

Turpentine as a source of perfume and flavor materials

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Over the centuries turpentine, either alone or in combination with other naval stores, has been used in many ways—as fuel for lamps and torches, for medicinal applications, and for embalming fluids. More recently it has been used chiefly as a solvent, especially by the paint industry. However, the development of water-based paints, as well as low-cost solvent streams from petroleum, has drastically reduced this demand. Only in the past few decades has the chemical industry begun to recognize turpentine as a wonderfully versatile raw material for enhancing product salability, and sometimes adding expensive and exotic effects. At present, chemical uses consume about ten times as much turpentine as all other uses combined.

Three types of turpentine—gum, wood, and sulfate—are produced commercially today. Gum turpentine is obtained by distillation from the oleoresin (incorrectly called gum) collected from wounds (scars) made in living pine trees. Wood turpentine is obtained by extraction of virgin pine stumps from which the sapwood has rotted away and further processing (steam distillation) of the extract. Sulfate turpentine is a by-product of the kraft (sulfate) pulping process for producing paper.

In this process wood chips (chiefly pine) are cooked in an alkaline liquor to produce pulp. During the cook the turpentine contained in the chips is volatilized and then condensed; the condensate contains crude sulfate turpentine and water.

Total U.S. turpentine production has declined from a high of 32.7 million gallons in 1968 to 24.2 million gallons in 1976. Gum turpentine production has been discouraged by high labor costs and also, to some extent, by lower-priced foreign imports. In any case, the price of gum turpentine largely prevents its use by the chemical processing industries (see fig. 1). Increased transportation and labor costs, and a dwindling supply of suitable stumpwood, mean that de-

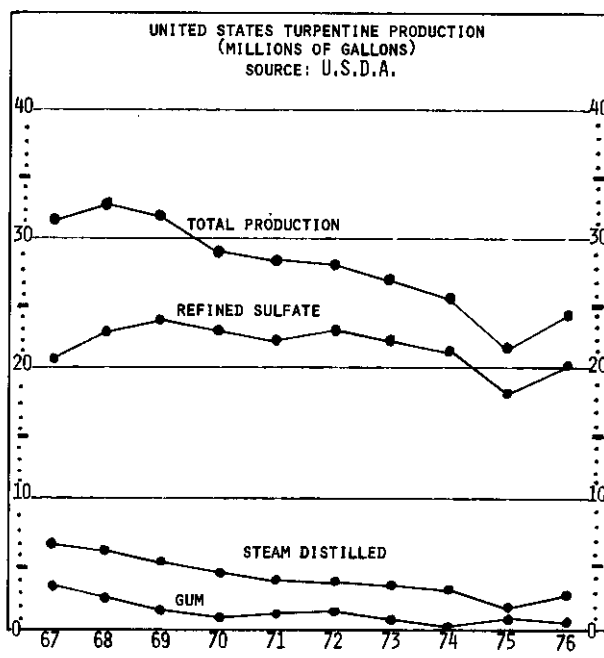


Figure 1

structively distilled wood turpentine is no longer important in the industry. In contrast, sulfate turpentine accounted for about 83.7% of 1976 production, and this percentage is likely to increase in the future.

In all three types of turpentine produced in the southern United States (which is the world's largest producing region), α -pinene is the most abundant constituent, varying from 60% to 80% (see Table I). β -Pinene is the second most abundant constituent in gum and sulfate turpentine, varying from 25% to 35% in the former, and 20% to 25% in the latter. Wood turpentine contains little, if any, β -pinene. Of the two pinenes, β -pinene is the most versatile chemically. Gum turpentine contains 5% to 8% of monocyclic p-menthadienes, commonly referred to as "dipentene," the trivial name for *dl*-limonene,

Table I - Composition of Southern Turpentines (%)

Component	Sulfate	Gum	Wood
α -Pinene	60-70	60-65	75-80
β -Pinene	20-25	25-35	0-2
Camphene	Trace	Trace	4-8
Others	6-12	5-8	15-20

which is the chief component of this p-menthadiene mixture. Sulfate turpentine contains 6% to 12% of this mixture, while wood turpentine contains somewhat more. Sulfate turpentine contains 5% to 10% of oxygenated material from which "natural" pine oil, mostly terpene alcohols, is separated. "Natural" pine oil is also produced in the processing of stumpwood to produce wood turpentine. Caryophyllene, methylchavicol, and anethole also occur in small amounts in sulfate turpentine.

