pertaining to odor and taste, e.g. volatile and nonvolatile.

Depending on the starting materials and the purpose for which their isolates are intended, oleoresins will be preferred in certain cases, whereas in other instances, particularly where the essential oils themselves contain all the sensory constituents, they will be the products of choice.

Classification

Essential oils can be classified in various ways.

- By botanical considerations: citrus oils, mint oils, oils of condiments (including spice oils derived from tropical plants such as clove, ginger, cinnamon, nutmeg, pepper), and seasoning oils derived from temperature zone plants (celery, caraway, dill, sage, cumin, onion, garlic, laurel).
- By chemical classifications. Essential oils are conglomerates of many diversified chemicals, both terpenic and nonterpenic. Terpenes are hydrocarbons having the structure $C_{10}H_{16}$. Among them are myrcene, limonene, p-cymene, dipentene, and ocimene. Sesquiterpenes, increasingly important to our industry, have the structure $C_{15}H_{24}$. Longifolene, patchoulene, and cedrene belong to this group. Terpenoids are the oxygenated derivatives of terpenes and sesquiterpenes. Among them are geraniol, linalool, alpha-, beta-, and gamma-terpineol, citral, citronellal, cedrol, cedrenol, vetiverol, and vetiverone. Nonterpenic constituents of essential oils include

benzyl alcohol (present in oil of clove, jasmine flowers)
phenyl ethyl alcohol (oil of roses)
acetic acid (free and mostly esterified in many essential oils)
tiglic acid (oil of star anise, as an ester in oil of geranium)
benzaldehyde (oil of bitter almond and many other essential oils)
cinnamaldehyde (oil of cinnamon)
anisic aldehyde (oil of anise)
beta hexenal (leaf aldehyde)
methyl n-amyl ketone (oil of clove and cinnamon)
methyl n-heptyl ketone (oil of rue)
coumarin (oil of lavender, various lactones in cold pressed citrus oils)
mono-, di-, and tri-sulfides (oil of garlic and onions)

The total number of known individual chemical components encompassed in essential oils is enormous.

Processing

Three production methods for essential oils are predominant today.

- Steam distillation
- Expression
- Extraction

In certain instances, various procedures applied to identical botanicals will render essential oils of different chemical compositions. An example is oil of lime. In steam distilled oil the citral content almost completely disappears, in contrast to expressed or solvent-extracted oil.

Essential oils are purified by fractional distillation according to the boiling points of their individual constituents. By this procedure, low boiling terpene hydrocarbons usually can be separated from the oxygenated constituents. It is also possible to separate higher boiling members, which might be unwanted in the final essential oil blend. In certain instances chemical separation of undesired components can be accomplished by chemical reactions. A simple example is to wash the essential oil with an aqueous caustic solution to eliminate acidic or sometimes phenolic constituents.

Conversion

Since essential oils are conglomerates of various and different chemicals, from an industrial economical point of view it was and is desirable to convert some of these chemicals, particularly those of lesser economic value, to more wanted, thus more expensive chemicals.

Two synthetic approaches are practiced for the utilization of such lesser valued essential oil constituents. The first is conversion to other, higher priced essential oil constituents, the second is utilization of essential oil constituents as reaction partners with other chemicals to obtain aroma chemicals found or not found in nature, such as

- Cinnamic aldehyde by the reaction of benzaldehyde with acetaldehyde
- Carvone from limonene
- Citral from geraniol
- Citronellol by partial hydrogenation of geraniol/nerol or hydrogenation of citronellal
- Ionones by condensation of citral with ketones followed by cyclization
- Esters of linalool, geraniol, citronellol and many more alcohols
- Esters of benzoic acid and other acids
- Acetals of benzaldehyde by reaction of benzaldehyde with alcohols or diols
- Alpha pentyl- and alpha hexyl cinnamic aldehydes by the reaction of benzaldehyde with the respective aldehydes
- Hydroxycitronellal by the hydration of citronellal

Many essential oil constituents today are mostly obtained by synthetic processes. Benzaldehyde, for instance, is produced in tonnage quantities by the aroma chemical industry.

