Menthol

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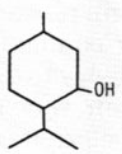
L-menthol can be described as unique for its cooling sensation on the skin and mucous membranes. Although other materials are known to display this cooling effect, almost all of them are derivatives of l-menthol.[11]

L-menthol displays a minty, light, refreshing odor that at most practical concentrations is complicated by the intense cooling sensation. This dual sensory effect makes the odor evaluation of menthol a difficult task. At very low concentrations, menthol displays a slight warming sensation along with the refreshing mint odor.[6] At moderate concentrations, the cooling effect develops, which, as concentration increases, becomes overwhelming and produces an anesthetic reaction. This numbing effect creates the soothing of the throat desired in cough drops. The overwhelming effect can best be illustrated by walking into a menthol production facility. One literally walks into a wall of menthol which registers in the eyes, nose and mouth first and as the vapor permeates one's garments, the whole body tingles.

The cooling-anesthetic effect interferes greatly in the odor evaluation of menthol for trace impurities, which can be critical in applications where menthol is used by itself and at low concentrations, i.e. tobacco products. The impurities are less critical where menthol is combined with other materials such as anethol, methyl salicylate

Menthol



MWt 156 $C_{10}H_{20}O$

CAS 89-80-5 **FEMA-GRAS** 2665

Classification

A cyclic, saturated monoterpenoid secondary alcohol, found in nature mainly in varieties of mint plants (Mentha family).

Additional Names (1,2,3)

The name menthol commonly refers to L-menthol, one optical isomer out of eight antipodes of 5-methyl-2-(1-methylethyl) cyclohexanol.

5-methyl-2-isopropyl cyclohexan-1-ol
3-p-methanol
hexahydrothymol
peppermint camphor

French = Menthol
Portugese = Mentol
German = Menthol
Spanish = Mentol

Physical Data[4,5]

Appearance: L-menthol U.S.P. grade is a clear colorless crystal; often large crystals with numerous faults which appear as white areas. Racemic (d,l) menthol U.S.P. is an amorphous fused colorless-white solid. The U.S.P. lists both products with their specifications,although they are really two different materials with respect to usage.
Specific Gravity: 0.890 (15°C)
Refractive Index: 1,458 (25°C)
Melting Point: l-menthol 43-44°C; the U.S.P. allows a melting range of 41-44°C. Racemic (d,l) menthol—this material displays a congealing point of two levels 27-28°C, which rapidly rises to 30.5-32°C
Boiling Point: 212°C
Flash Point: 93°C
Solubility: H_2O (20°C) .04%. Soluble in ethanol, essential oils, esters, chlorinated solvents, mineral oil DEP, etc.

or carvone, i.e. oral hygiene products. However, there are cases where even in such products the trace impurities stand out.

Since all commercially available 1-menthol production involves a last crystallization step, small amounts of the mother liquor and impurities are trapped in the menthol crystal matrix. Menthol crystals contain many faults or pockets of these impurities. Large crystals of natural menthol best illustrate these faults. However, even small crystals contain these inclusions. Thus, each process colors the basic menthol impression with impurities generated or present in the system. For natural menthol, which is crystallized from peppermint oil, the impurities are considered beneficial as they impart a pleasant fresh peppermint note which has become critical for some applications.

Synthetic menthol crystals will display off-odors reflecting the materials used to produce the product and impurities utilized in the final production steps, i.e. citronellal, thymol, methyl benzoate, and solvents such as acetone. These impurities often go undetected if the product is smelled neat from the bottle, yet they can cause severe problems in the end application. Two methods which help detect these off-odors, aside from GLC, are head space smelling and diluted samples on a blotter usually from clean ethanol solutions.

Racemic menthol presents the same odor problems as pure l-menthol, but with the further complication of increased impurities and the presence of 50% d-isomer which gives a musty, unpleasant impression.

