The Chemistry of Detergent Perfumery

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Abstract

Detergents constitute a low-price, bulk item, which consumes a large quantity of aromatic materials. Detergent perfumes must not only meet the normal requirements of odor and stability but also strict demands in low price and high availability.

The perfumes used in detergents are normally a complex mixture consisting of synthetic materials produced from either petroleum or coal tar products, isolates of natural products or synthetics derived from isolates, and natural products such as the essential oils.

The synthetics and isolates which are commonly used in detergent perfumery are discussed with their methods of production. The essential oils that can meet the demands of price and availability are listed.

Discussion

DETERGENTS AMOUNTED to a volume of 4,298,273,000 lb in 1966 (1). Even though the perfumes are added at a low percentage, these products consume a large quantity of aromatic materials. The perfumes used in these solid or liquid products must not only meet the normal requirements of fragrance and stability but also the stringent demands of low price and high availability. The discussion will concern some of those materials which are commonly used in detergent perfumery and are especially able to meet these economical requirements.

The perfumes for detergents and other products are normally complex mixtures of many components. These can be considered to be dependent upon three sources: a) petroleum or coal tar products, b) isolates of readily available natural materials, and c) readily available natural products such as the essential oils. In Table I are listed some of the materials that are commonly used. These will be discussed in terms of their production, availability, and their suitability for detergent perfumery.

Petroleum or Coal Tar-Derived Chemicals

Since the chemicals obtained from petroleum or coal tar products are economical and plentiful, any perfumery item that can be readily manufactured from this source would be able to meet the demands of price and availability. Some of the more important synthetics are discussed.

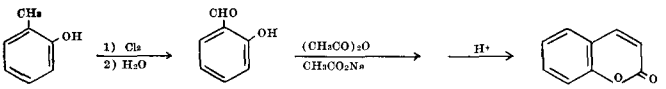
Phenyl Ethyl Alcohol. This alcohol is an important synthetic used in the rose type of fragrances. It has a pleasant floral rose odor and is found as a component in many natural oils, including rose oil. Since phenyl ethyl alcohol is slightly soluble in water, it is found in the recovered rose distillation water which is sold as rose water.

The alcohol is manufactured by the Friedel-Crafts condensation of benzene and ethylene oxide by using aluminum chloride as catalyst. Since it is manufactured from available material and has a desirable odor, it is used extensively in detergent and soap perfumery. It can be supplied in a pure state (99+%) and has excellent stability. The esters of phenyl ethyl alcohol are also used.

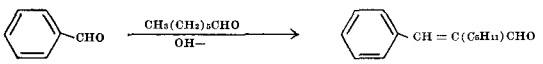
Benzyl Alcohol. This is another popular alcohol which is derived from a petroleum product. It is easily manufactured by the hydrolysis of benzyl chloride, which is prepared by the chlorination of toluene. It is manufactured on a large scale and used in many industries. It has only a faint odor but finds wide application in perfumery for its solvent and fixative properties. This alcohol is a component of many essential oils, such as the oils of jasmin and ylang ylang. It has excellent stability and can be supplied in a pure state.

Benzyl Acetate. Manufactured by the acetolysis of benzyl chloride, benzyl acetate is the major component of jasmin oil and has a strong pleasant jasmin odor. Like the benzyl alcohol, it is available in a pure state at a low price and is used to a large degree in detergent perfumery. The acetate is only moderately stable, being susceptible to hydrolysis. Because of its easy hydrolysis, jasmin oil is obtained through extraction procedures rather than by steam distillation.

Coumarin. This is a lactone which is important in most types of perfumery owing to its pleasant, sweet hay-like odor. Its manufacture is based on o-cresol, a product of coal tar. The cresol is converted to o-hydroxy benzaldehyde, which is condensed with acetic anhydride and then cyclized to the lactone. Coumarin occurs widely in nature and is found in many oils including tonka bean and lavandin.