Oleoresins

As their name indicates, oleoresins are composed of essential oils and resinous materials. They can be divided into two main groups.

- Those prepared by extraction with volatile solvents of spices and herbs. These materials are mostly or exclusively used by the flavor industry. Examples of oleoresins are black pepper, ginger, nutmeg, turmeric, cinnamon, capsicum, and vanilla beans. Since these products are used in foods, they have to meet strict regulatory specifications.
- Those oleoresins used in perfumery (resinoids) can be obtained from any odorous part of the plant except the flower. Resinoids prepared from pathological products of plants (exudations such as gums, resins, and balsams) are of special interest. Examples well known and widely used in perfumery are the resinoids of labdanum, olibanum, and galbanum.

Odorous animal products (civet, castoreum, and natural musk) are very much appreciated for their intense and lasting odor and fixation qualities.

Production

Selection of the appropriate solvent is one of the most important factors in the process of extraction of oleoresins for the flavor industry. The valuable constituents must be separated from unwanted ballast such as cellulose. The extract is then liberated from its volatile solvent under the mildest possible conditions (to avoid such problems as spot overheating) by vacuum distillation, leaving the desired oleoresin as the residue.

In the production of resinoids, selection of the extractive solvent is again of great importance. Ether extracts, acetone extracts, alcohol extracts, or those achieved by the application of hydrocarbons such as hexane, benzene, or toluene, will yield products of different odorous properties from the same material. On removal of the solvent, some low boiling odorous components might co-distill. They have to be captured in a cold trap and are eventually returned to the main product.

In specific cases high molecular resinous components are desirably eliminated by selective extraction procedures or by treatment with activated carbon. Lower molecular resinous products, of value as fixatives, have to remain as part of the final product. Valueless waxy materials can be precipitated from alcoholic solutions of the resinoid at low temperatures followed by filtration using a filter aid such as a diatomaceous earth. Chlorophyll, if not wanted in the final product, is best eliminated by adsorption on activated carbon. In all these cases the application of mixed solvents could or should be considered.

The various production methods explain the different properties of oleoresins obtained from identical starting materials.

Concentrated fruit juices

Fruit juice concentrates are produced by the reduction of water content. Special care and techniques must be exercised in processing to preserve flavor. In many instances the pectin content of the concentrates is removed. This process is an example of the usage of an enzyme (pectinase) in our industry.

Natural vs. synthetic products

Although organic chemistry and technology have advanced tremendously in the last decades making the synthetic production of a great number of aroma chemicals possible, essential oils, oleoresins, and fruit juice concentrates still occupy a prominent position in perfumery and in flavors. There are various reasons for this fact.

- Perfume and flavor compositions must contain at least some of these natural products to exhibit life, luster, and brilliance. Compositions made up solely of synthetics lack these necessary and important properties.
- The back to nature trend implies the use of natural products, particularly in foods. This increases demand for essential oils and oleoresins.
- Natural products such as essential oils and oleoresins are harmonious blends of main constituents and trace substituents. In many instances it is next to impossible now to produce all of these chemicals. Not all of them have been isolated yet, thus their chemical structures are

not known. There are difficulties in the syntheses of some substances, such as duplicating exact chemical configurations. Even where production would be possible, it remains at present economically unfeasible.

- In many instances nature is still a more economical producer than the chemical industry.

However, the chemical industry has in some cases produced synthetic duplications of natural isolates at consistent quality and at lower prices than natural products. Examples are methylsalicylate, thymol, vanillin, linalool, geraniol, benzaldehyde, cinnamic acid, and aldehyde.

Obviously there are several major differences between agricultural products and those of the synthetic chemical industry.