The composition of turpentine depends not only on the method of isolation, but also on the species and the geographic location of the trees. For example, some western turpentines, as well as certain foreign turpentines, contain appreciable amounts of 3-carene, which finds little other use than as a solvent.

Nearly all crude sulfate turpentine and some wood turpentine are processed before further use.

α -Pinene and derivatives

Pine oil

The lowest boiling and largest fraction from turpentine fractionation is α -pinene. One use of α -pinene lies in the production of pine oil, which has a refreshing piney odor and finds high volume usage in cleaners, odorizers, and sanitizers. Today 80% to 85% of the pine oil produced is made by hydration of α -pinene with aqueous mineral acids; the remainder, the so-called "natural" pine oil, comes chiefly from the processing of stumpwood to wood turpentine and from sulfate turpentine fractionation. Synthetic pine oil is a mixture of terpene alcohols, chiefly, α -terpineol, along with smaller amounts of other mono- and bicyclic terpene alcohols. Commercial pine oils contain 50% to 90% terpene alcohols, the remainder being a mixture of p-menthadienes (plus some 1,4- and 1,8-cineoles) produced as by-products in the hydration. Perfume grade α -terpineol is produced by fractionation of pine oil (see fig. 2). High-grade α -terpineol has a delicate floral, lilac-type odor and is one of the most widely used of all perfume chemicals because of its low cost and stability; it also finds use in the flavor industry. α -Terpinyl acetate has a herbaceous bergamot-lavender odor and considerable quantities of it are used in low cost fragrances for household products.

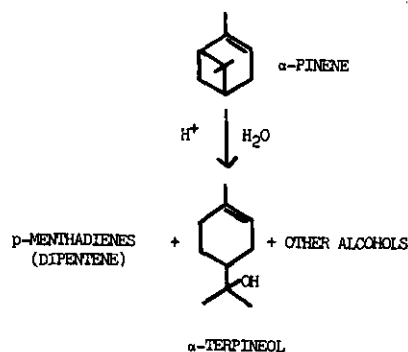


Figure 2

Camphene and Isobornyl Acetate

Another substantial use for α -pinene is in the production of camphene. This is accomplished commercially by the isomerization of α -pinene over an acid catalyst in the absence of water. Camphene itself is used in a variety of fragrance and flavor applications, and is the starting material for the manufacture of isobornyl acetate.

Isobornyl acetate is a perfumery compound used extensively in low-cost soaps, detergents, and perfumes because of its pleasant piney fragrance. This acetate is produced by the reaction of camphene with acetic acid in the presence of a strong acid catalyst (see fig. 3). *dl*-Camphor can be made by saponification of isobornyl acetate and oxidation of the resulting isborneol. This process is not used commercially in the U.S. today, but is still practiced in Germany, the United Kingdom, China and India.

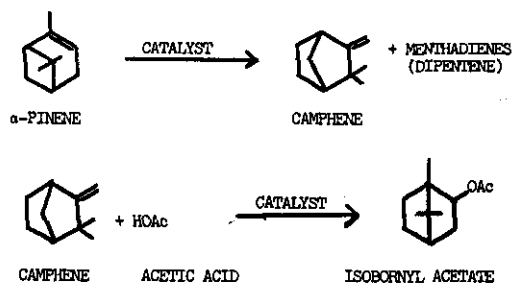


Figure 3

Chief components of dipentene

In both pine oil and camphene manufacture a mixture comprised mostly of p-menthadienes is obtained as a by-product; the by-product from pine oil production also contains 20% to 25% cineoles. This mixture is called "dipentene" in the trade. A limited amount of dipentene is used in the fragrance industry. Additionally, dipentene has been cleared by FDA for use in chewing gum base, in various resinous and polymeric coatings coming in contact with foods, and in certain adhesives. Dipentene can also be produced "on purpose" by proper acid treatment of α - or β -pinene. γ -Terpinene can be isolated from dipentene or isomerized dipentene by efficient fractionation and is used in modest quantities in both flavors and fragrances (see fig. 4).