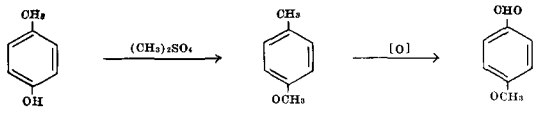
α-Amyl Cinnamic Aldehyde. This is prepared from benzaldehyde, which is manufactured by the hydrolysis of benzal chloride, a secondary chlorination product of toluene. On condensing benzaldehyde with heptaldehyde, a product from the pyrolysis of castor oil, α-amyl cinnamic aldehyde, is formed. This material has been used for many years and is still popular in detergent perfumery. It has a strong floral odor with moderate stability. It has never been reported as occurring in nature.



Anisaldehyde. This material is also referred to as aubepine, a French word meaning hawthorne, to which this aldehyde is similar in odor. It is manufactured from p-cresol by methylation, followed by careful oxidation. A finer and more expensive grade of the material is available by the oxidation of anethole. The material is found as a component in many oils, especially those containing anethole, such as fen-

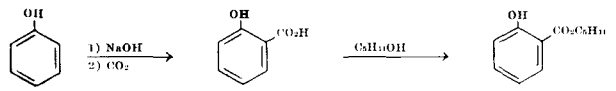
TABLE I
Detergent Perfumes

A. Petroleum or Coal Tar-Derived Chemicals	2. Isobornyl acetate
1. Phenyl ethyl alcohol	3. Nopyl acetate
2. Benzyl alcohol	4. Rose alcohol
3. Benzyl acetate	5. Ionones
4. Coumarin	Citronella
5. α-Amyl cinnamic aldehyde	6. Citronellal
6. Anisaldehyde	7. Hydroxycitronellal
7. Amyl salicylate	8. Menthol
8. Synthetic musks	9. Geraniol
B. Isolates or Synthesized from Isolates	Ocotea Cymbarum or Camphor
Turpentine	10. Heliotropin
1. Terpineol	C. Essential Oils
2. Isobornyl acetate	1. Lavandin
3. Nopyl acetate	2. Pine oil
4. Rose alcohol	
5. Ionones	
Citronella	
6. Citronellal	
7. Hydroxycitronellal	
8. Menthol	
9. Geraniol	
Ocotea Cymbarum or Camphor	
10. Heliotropin	
C. Essential Oils	
1. Lavandin	
2. Pine oil	



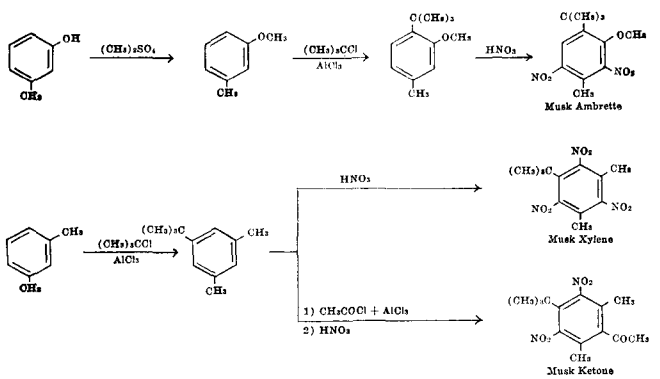
nel and anise, which indicates that it is probably formed in nature by the oxidation of anethole. Because of its pleasant powerful odor and its availability from p-cresol, it finds extensive use in all forms of perfumery.

Amyl Salicylate. Two esters of salicylic acid are commercially important in the flavor and perfumery industries, namely, methyl salicylate and amyl salicylate. Methyl salicylate is used in flavor work as a synthetic wintergreen oil, and amyl salicylate is employed throughout perfumery. Amyl salicylate is manufactured on conversion of phenol by the Kolbe reaction to salicylic acid, which is then esterified. Since the alcohol in the esterification is a mixture of amyl and isoamyl alcohols, the final product is a mixture of these esters. Because of its lasting floral odor and its low cost, it is widely used in detergent and



soap perfumery. Although the methyl salicylate is found in nature, amyl salicylate has never been reported as a naturally occurring compound.