- Natural products contain a multiplicity of chemicals. In contrast, the synthetic aroma industry is aimed at the production of a single item at a time.
- Production in the chemical industry is independent of climatic conditions. Chemical processes are far less time consuming than agricultural processes, which are confined to at most three crops a year. The chemical industry occupies much less land than agriculture. And the chemical industry has produced many chemicals that are not found in nature. Many of these are extremely valuable fragrance and flavor materials. Examples are

Nitro musks: Musk Xylene: 2,4,6-trinitro-1,3-dimethyl-5-tert. butyl benzene, Musk Ambrette: 2,6-dinitro-3-methoxy-4-tert. butyl benzene, and Musk Ketone: 3,5-dinitro-2,6-dimethyl-4-tert. butyl acetophenone
Cyclamal: alpha-p-isopropyl-hydrocinnamic aldehyde
Lilial: alpha-methyl-p-tert.butyl-hydrocinnamic aldehyde
Lyral: 4-(4-methyl-4-hydroxy-amyl)-3-cyclohexencarboxaldehyde
Sandella: trans-3-(exo-5-exo-isocamphyl)-cyclohexanol
Hydroxycitronellal: 3,7-dimethyl-7-hydroxy-octan-1-al
Hexyloxyacetaldehyde dimethylacetal

Essential oils, oleoresins, and fruit juice concentrates—representing natural products—are indispensable in the fragrance and flavor industry. However, presently more aroma chemicals (in quantities and money values) are produced by syntheses than by agriculture. It would be impossible to satisfy today's demand for aroma chemicals from natural sources only.

Synthetic organic materials

The last century and the beginning of this one is classified as "the Golden Age of Organic Chemistry," during which numerous important discoveries and inventions were made. Synthetic organic chemistry now emerged as a well organized science. Novel approaches resulted in the reactions of different molecules with each other to produce new molecules of known and unknown structures. Many of these synthetic methods remain part of today's organic chemistry and are of great value in the syntheses of essential oil constituents and other aroma chemicals.

A few examples of the many synthetic methods follow.

The Grignard Reaction

The Grignard reaction is particularly valuable because of its versatility.[1] In this reaction a halogen compound is reacted with magnesium to form a Grignard reagent which can be reacted with almost any functional group.

One of the earliest applications of the Grignard reaction was in the preparation of phenyl ethyl alcohol by the reaction of phenyl magnesium bromide with ethylene chlorohydrin.[2] Since then several more advantageous processes for this alcohol were developed and have replaced the Grignard reaction in this case. However, in many other instances this reaction is still widely used in our industry for example for the preparation of tertiary alcohols such as dimethyl benzyl carbinol and phenyl ethyl dimethyl carbinol.

While the original Grignard reaction was conducted in ether solution, the benefit of other solvents, particularly tetrahydrofuran, was more recently realized. This solvent was applied by Normat in a one-step synthesis of linalool by the action of magnesium vinyl bromide or chloride on methylheptenone.[3] The Grignard reagent, e.g. magnesium vinyl bromide or chloride is formed only in THF solution but resists formation in ether.

A recent example gives further evidence of the applicability of the Grignard reaction to our industry. In a modified Grignard reaction, Ramsden condensed prenyl chloride and isoprene with magnesium to obtain lavendulyl magnesium chloride which on oxidation with air or oxygen, followed by hydrolysis, yielded lavendulol.[4]

The Friedel-Crafts Reaction

In their original report, Friedel and Craft described the condensation of alkyl or acyl halides with different aromatic compounds catalyzed by anhydrous aluminum chloride. This procedure results in the substitution of an alkyl or acyl group of one or more hydrogen atoms of the aromatic compound. Important aroma compounds are produced. Examples are aromatic ketones such as acetophenone. In a broad sense any reaction which is catalyzed by anhydrous aluminum chloride is today classified as a Friedel-Crafts reaction.[5] An example is the preparation of phenyl ethyl alcohol by the reaction of benzene with ethylene oxide, catalyzed by aluminum chloride and hydrochloric acid. This process was first described by Schaarschmidt and coworkers[6] but has since then been improved and developed to an important, practical production process.