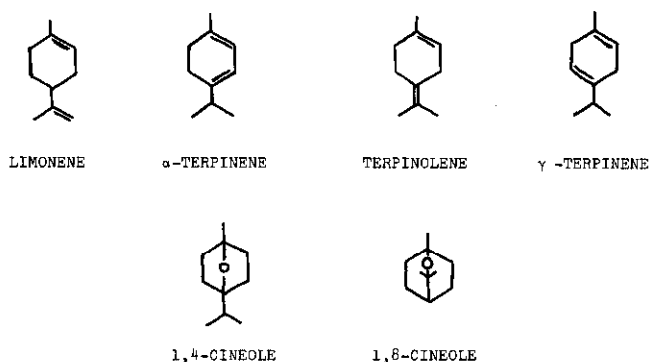


Figure 4

Either α -pinene, β -pinene, or dipentene can be readily dehydrogenated to p-cymene. p-Cymene finds use in industrial masking agents and in certain synthesized essential oils for perfume and flavor applications.

Alloocimene

Alloocimene is produced (along with *d,l*-limonene) by pyrolysis of α -pinene (see fig. 5). This acyclic triene has limited use in the production of perfumery alcohols and to some extent in perfumes.

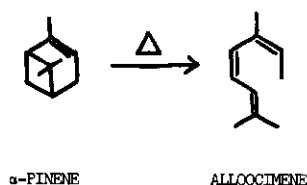


Figure 5

Linalool

Recently, α -pinene has been used on a commercial scale for the manufacture of linalool. In this process, α -pinene is hydrogenated to produce chiefly cis-pinane, which is then oxidized with air or molecular oxygen to produce pinane hydroperoxide. The hydroperoxide is reduced to obtain a mixture of cis- and trans-pinanol which on pyrolysis is isomerized to linalool (see fig. 6). Linalool and its acetate possess pleasant flowery fragrances and are widely used in perfumery. They are major components in certain natural and synthesized essential oils. Synthetic linalool

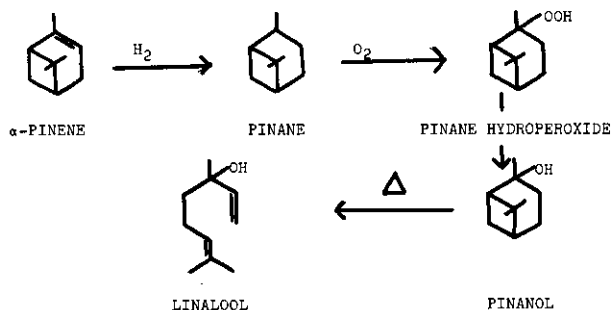


Figure 6

also has large usage as an intermediate in the synthesis of vitamins A and E. The pinanols may find use in perfumery, as they have subdued piney-camphoraceous odors with a somewhat minty overtone.

Dihydromyrcenol

Dihydromyrcenol, a perfumery compound which has a citrus floral fragrance, can also be made from α -pinene. One way to synthesize this compound is to hydrogenate α -pinene to pinane, pyrolyze the pinane to produce 3,7-dimethyl-1,6-octadiene, react the latter with formic acid, and saponify the product (see fig. 7). The exact volume of commercial production is not known. Dihydromyrcenyl acetate is not a commercial product of great importance.