Synthetic Musks. Although the majority of scents in perfumery are of vegetable character, no discussion would be complete without mention of the legendary animal notes. The history of perfumery is filled with adventurous tales of the ancient products of musk, the glandular secretion of the male musk deer of the Himalayas, and ambergris, the wax-like secretion of the sperm whale. Though musk, ambergris, and civet are still important in perfumery, they are far too expensive for use in detergents. In detergent perfumery these scents are provided by synthetic musks such as musk ambrette, musk xylene, and musk ketone. Since these three synthetics do simulate the powerful odors of the natural animal products and can be derived from petroleum or coal tar products, they represent practical and economical substitutes for their natural counterparts. These synthetic musks are manufactured by the following reactions:



Isolates of Natural Products

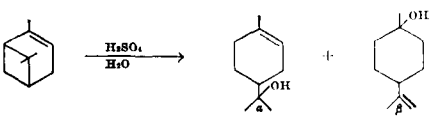
Several natural products can be produced cheaply and on a large scale. Some however are not of a suitable odor for wide-scale use in perfumery but are used in the manufacture of more important perfumery items. The largest and most important of these natural products is turpentine.

Turpentine

Turpentine is the volatile oil obtained from the resinous exudates or resinous wood of living or dead pine trees. These are four approved types of turpentine: a) gum spirits of turpentine, which is the volatile oil steam distilled from the oleoresin that exudes from the living pine: b) steam-distilled wood turpentine, which is the terpene fraction of the volatile oil extracted from the dead pine stumpwood remaining after lumbering operations; c) sulfate wood turpentine, the volatile terpenes recovered during the sulfate wood pulp process; and d) destructively distilled wood turpentine, which is the terpenic material recovered in the carbonization of wood. At the present time the sulfate turpentine is the most important, and its production appears to be increasing as a result of improved yields in turpentine recovery in the pulp mills. The destructively distilled wood turpentine is relatively unimportant. The composition of turpentine varies widely, depending largely on the type of turpentine and/or the species of pine (2). The major component is generally α-pinene with smaller amounts of β-pinene and numerous other terpenes. A typical composition of a sulfate wood turpentine is 65% α-pinene, 23% β-pinene, and 12% other terpenes.

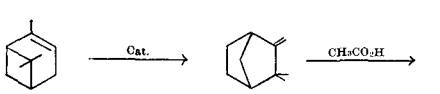
Although these terpenes are found in most essential oils in low amounts, turpentine itself is not an important perfumery material. However, since the major components of turpentine are the pinenes, which possess terpenic structures that are easily rearranged, turpentine has become a major starting material for the manufacture of the most important items in perfumery.

Terpineol. Terpineol, the largest manufactured perfumery material, is prepared from turpentine or α-pinene by treatment with aqueous sulfuric acid. This commercial terpineol is a mixture of isomeric



terpenic alcohols; the α- and β-isomers predominate. Being prepared directly from α-pinene, the material is readily available and is very economical. Terpineol has a sweet lilac odor and is one of the most popular items in the perfumery of detergents. The major isomer, α-terpineol, is found as a component in many essential oils.

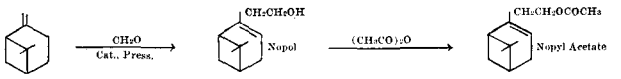
Isobornyl Acetate. The next most popular material in perfumery is isobornyl acetate. It is also derived from α-pinene, which is isomerized under catalytic conditions to an isomeric terpene, camphene. Camphene, when refluxed with acetic acid, is converted to isobornyl acetate. Camphene occurs in turpentine



and in numerous other oils but only in small amounts; therefore it is commercially dependent on α-pinene. Isobornyl acetate has a pine needle odor and is popular in detergents and cleansers. It has not been reported as a natural component, but the corresponding exo isomer, bornyl acetate, is found in all pine needle oils. The bornyl acetate and isobornyl acetate have nearly identical odors.