The Diels-Alder Reaction

In the "Diene" synthesis, a chemical having a double or triple bond is reacted with the 1,4-position of a conjugated diene system. A six-membered hydroaromatic ring results. This process, known as the Diels-Alder reaction, is widely used in the aroma industry and examples are well known and plentiful.[7] In a more recent example, Cookson and coworkers prepared certain terpenes such as tagetonen, atlantonen, ocimenen, and filifolonen by using isoprene in a Diels-Alder reaction.[8] Cookson and coworkers also reported the preparation of terpene-ketones, among them atlantone which was synthesized by an acid catalyzed Diels-Alder reaction and isoprene.[9]

The versatility of the Diels-Alder reaction is also shown by a paper entitled "Recent applications of the Diels-Alder reaction to the synthesis of natural products," which was presented at the Metrochem meeting of the American Chemical Society in Fallsburg, NY, October 1978 by S. Danishefsky.

Advances in synthetics

The chemical industry is in constant search of less expensive and readily available starting materials and novel technological and synthetic advances to produce identical materials at lower or competitive prices. There are several well known examples.

- Phenyl ethyl alcohol has been synthesized for the past century. During this period it was produced by many diversified processes which one by one were replaced by more economical processes. Today only two production methods remain predominant: the Friedel-Crafts process in which benzene is reacted with ethylene oxide, and the hydrogenation of styrene oxide.
- Vanillin is probably the most widely used synthetic flavor aroma chemical. It was first prepared by Tiemann and Haarmann in 1874 from coniferin.[10] The ever increasing demand for vanillin was the catalyst for much research resulting in a variety of production processes, among them those starting with guaiacol. A significant success of chemical technology was the production of vanillin from sulfite liquor, a by-

product in the manufacture of paper.[11] For many years almost exclusive, this process is challenged today, to be at least partially replaced by the rational availability of guaiacol and by improved technological advances made for its application in the vanillin and ethyl-vanillin syntheses.

From the above examples it becomes evident that identical chemicals can be synthesized today by different approaches. This is a striking example of the great advances organic chemistry and its synthetic applications have made. Our industry is an active partner in this progress.

- Synthetic musk has had a long history, from nitro-musk "Bauer" in 1888 (trinitro-m-tert.butyltoluene) to nitrile-musk (in 1975) (1,1,4,4-tetra-methyl- alkyl-nitriles- tetrahydronaphthalene).[12] During this time many chemicals having musk odors were invented. In contrast to phenyl ethyl alcohol and vanillin, the family of musks comprises a great variety of chemicals having different basic chemical structures and functional groups. This demonstrates that no one specific functional group or molecular configuration can claim sole responsibility for a certain basic odor. There are many musks produced that differ in sensory properties from each other. In other words, there are specific by-notes which are desirable for one or another application.
- Menthol is one of the unique chemicals of our industry. It can exist in four isomeric forms: menthol, neomenthol, isomenthol, and neoisomenthol. Each of these isomers can exist in the two optical forms: (−) or (+) or as the racemate (±). In menthol all the substituents of the hexane ring are equatorial, whereas in all menthol isomers one or two substituents of the hexane ring have the axial conformation. The isopropyl group in all menthols has the equatorial conformation—as expected—because bulky groups usually have this conformation. Among the menthols, (−)-menthol is the most widely used. Its predominant and desired property is its well known cooling effect. Its natural main source is the essential oil of Mentha Arvensis, where it is present in 75-90%. (−)-Menthol and its isomers are the classical examples to demonstrate stereoisomerism and to give proof that such isomers can differ greatly from each other in sensory properties.

Many syntheses for menthols have been reported; some of them are even today in commercial production. An example is a stereospecific reduction of a menthone to (−)-menthol. A specific example is the sodium reduction of the (−)-menthone content to (−)-menthol in dementholized peppermint oils.

In chemical terms (±)-menthol is hexahydrothymol. The racemic menthol can be actually prepared by the direct—thus most elegant—procedure, which is the catalytical hydrogenation of thymol.

The problem of resolving a racemate into its two optically active components was and is one of the challenging and important projects of organic chemistry. While much progress in this direction was made, commercial processes (which are the final goal of any type of research) are rare. In the case of racemic menthol, a commercially feasible solution seems to have been achieved. In this regard the publication of Bauer and coworkers of Haarmann & Reimer,[13] and a paper presented by Bauer and coworkers at the IV International Congress of Essential Oils in San Francisco, is worthy of note. It is stated that the partial crystallization of menthyl benzoates or their derivatives and inoculation of their supersaturated solution in methanol or other solvents is now used as the most important step in the large scale production of (−)menthol from (±)-menthol by Haarmann & Reimer.