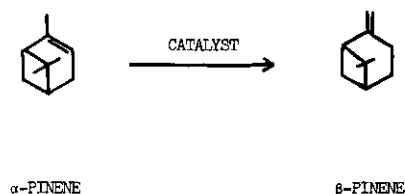


Figure 7

Osyrol, Methoxycitronellal

Methoxyelgenol is made from 3,7-dimethyl-

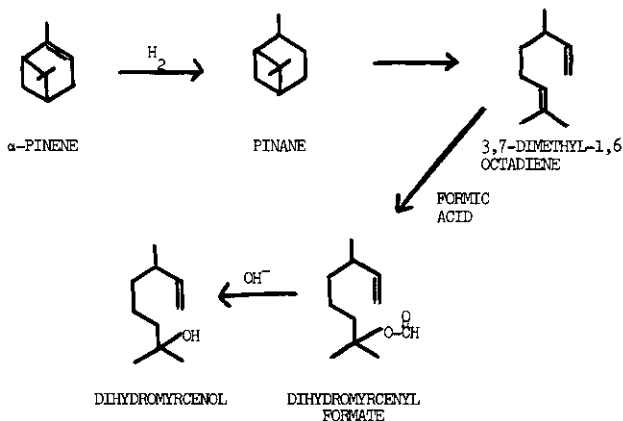


Figure 8

1,6-octadiene. It has a fine sandalwood odor, and is known to perfumers as Osyrol. To produce this compound the diene is reacted with methanol under acidic catalysis, and the resulting product is epoxidized. Hydrogenation of the epoxide can be directed to produce chiefly methoxylgenol, or, if desired, methoxycitronellol. On dehydrogenation the latter produces methoxycitronellal (see fig. 8). Methoxycitronellol can also be converted to citronellol by acid treatment.

Patent literature indicates that α -pinene also can be converted to citronellol via aluminum alkyl or ozonolysis technology.

α -to β -Pinene

A recent commercial use of α -pinene is its conversion to β -pinene. The β -isomer is chemically more versatile than the α -isomer and has a higher commercial value. The isomerization is accomplished over a noble metal catalyst with high selectivity (see fig. 9). The production of synthetic β -pinene will not only increase its availability, but will tend to stabilize the price of turpentine by making all of the world's turpentine more useful as a chemical raw material.

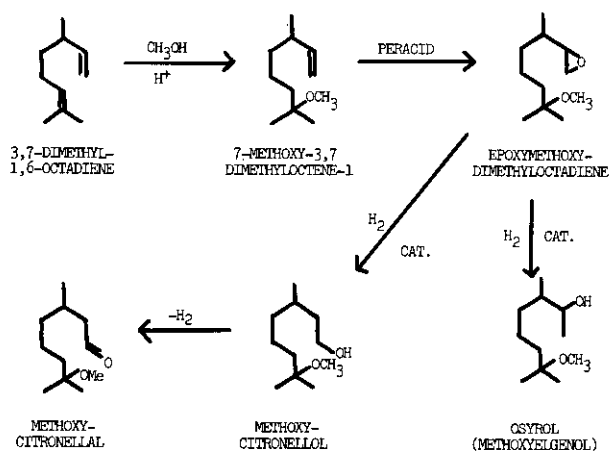


Figure 9

β -Pinene and derivatives

β -Pinene undergoes many of the same reactions as α -pinene (that is, camphene, pine oil, etc.), but is rarely used for these reactions because it is of greater value in other applications. When optical activity is important, natural β -pinene is the starting material of choice. In southeastern U.S. turpentine β -pinene is 90-95% optically pure *laevo*-isomer, whereas the α -isomer is only 30-40% optically pure *dextro*-isomer.

Geraniol, Nerol, Linalool

When β -pinene is pyrolyzed, an acyclic triene, myrcene, is formed. Myrcene is the key intermediate in the manufacture of a number of important commercial alcohols, esters and al-

dehydes. Hydrochlorination of myrcene produces a mixture of geranyl, neryl and linalyl chlorides. The geranyl and neryl chlorides are *cis-trans*-isomers. The ratio of primary and tertiary chlorides can be changed somewhat by varying reaction conditions. Reaction of the chloride mixture with sodium acetate produces a mixture of geranyl, neryl and linalyl acetates, which when saponified gives a mixture of the corresponding alcohols, geraniol, nerol and linalool (see fig. 10). Both the esters and alcohols have rosy, floral, fruity-type odors and find wide use in perfumery.