Nopyl Acetate. This is the ester of the condensation product of β-pinene and formaldehyde by the Prins

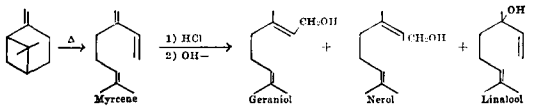
reaction. Its popularity is attributed to the relationship of its odor to bergamot oil and its low cost. It



is also called lignyl acetate or citroviol. Nopol is not as popular in perfumery as its acetate.

Rose Alcohols. One of the more recent developments in the perfumery industry has been the manufacture of the so-called rose alcohols, again from turpentine. These are the terpene alcohols known as geraniol, nerol, linalool, and citronellol. These materials have been used for many years as isolates of various essential oils. Their price and usage vary, depending upon the availability of the particular essential oil. They have now been manufactured by the hydration of myrcene to produce, depending upon reaction conditions, geraniol, nerol, or linalool. Myrcene is manufactured by the pyrolysis of β-pinene. Because of recent demands in both the perfumery and resin industries for the less plentiful β-pinene, a process has been developed to obtain β-pinene from the catalytic isomerization of the more available α-pinene (3).

Geraniol was previously obtainable from the oils

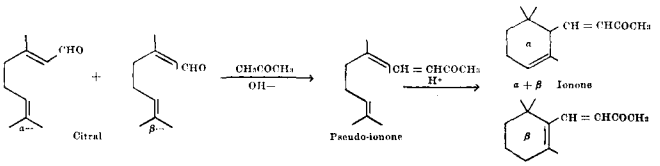


of palmarose and citronella. Geraniol ex palmarosa is the more expensive type, having a very pleasant rose odor that is used in fine perfumery. Although this geraniol is fairly pure, it contains numerous trace impurities which contribute much to its prized odor. Geraniol ex citronella is a cruder material, containing a large amount of citronellol, and consequently is not as fine or expensive as the former. This material is used widely in detergent perfumery. Synthetic geraniol ex turpentine can be produced in a pure state and is becoming popular in detergent perfumery. Although pure, it is not comparable in odor with the palmarosa geraniol because of the differences in their minute impurities.

Nerol, the *cis* isomer of geraniol, is not as popular in perfumery as geraniol but is found in numerous essential oils. Although it also has a rose-like odor, it is distinctly different in odor from geraniol.

Linalool is a familiar terpenic alcohol previously isolated from oils of bois de rose (rosewood), ho or shiu, linaloe or coriander where it is the major component. This alcohol has an asymmetric center and can occur in dextro or levo forms, depending upon the oil. Synthetic linalool from turpentine is racemic and is nearly identical in odor to the linalool isolated from bois de rose oil, which was the major source of natural linalool. Bois de rose oil is commercially obtainable only from the Amazon region of Brazil and Peru by the steam distillation of the wood. The synthetic linalool is now replacing, to a large extent, the linalool isolated from the bois de rose oil. Synthetic linalool is also available from an alternate synthetic process which starts with acetylene. The two processes are competitive. Recently citronellol has been synthesized from pinene, but this process has not yet achieved the commercial status of the above process.

Ionones. Since both geraniol and nerol are now available under economical manufacturing procedures, they can be used in the manufacture of citral through oxidation. By using a mixture of geraniol and nerol, citral with α- and β-isomers can be manufactured. Citral is also commercially available from lemongrass oil, an essential oil obtained from the grass grown in the state of Kerala of India, and synthetically from dehydrolinalool, which is manufactured from acetylene. Citral has a characteristic lemon-like odor and is used largely in flavor applications. The chief perfumery use is in the manufacture of the ionones. On condensation with acetone in base, citral can be converted to pseudo-ionone. The pseudo-ionone is generally not used as such but is cyclized with acid to



the ionones. Depending upon the reaction conditions, either the α- or β-ionone can be made to predominate. The ionones with a pleasant woody-violet fragrance are popular in detergent and soap perfumery.