- Carveol, an unsaturated secondary alcohol having the structure $C_{10}H_{16}O$ has two asymmetric centers. Thus, it exists in four optically and two racemic forms. However the isomeric ketones of carveol, the carvones, are of greater importance as flavor and fragrance contributors than their isomeric alcohols. Carvones are main constituents of certain essential oils. (−)-Carvone is the principal constituent of spearmint oil where it is present up to 70%, whereas (+)-carvone is the main constituent of caraway oil and dill seed oil. A sensory examination of these oils immediately reveals their pronounced differences in odor and taste. Teranishi and coworkers synthesized the two enantiomeric carvones in pure form by standard methods from (−)-limonene and (+)-limonene, and described their organoleptic differences.[14]

Enzymes

Enzymes are proteins which catalyze biological functions of (or in) animal and plant life. Their importance to our industry is obvious. They are coresponsible for the growth of plants and the development of their constituents such as the terpenes and oxygenated materials and other elements present in these constituents. In contrast to many synthetic processes, enzymatic reactions are stereospecific. However many synthetic stereospecific syntheses are also known. Our basic knowledge concerning the functions of enzymes, as well as intensified research, gives hope that biologists in collaboration with chemists will be able to synthesize valuable plant materials in the laboratory.

Enzymes are used on a large scale in our industry. The development of odor and taste by the "curing" process is an enzymatic reaction and is applied to vanilla beans, patchouli leaves, tobacco, etc. In rose oil production, an enzymatic procedure boosted considerably the yield and quality of this all-important essential oil. V.

Staikov and coworkers stored rose petals under different conditions and observed and analyzed the development of their aroma and constituents.[15] Best results were obtained by keeping the petals for 24 hours at a temperature of 4-11°C. under water. Under these conditions the essential oil content (consisting among others of citronellol/nerol and geraniol) rose 154% while the stereopten content decreased.

The nomenclature of enzymes is based on their action. Urease attacks urea, dehydrogenase acts as a dehydration catalyst. Older names such as pepsin, tripsin, etc. are still in use. The material upon which an enzyme acts is called the "substrate."

According to their bio-chemical reactions, enzymes can be divided into several general groups:

Oxidoreductase: for oxidation-reduction reactions
Transferase: for transfer of a chemical group from one molecule to another
Hydrolysase: for hydrolytic reactions such as the promotion of hydrolysis of proteins, glycosides, esters and phosphates
Lyasase: for the addition of a chemical group to a double bond
Isomerase: for intramolecular rearrangements
Ligase (synthesase): for catalysing the condensation of two molecules coupled with the cleavage of a pyrophosphate-bond of a ATP (adenosine-triphosphate) or similar phosphates

Each of these groups consists of many individual members; thus a great number of enzymes are in existence. The chemical structure of each enzyme is different, thus enzymology is complex, involved and somewhat complicated.

As can be imagined, in enzymology, as in any other science, great progress has been made and many scientific questions have been answered and are today common knowledge. An interesting progress in the development of enzyme technology was recently reported by Whitesides who described a practical process for the preparation of the enzyme co-factor ATP (adenosine triphosphate).[16] From a possible synthetic point of view this development is worthy of note.

Offhand, there are various possible applications of enzymes of interest to our industry. These include the addition of these materials to food products to improve their flavors, the possibility of applying enzymes as stereospecific catalysts in organic syntheses, and the curing process, already mentioned.

Terpenes

In dealing with natural products, the question of how nature produces them has always intrigued academic researchers and industrial scientists. Regarding the biosynthetic formation of terpenes, a paper by Agranoff, Eggerer, Henning and Lynen is of great importance.[17] It was stated that delta-3-isopentenol pyrophosphate (also somewhere else described as "active isoprene") a product of mevalonic acid metabolism was isolated. This product was also established to be related to farnesol pyrophosphate. The interpretation of these findings was that terpenes are actually biogenetically formed in accordance with the isoprene rule.