Natural Sources

The sole source of the world's supply of commercially available natural l-menthol is from plantations of numerous subspecies of mentha arvensis plants grown in Brazil, Paraguay, China, India, Japan and Taiwan. Production of natural menthol worldwide is estimated at 3,600 M tons or more for 1988. Two essential oils are rich in l-menthol content: mentha arvensis (corn mint)-46-80% and mentha piperita (peppermint)-50-60%. Menthol is not widely distributed in commercially available essential oils, and is found in minor or trace amounts in: lemon balm, tagetes minuta and yarrow.[7,8]

History of Menthol

Peppermint and menthol have been known to man since ancient times. Prior to World War II, China and Japan were the only sources for natural l-menthol. Synthetic l-menthol was produced by European and American flavor and fragrance houses usually from citronellal based feed stocks. The sudden disruption in supply of menthol which occurred in 1941, encouraged Brazilian entrepreneurs to begin planting mentha arvensis mint and producing cornmint oil and menthol. The war brought urgency to that need as menthol cigarettes found their way around the world. Today, mentholated cigarettes are still an American phenomena, consuming more than 60% of U.S. usage.

Brazil rapidly replaced both China and Japan in occidental markets and in the 1960's reached a zenith of production of over 3000 M tons per year of menthol. Coincidentally, China began supplying menthol, but was prohibited by United States foreign policy from selling their products in the U.S.

The severe competition for the menthol markets of the late 1960's resulted in a depressed price ($3.50-4.00/lb.) and interest dwindled in planting cornmint in Brazil. This price depression eventually led to the menthol shortage of 1974 when prices of up to $26.00/lb. were extracted by some dealers. Keep in mind that the menthol market, as the potato market, is inelastic.

During and since the 1960's, various chemical companies have investigated the production of synthetic l-menthol, as this aroma chemical, after vanillin, has the highest volume of consumption in the world. Some firms entered the synthetic market only to withdraw later, i.e. Newport, Norda and SCM. Those interested in the chemistry reviewed in synthetic menthol should consult Bedoukian[9] and Leffingwell's[10] publications.

By 1974 Glidco (SCM), Haarman & Reimer (H&R) and Takasago had entered the synthetic menthol market. China had expanded its production and Brazil had decreased its plantings. The menthol market received its greatest supply shock in 1978 when H&R opened a 700 M ton synthetic menthol plant in Charleston, South Carolina (since expanded to 1,100 M tons) and China increased its plantings of mentha arvensis simultaneously. This over-supply led to depressed prices in 1980-82 and forced H&R to file a dumping action against Japan and China claiming their sales had depressed prices and, hence, H&R's profit potential.

More recently, Takasago has built a new synthetic menthol plant based on pinene feed stock. China has had supply problems due to socio-political restructuring of its society. India has emerged as a source of both synthetic and, more importantly, natural menthol. More significantly, the Brazil-Paraguay situation has been reversed. The oil of mentha arvensis, like its cousin mentha piperita, has found worldwide demand. With it, natural l-menthol has begun to increase in supply.

This resurgence of natural menthol is due to higher prices and a change in demand. Once menthol was the only saleable product and dementholized cornmint oil was of no value. Today world consumption of dementholized cornmint oil for toothpaste and chewing gum, etc. has resulted in great demand for the oil. Favorable prices have allowed South American growers to continue planting. In Brazil-Paraguay, the farmers are beginning to fertilize and maintain their plantations just as China has done. The economics of production based on two saleable products have guaranteed that natural menthol will continue to be available.

Eventually, Brazil will develop a large scale mechanized plantation system for the growing of mint, similar to the practice in the mid- and far-west farming of mint carried out in the U.S., and at far more favorable economics. It should be noted that mint growing in the U.S. has not exhausted the soil and destroyed ecology, as maintained by some synthetic manufacturers.

World Consumption

Consumption in 1988 of both natural and synthetic l-menthol in the flavor, fragrance, pharmaceutical, tobacco and oral hygiene industries is estimated at 5,600 M tons (12,346,000 lbs.) worldwide. Regional consumption figures are estimated as follows:

North America 1,500 M tons (3,307,000 lbs.)