If methyl ethyl ketone is employed in the condensation rather than acetone, the resulting product is the methyl ionone, which is also important.

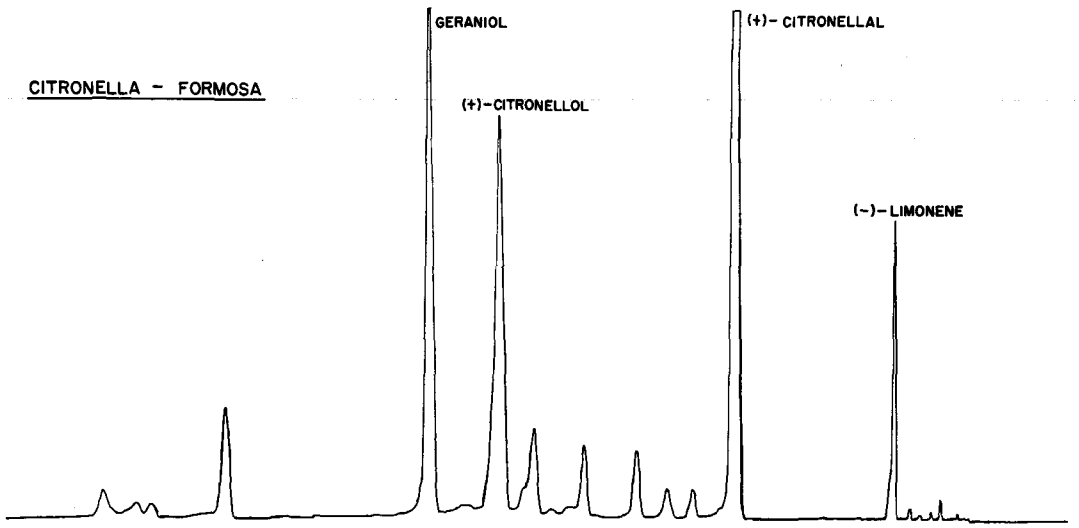


FIG. 1. Chromatogram of citronella oil.

Citronella

Next to turpentine, the most important natural source of perfumery synthetics is citronella oil. This oil is obtained by the steam distillation of the grass native to the Far East, mainly on the island of Formosa. There are two species of this oil, the Formosan or Java type and the Ceylon type. The Formosan or Java type is the more important of the two because of its higher citronellal content, an important chemical intermediate. A chromatogram of the oil is shown in Fig. 1 with the major components of citronellal (35%), citronellol, and geraniol indicated.

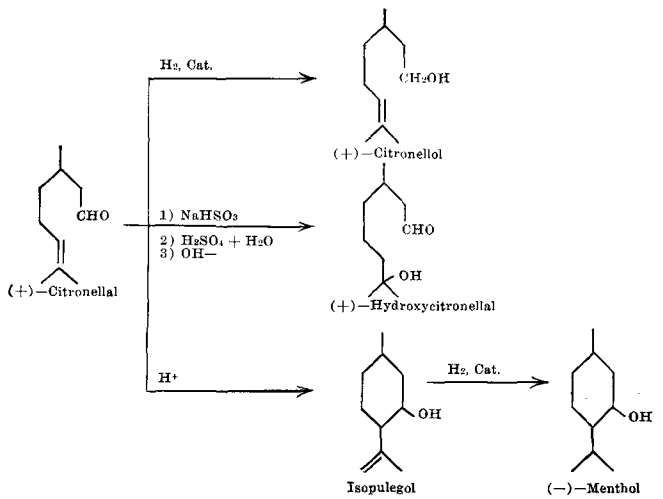
The oil is processed into essentially four fractions: a) a terpene fraction which is largely (−) −limonene and is relatively small; b) a fraction that is largely citronellal, the principal and most valuable component, which has a refreshing lemon-rose type of odor but is used largely for conversion into other materials; c) a fraction rich in both citronellol and geraniol, which is sold as geraniol for soap; and d) a higher-boiling fraction sold and used largely as a fixative.