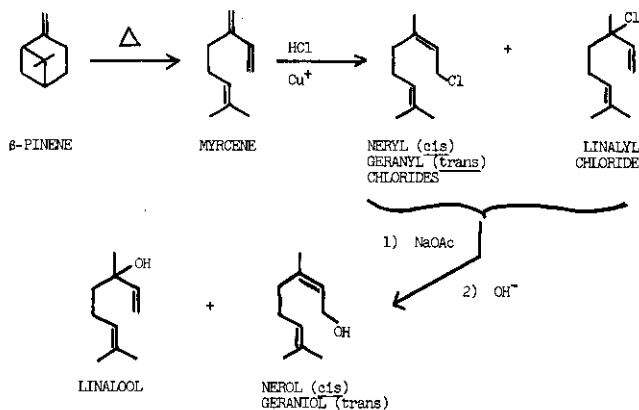


Figure 10

Citronellol, Dimethyloctanol

Geraniol and nerol can be selectively hydrogenated to produce citronellol, tonnage quantities of which are used in fragrances by the soap and detergent industries. Further hydrogenation gives 3,7-dimethyloctanol-1 (fig. 11) which is used in perfumery to a lesser extent.

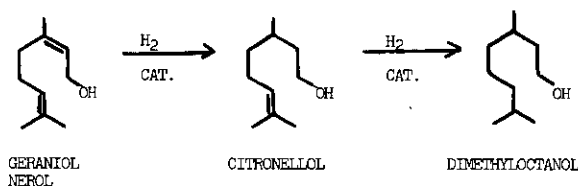


Figure 11

Citronellal

Citronellol is dehydrogenated or oxidized to produce citronellal. The chief uses for this compound lie in the production of menthol, hydroxycitronellal, and methoxycitronellal (fig. 12). Hydroxy- and methoxycitronellal can be made by addition of water or methanol to citronellal over acid catalysts after protection of the aldehyde group and subsequent regeneration. Alternately, the latter two aldehydes can be made by reacting citronellol with water or methanol and dehydrogenating the resulting products. Hydroxycitronellal has a lily-of-the-valley fragrance, and usage in perfumery has substantially passed the million pounds per year mark.

Methoxycitronellal is a relative newcomer to the perfumer's shelf, but is gaining in popularity. It is also a building block in the synthesis of certain juvenile hormone mimics, a use which is expected to increase.

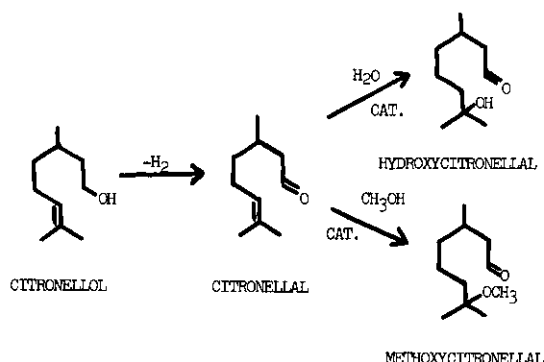


Figure 12

Citral

Geraniol and nerol are dehydrogenated or oxidized to produce citral (fig. 13), a mixture of geranial and neral, which are *cis-trans*-isomers. Wet oxidation of linalool also produces citral via an intermediate allylic shift. While a significant amount of citral is highly purified for use by the flavor and fragrance industries, the biggest use is in the manufacture of vitamins A and E. Tonnage quantities of citral extract go into the manufacture of these vitamins.