	M tons
Tobacco	800
Oral Hygiene	350
Pharmaceuticals	200
Confectionaries	80
Shaving Products	50
Miscellaneous	20

Europe (including the East Block) 1,200 M tons

	M tons
Tobacco	100
Oral Hygiene	500
Pharmaceuticals	400
Confectionaries	100
Shaving Products	80
Miscellaneous	20

Asia (including Indonesia, Philippines, Japan and India) 1,700 M tons

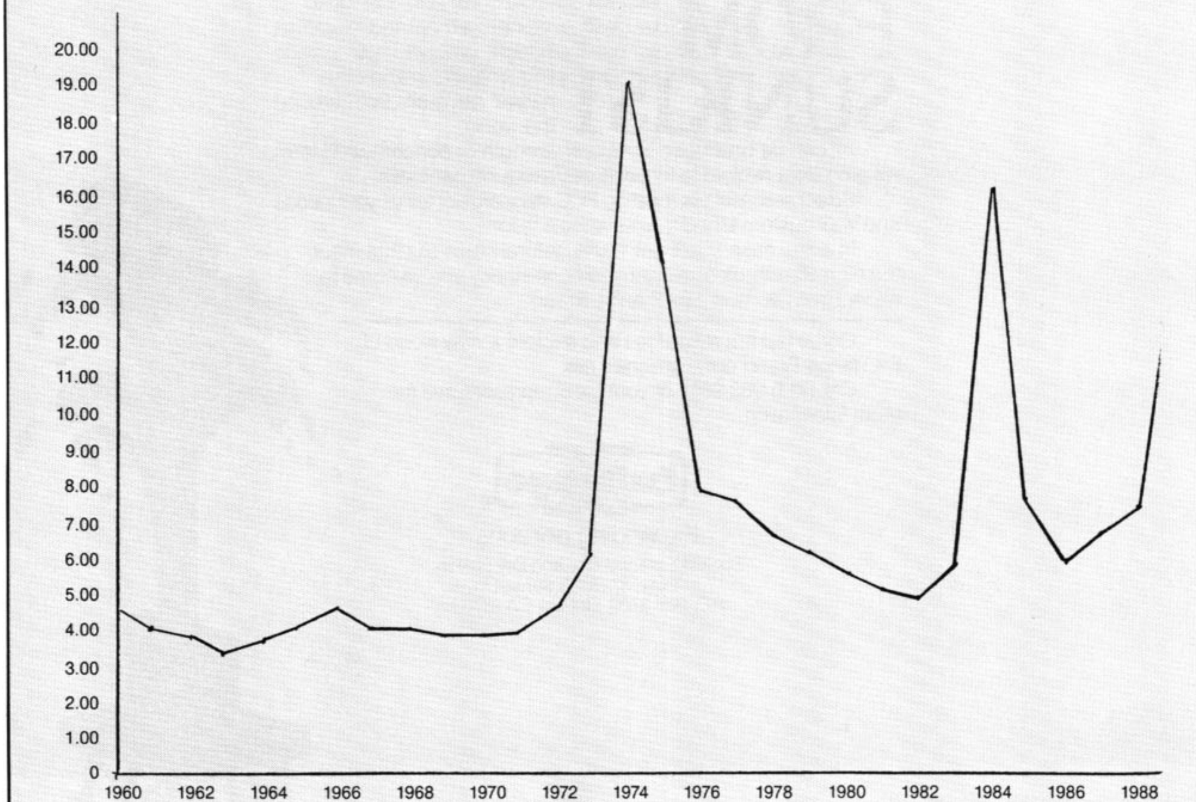
	M tons
Tobacco	300
Oral Hygiene	450
Pharmaceuticals	750
Confectionaries	200
Shaving Products	40
Miscellaneous	10

South and Central America 700 M tons

	M tons
Tobacco	100
Oral Hygiene	300
Pharmaceuticals	100
Confectionaries	140
Shaving Products	50
Miscellaneous	10

Others (includes near East, Africa, Australia, New Zealand 500 M tons

	M tons
Tobacco	50
Oral Hygiene	250
Pharmaceuticals	100
Confectionaries	50
Shaving Products	30
Miscellaneous	20



L-MENTHOL
MARKET PRICES IN THE U.S.
1960-1988
US $/LB

Pricing

This graph illustrates the problem that cyclically appears when an agricultural commodity suffers from underpricing over a number of years. As the demand for menthol is inelastic, very slight reductions or surpluses of supply result in very low prices or sudden rises. The steep rise always results in overproduction and low prices. It is interesting that the market price highs experienced in 1974, 1983 and 1988 all occurred when significant synthetic volume was available to the market.