There are two groups, one headed by Cornforth in England and the other by Eggerer in Germany, actively engaged in research regarding the biosyntheses of terpenes. Several papers were published between 1970-1975. Among them, one is entitled "Enzymatic Generation of Chiral Acetates, a Quantitative Evaluation of their Configuration Assay" and another deals with the isopentenyl-pyrophosphate isomerization, seem to be of particular interest.[18,19]

However, the present synthetic approaches for the production of terpenes and their oxygenated derivatives do not follow their biogenetic pathways. There are several well-known, efficient syntheses for monoterpenes and their derivatives. The utilization of myrcene for the preparation of geraniol and to a lesser extent to linalool seemed to be a logical way on account of the structural similarities of the carbon skeletons of these products. However, hydrolysis of myrcene, the most logical approach, failed. The application of a copper catalyst in conjunction with HCl and sodium acetate, which brought the desired result, has to be considered as a significant technological achievement.

Recent research and developments in the pharmaceutical industry have contributed greatly to the availability of monoterpenoids by total syntheses of these chemicals. More specifically, reference is made to the important vitamin A and E syntheses where acyclic monoterpenes are required in large amounts. Starting with methylheptenone as the anchor-chemical, various synthetic methods are used to provide materials which are also basic to our industry.

From an industrial point of view it is obvious that sesquiterpenes and their oxygenated derivatives are important materials. Several of these materials, such as alcohols, esters, ketones, are well known for their interesting and valuable odorous properties. The versatility of these materials in organic syntheses makes them interesting and valuable for the preparation of known and novel aroma chemicals. Most sesquiterpenes are readily available.

As can be assumed, there is a vast literature dealing with sesquiterpenes in general and with specific members of this chemical group. Three helpful papers present these structures and important facts of this important part of the chemistry of our industry. They are

The Chemistry of Essential Oils by Kurt Kulka, Perfumery & Essential Oil Record, March 1962
Synthesis of Sesquiterpenes by J. M. Mellor and S. Munavalli, Quarterly Reviews, Vol. XVIII, No. 3, 1964
Sesquiterpenes in the Perfumery Industry by H. R. Ansari and A. J. Curtis, J.S.C.C. 25, 203-11, 1974

In addition to the above dealing with terpenes, it should be remarked that isoprene is one of the most versatile chemicals. It has found many applications in organic syntheses in the past, and more usage of this valuable chemical can be contemplated in the future. A great advantage of this product is its availability. A paragraph entitled "Research in Isoprene Derivatives" in Bedoukian's 34th Annual Review, published in the April/May 1978 issue of *Perfumer & Flavorist* gives witness to the importance of this product.

Analytical procedures

The analytical procedures practiced today by the essential oil-aroma chemical industry can be divided into two groups:

- wet analyses,
- physicochemical analytical procedures (instrumental analyses)

The main objective of today's wet analyses is the examination of the physical constants of aroma materials. The purpose of these examinations is to establish whether the products of investigation are acceptable, that is, whether they meet established standards or have to be rejected. When dealing with novel products the task becomes the establishment of physical constants for future references. Properties such as refractive indexes, specific gravities, optical rotations, boiling points, melting points, solubility in various solvents, etc., are routinely obtained.

In our industry sensory evaluation with regard to odor and taste by comparison of these phenomena with those of previously accepted standard products is required. The determination of purities of aroma materials based on their functional groups requires individual chemical operations, such as saponification, esterification, or titration. The reaction methods and calculations for many individual aroma products and for functional groups in general are well established.

The elucidation of chemical structures was previously a tedious, complex and time-consuming chemical procedure which required large amounts of a chemical to be analyzed. In contrast, the physicochemical methods of today require only small quantities of chemicals; they are fast, precise and relatively simple operations.