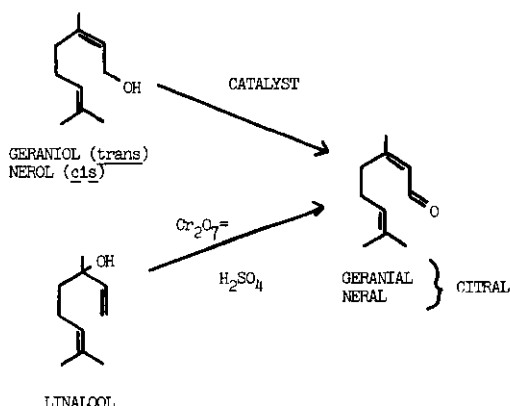


Figure 13

Ionones

Reaction of citral with acetone under basic conditions produces pseudoionone. The latter cyclizes under the influence of acid to produce α - and β -ionone (fig. 14); one isomer or the other can be made to predominate by proper selection of the cyclizing acid. γ -Ionone, the isomer with the double bond at the single ring-methyl group, is formed in only minor amount. α -Ionone can be isomerized to the β -isomer under the influence of acid. The ionones are widely used in perfumery, but the large scale use is for β -ionone which is an intermediate used in all syntheses of vitamin A and carotenoids.

Hexahydropseudo-ionone is a common starting material for vitamin E synthesis.

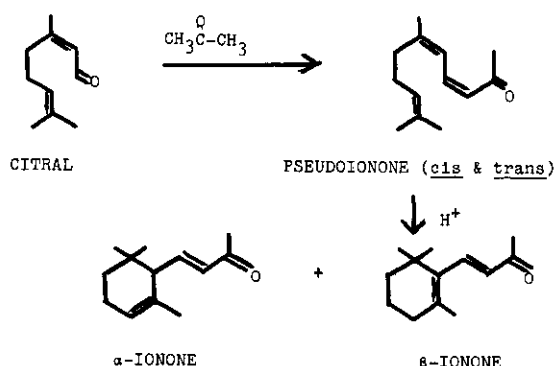


Figure 14

Methylionones

If citral is condensed with methyl ethyl ketone, instead of acetone, pseudomethylionones result. In this case the condensation occurs involving either a methyl or a methylene carbon to give a mixture of pseudo-*n*-methylionone and pseudo-*iso*-methylionone (fig. 15). Cyclization of this mixture gives four methylionones. The α -to β -ratio again can be varied within limits by varying the cyclization conditions; only small amounts of the γ -isomer are formed. The methylionones have extensive perfumery usage, with the α -isomethyl isomer being the most highly prized.

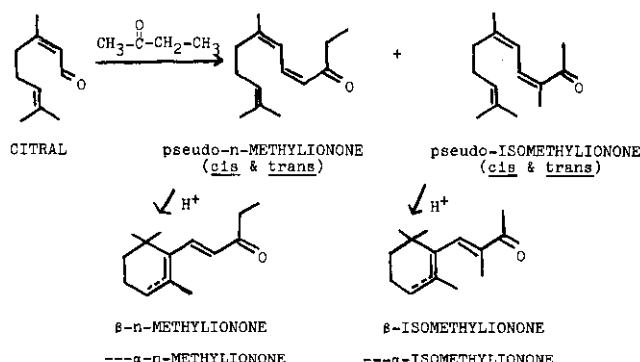


Figure 15

l-Menthhol

l-Menthhol has been produced from turpentine constituents by a variety of methods. One of these started with optically active β -pinene and involved its conversion to *d*-citronellal and cyclization to *l*-isopulegol which can be hydrogenated to *l*-menthol (fig. 16). A domestic company has recently built a plant for producing *l*-menthol from turpentine by a new proprietary process. *l*-Menthhol is widely used in the tobacco, proprietary drug, flavor, and toiletries industries, because of its minty characteristic and its physiological cooling effect. It is estimated that world consumption of *l*-menthol is over 3,000

Turpentine

tons per year, with the U.S. accounting for about 40% of this.

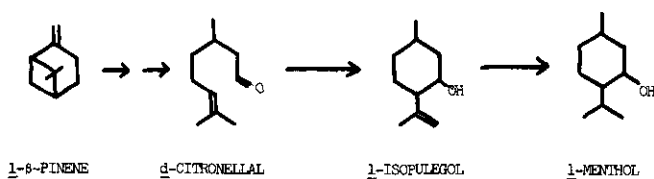


Figure 16

dl-Menthhol is prepared when optically inactive starting materials are used, for example from *dl*-citronellal *ex* myrcene. *dl*-Menthhol has only about half the cooling effect of *l*-menthol and has a considerably smaller usage. It is used mostly in skin care products, such as shaving creams and various types of lotions, as well as in pharmaceutical rubs. *l*-Menthhol is produced on a commercial scale by resolution of the *dl*-isomer.