Supply of Menthol

Of the 5,600 M tons of menthol consumed in the world in 1988, the majority will be natural menthol (3,600 M tons), while synthetic menthol producers will furnish 2,000 M tons. Natural suppliers have the advantage of decentralized supply both in crop acreage and oil production from small local still's. This system is based upon low capital investment and potential for rapid expansion of output. Even the factories to crystallize menthol from the cornmint oil are relatively low cost investments that can be quickly repaired or expanded. As the economics of supply become favorable to local producers, they encourage expansion of planting acreage and the establishment of permanent plantations. Land available for growing mint is more than enough needed, especially in Brazil-Paraguay; contrary to assertions by synthetic producers that they are running out of "jungle" in South America.

Synthetic producers have the advantage of certain raw material bases as feed stocks. However, they suffer from the jeopardy of centralization of production facilities, which could result in a major disruption of supply due to equipment failure. Other problems faced are investment costs due to the expensive and tailor-made sophisticated equipment needed in order to produce l-menthol. The recent past experience of synthetic producers, especially those using benzenoid (racemic) feed stocks, indicates their investments have not yielded the returns necessary for justifying new facilities or to replace aging equipment. Some of these synthetic plants are more than 15 years old and will require extensive capital to replace worn-out equipment in the near future.

The future for the supply of menthol will see expanded production of natural menthol in Brazil-Paraguay and India. China, after a few years of adjustment, will return as a stable and reliable source. Synthetic producers will remain in the market for the near future, especially those manufacturing menthol from natural feed stocks which allow production with less capital investment than those using racemic intermediates.

Natural Menthol Producers and Estimated Production

Brasway S.A.—The largest producer in Brazil has a crystallization capacity of 3,500 M tons/year of menthol and 4,000 M tons/year of dementholized cornmint oil. Recent actual production has been estimated at 800-1000 M tons menthol.

Yah Sheng Chong S.A.—One of the last of more than twenty small crystallizers that were active in Brazil 20 years ago has an estimated capacity of 100 M tons/year of menthol.

Amigo and Arditi S.A.—Estimated capacity is 30 M tons/year of crystallization volume.

China—The capacity of each crystallizer is difficult to estimate, although China in total is estimated to produce more than 2,000 M tons/year of menthol. The largest factory is in Beijing and was built before the second world war. It is estimated to produce 1,000 M tons/year of menthol. At least four other smaller plants produce menthol in other areas.

Mentha and Allied Products, Ltd., India—Capacity is estimated at 200 M tons/year of l-menthol crystallized from locally produced Indian mentha arvensis.

Bhagat, India—This company is producing derivatives of menthol and peppermint oil. Their capacity to produce l-menthol is unknown.

Dayspring Co. Ltd., Taiwan—Capacity of the last crystallizer left in Taiwan is rated at about 100 M tons/year of l-menthol, produced from imported crude mentha arvensis oil.

Nagaoka & Co. Ltd., Japan—Capacity is estimated at 300 M tons/year of l-menthol using both locally grown oil (100 M tons) from Hokuren on the Island of Sapporo and imported crude mentha arvensis from China.

Other Natural Sources—Significant quantities of supposedly natural menthol have been sold from such areas as Singapore over the last decade. Most of the l-menthol from these sources, without native production of mentha arvensis oil, is in reality synthetic menthol recrystallized from peppermint oils.

Synthetic Producers

There are only two major manufacturers currently left producing synthetic menthol, Haarmann & Reimer and Takasago, and three minor producers, Keith Harris of Australia, Camphor and Allied of India and Bordas of Spain.

Haarmann & Reimer. Estimated menthol capacity worldwide is 1,520 M tons/year, 1,100 M tons/year in the U.S. and 420 M tons/year in Germany. H&R also supplies racemic menthol USP and liquid menthol.