These analytical processes can be divided into three groups:

- Chromatographic separations, consisting of gas, liquid, and thin layer chromatography. The purpose of these procedures is to separate any mixture of chemicals—for example, an essential oil—into its individual constituents.
- Spectroscopic methods, consisting of infrared spectroscopy, nuclear magnetic resonance spectroscopy, mass spectroscopy, and raman spectroscopy. The spectroscopic methods are intended to produce a picture of the structural architecture of the individual isolates or any single chemical.
- X-ray diffraction, which is applied to solid materials. Because most of the products of our industry are liquids, in order to make use of this technique, the liquid products have to be converted by syntheses to solid derivatives. In spite of this apparent disadvantage, there are examples, such as longifolene and geraniol, where X-ray diffraction was successfully used to establish the exact structures of these chemicals.

It is significant that our industry immediately recognized the great value of these instrumental analytical methods. Using a combination of gas chromatography and infrared spectroscopy many essential oils were investigated in the 1950s and 1960s, by Leo Levi of the Canadian Research Council, Y. R. Naves of Givaudan, James A. Rogers, Jr. of Fritzsche Dodge & Olcott Inc., E. Theimer, W. T. Somerville, B. M. Mitzner and S. Lemberg of IFF, and other scientists.

Looking at today's state of the art it is interesting to observe that the basic principle of chromatographic separation-infrared spectroscopy for identifications remains the workhorse in the laboratories of our industry. Significant improvements in equipment for and execution of the before-mentioned procedures are made continuously. More efficient chromatographic columns and packing, automatic samplers, and detectors are among the variety of accessories which contribute to the increased efficiency of physicochemical analytical instruments. Thus, more efficient and precise resolutions are achieved.

Other improvements due to developments in other scientific fields were adapted to instrumental analytical equipment. A logical consequence was to combine a separation technique method with a spectrographic method and add the advantages of automation and computerization. Thus, a sophisticated instrument comprising chromatography with mass spectrometry in an automated and computerized system was created and is used by many laboratories.

An ever-increasing list of important publications pertain to this field. The following recent papers are examples.

Analytical Science (A Science Update) by Worthy gives a general view of today's standing of analytical chemistry[20]

Mobile Phase for High Performance Liquid Chromatography by Bakalyar describes most concepts of this analytical tool[21]

"Synchrotron" (radiation) A Novel Tool for Chemical and Structural Studies by Hodgson and Doniach contains information worthy to be kept in mind for future possible developments[22]

Gas Chromatography with Glass Capillary Columns by Jennings explains general considerations and theories of chromatographic processes as well as giving a very authoritative description of gas chromatography with glass capillary columns[23]

How chemistry profits from other technological achievements is also demonstrated by the adaptation of laser technology to spectrographic methods. A more specific example is the magnetically tunable spin-flip Raman infrared laser used in high-resolution spectroscopy, which was introduced in 1969 by Bell Laboratories.[24]

Without the benefits of instrumental analyses the tremendous advances of our industry—which we have witnessed during the last decades—would have been impossible. Besides the separation and structural elucidation of many components of natural products such as found in rose oil, jasmine, etc., a great number of trace substances such as the pyrazines were detected, identified and prepared.[25]

Any product isolated from natural sources that has found importance as an odor or flavor contributor automatically becomes the target of synthetic duplication. Such projects not only activate the knowledge of the organic chemist, but also inspire creative imagination to search for or produce novel and useful chemicals having similar structures.

Another important aspect of analytical procedures is that they are able to guide the organic chemist in synthetic work. They will indicate whether a synthesis is going in the right direction or whether the experimental conditions have to be corrected or a specific approach has to be abandoned.

Conclusion

If the many sources from which essential oils, oleoresins, fruit juice concentrates, and aroma chemicals are derived are considered and the ever-increasing demand for such products is noticed, one will not be astonished that today 3,000 to 4,000 of such individual chemicals are known.[26] In addition there are at least several hundred aroma chemicals in existence which are not for sale but are reserved for internal use by the perfume and flavor divisions of essential oil houses and aroma chemical manufacturers for incorporation in their exclusive perfume bases and specialties.

Our industry is unique because it is concerned with agriculture, chemistry, physiology, bacteriology and other sciences. No other industry, chemical or otherwise, produces such a diversified and great number of individual materials. It is also understandable that these operations require the application of various chemical reactions and analytical procedures.

The future of the essential oil-aroma chemical industry can be predicted in two words: Continuous Progress.

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