A commercial balance must be reached with the isolates of this oil. A large demand for citronellal must be met with a similar demand for geraniol. The three most important synthetics that are obtained from citronellal are citronellol, hydroxycitronellal, and menthol.

Citronellol, which is prepared fairly pure by the hydrogenation of citronellal, has a rose-like fragrance and is found in numerous essential oils. The esters of this alcohol are also popular in detergent perfumery.

Hydroxycitronellal is manufactured by the acid-catalyzed hydration of the sodium bisulfite addition product of citronellal. This material can be manufactured in a pure state and is used in perfumery for its sweet floral fragrance.

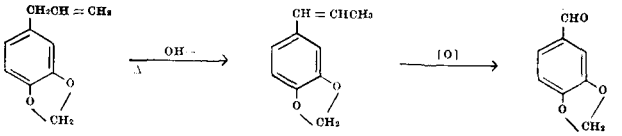
Menthol is used chiefly for flavor purposes, largely in toothpastes and cigarettes, and is mentioned only to complete the citronella story. The (+) − citronellal, on cyclization with acid, is first converted to isopulegol, which is hydrogenated to (−) − menthol. At the present time this (−) − menthol process is not competitive with the (−) − menthol isolation from Brazilian mentha arvensis. This species of mint is often referred to as cornmint and yields an oil high in (−) − menthol.



Ocotea Cymbarum

Safrole is an important chemical intermediate which is commercially available only from natural sources, such as the ocotea cymbarum oil of Brazil and the camphor oil of the Far East. Currently, ocotea cymbarum oil is the major source of this compound. This oil is obtained by the steam distillation of the cut wood from the wild tree native to Brazil. Ocotea cymbarum oil is also known as Brazilian sassafras oil and has more than 90% of safrole. Safrole, which has a strong sassafras odor, congeals at 10C and is removed from the oil by cooling. Its major importance is in the manufacture of heliotropin.

Safrole is isomerized to isosafrole on treatment with base in the presence of a catalyst. On oxidation of the isosafrole, heliotropin is produced.



This compound is named after the blossoms of heliotropin, which it resembles so closely in odor. Heliotropin is also referred to as piperonal.

Essential Oils

The final category of detergent perfumes concerns the essential oils that are commonly used per se. Although many essential oils can be used at low levels, pine oil and lavandin oil can be used in higher percentages and are two of the largest oils used in detergents.

Pine Oil. Pine oil is obtained by the solvent extraction of the pine stumpwood, that is, the pine wood which remains in the forests after lumbering operations. On removal of the solvent, the crude oleoresin is steam-distilled to yield several fractions. The major fraction is the most volatile and is largely α-pinene; it is called steam-distilled wood turpentine. A second higher-boiling fraction, amounting to nearly 7% of the oleoresin extract, is pine oil. Pine oil is a by-product of the steam-distilled wood turpentine and was at one time discarded.

The major component of pine oil is α-terpineol. It is used largely in cheaper perfumes, such as the perfume of disinfectants and liquid cleansers. Being an economical item, it is also used in the production of terpineol and competes with synthetic terpineol from α-pinene.

Lavandin. Lavandin oil is a much finer perfumery material than pine oil and is employed in the better household product perfumes. It is obtained by the steam distillation of the shrub that grows in southern France. The plant is a hybrid of aspic and true lavender and is a hardier plant than true lavender. Because of this hardiness and its higher yield of oil, the oil can be produced in large quantities and at a fairly low cost. The major components are linalool, linalyl acetate, and camphor.

In conclusion, it should be emphasized that only a few of the more important materials have been discussed, and certainly many important items have been omitted.

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