The H&R process begins with byproduct meta-creasol, produced by Bayer AG at their Uedingen/Germany works, which supplies both H&R plants. The creasol is alkylated to thymol and then hydrogenated to a racemic mixture of menthol isomers (hexahydrothymol) at Uedingen. Racemic menthol is separated from the isomers by high-platage distillation and the isomers are recycled. It is interesting that the alkylation of meta-creasol produces some n-propyl derivative which accompanies the racemic menthol and is carried through the process and removed in the final steps.

The resolution of the optical isomers of menthol is accomplished by converting the racemic menthol to the benzoate via transesterification with methyl benzoate. The racemic menthyl benzoate is revolved into pure l and d esters by selective crystallization using controlled seeding in specially designed equipment with exacting temperature control. The isolated crystalline esters are converted back to the alcohols, yielding pure d and l menthol. The l-menthol is further crystallized to remove impurities while the d-menthol is recycled.

Takasago. Estimated l-menthol capacity is 1,000 M tons/year at their one production facility in Japan. Takasago has produced l-menthol by a number of processes over the past 20 years using such feed stocks as thymol, isoprene, limonene and citronellal. Their current process is based on beta-pinine which is converted to myrcene, which is further converted to d-citronellal and subsequently to l-menthol. As their feed stock is optically active, there is no need to resolve a racemic mixture as in the H&R process.

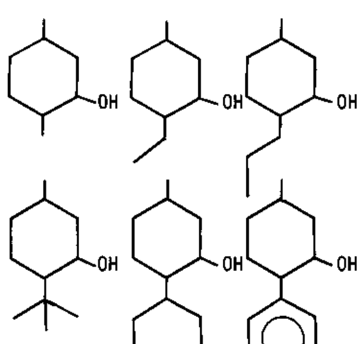
Camphor and Allied. Capacity is estimated at less than 200 M tons/year. Little of their production has been seen outside of India. The process uses delta-carene which is found in Indian turpentine. Through a multi-step process involving pyrolisis, addition of HCl and subsequent generation of cis-pulegol, from which l-menthol is derived.

Keith Harris. Capacity is estimated at 30 M tons/year of l-menthol and levo-racemic menthol generated from l-piperitone, found in native Australian eucalyptis dives oil.

Bordas. Capacity is estimated at 20 M tons/year of l-menthol and racemic menthol. Their feed stock is d-pulegone, obtained from Spanish pennyroyal oil.

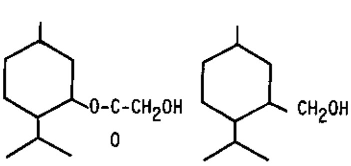
Analogs

Little work has been published on the attempts, if any, to develop analogs of menthol. Certainly, the industry would like to see the effect of modifying the basic structure of the menthol molecule and how these modifications would affect both odor and the cooling effect. The presence of n-propyl methyl cyclohexanols in H&R's feed stocks have not been explored, but this author projects that optically active analogs of l-menthol should show varying and possibly surprising cooling effect phenomena. In particular, the following products should be of interest as the 2-hydroxy group next to the alkyl grouping of varying bulks are thought to be the key determinant of the cooling effect.

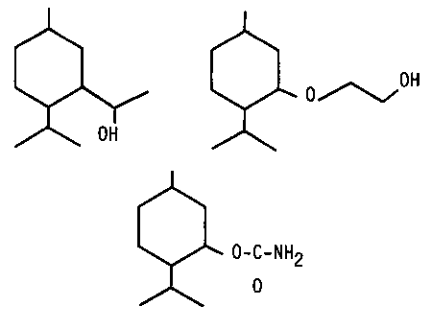


Substitutes

The following materials have been offered or suggested as substitutes for menthol in the literature and[11] were known in the industry as the Wilkinson Sword chemicals.



Frescolat H&R



Derivatives

Menthol is used in flavors and fragrances in the form of the following derivatives:

Acetate	GRAS 2668
Isovalerate	GRAS 2669
Propionate	
Menthone	GRAS 2667
d-neo-menthol	GRAS 2666
Menthofuran	GRAS 3235

In addition, the lactic acid ester (FRESCOLAT) of H&R has found some use in fragrances due to its cooling effect and menthyl salicylate has been used as a sun screen agent. In Europe the valerate ester was previously used as a mild sedative (VALIDOL) Merck Index 5667.

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