Nopol, Lyrall

Condensation of β -pinene with formaldehyde produces nopol (fig. 17), a perfumery alcohol with a woody camphoraceous odor. Its acetate, which is more widely used, has an odor reminiscent of linalyl acetate. Condensation of myrcenol (produced indirectly from β -pinene) with acrolein yields Lyrall (fig. 17), another specialized perfumery material with an odor not unlike that of hydroxycitronellal.

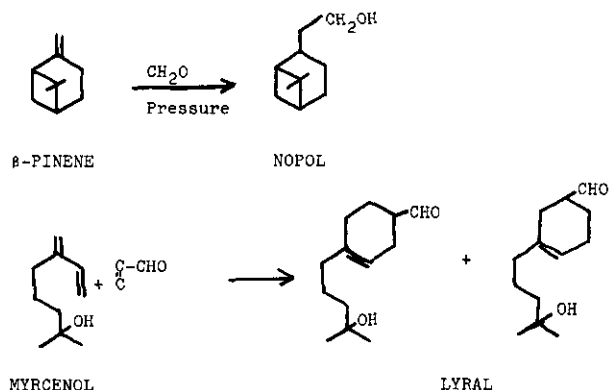
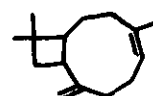
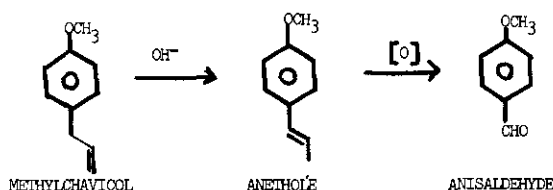


Figure 17

Miscellaneous Compounds

Anethole and methylchavicol occur in the "bottoms" from fractionation of sulfate turpentine and can be isolated by efficient fractionation (see fig. 18). Highly purified anethole finds use in licorice-anise type flavors, but its chief use involves its oxidation to anisaldehyde which is widely used in perfumery for its hawthorne-type odor and resistance to oxidation. Methylchavicol has a strong root beer odor and can be converted to anethole by isomerization under basic conditions. Another high-boiler in sulfate turpentine is the sesquiterpene caryophyllene, along with its isomer, isocaryophyllene. This sesquiterpene has a pronounced clove odor and

is used in perfumery (e.g., soaps, cosmetics) and to a lesser extent in flavor applications.



CARYOPHYLLENE
Figure 18

β -Pinene, and to a lesser extent α -pinene, serve as starting materials for a number of useful flavor compounds, or as components for the manufacture of synthesized essential oils. These oils replace or extend the natural oils, which are subject to wide variations in quality, price and availability. Some such synthesized oils currently on the market include spearmint, peppermint, lemon, lime, bergamot, lavandin, nutmeg, ylang ylang, pine needle, and bois de rose. All of these contain substantial amounts of terpenes and their derivatives.

Conclusion

Labor and land costs for producing natural oils are rising. Other crops, as they become more profitable, compete for available space. These factors combine to drive up the price of natural oils; as the world becomes more affluent and new markets develop, the use of synthesized oils can be expected to grow.

The future for the turpentine-based chemical industry is bright. Unlike petroleum, turpentine is a renewable resource. Efforts are underway to increase the availability of turpentine by paraquat or other treatment of living trees, by improvement of recovery techniques, by recovery from new sources, and by developing methods for preserving turpentine in wood going to paper mills from harvest to digester. Success of these efforts could conceivably result in as much as a two-fold increase in world turpentine production as early as the 1980s. And since all turpentines, both foreign and domestic, are rich in α -pinene, the increased chemical versatility developed for this compound makes all turpentine of commercial interest to the chemical processing industry.

Acknowledgement

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