

An Aroma Chemical Profile

Menthol

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The menthol molecule is comprised of four isomers: menthol, isomenthol, neo-isomenthol and neo-menthol. These are complicated by the fact that each isomer has two chiral antipodes having positive and negative rotation. What is commonly called menthol in nature and in commerce is the l-menthol chiral isomer.

L-menthol can be described as unique in the aroma-chemical world for the cooling sensation it imparts to the skin and mucous membranes. This cooling effect is far greater than the cooling that occurs when a solvent, such as ethanol or hexane, is placed on the skin. Although other materials are known to display such a cooling effect, almost all of them are derivatives of l-menthol.⁶

Organoleptically, l-menthol displays a minty, light, refreshing odor that at most practical concentrations is complicated by an intense numbing-cooling sensation. At very low concentrations, menthol displays a slight warming sensation, along with the refreshing mint odor.^{7,8} At moderate concentrations, the cooling effect develops. As concentration increases, the cooling effect becomes overwhelming and desensitizing, producing a cooling-anesthetic reaction.

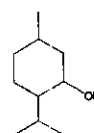
This numbing of the nerve sensation creates the throat-soothing effect desired in cough drops. The desensitizing effect can best be illustrated by walking into a menthol production facility. One literally walks into an invisible wall of menthol. It registers in the eyes, nose and mouth first. As the vapor permeates one's garments, the whole body tingles and then numbs.

Problems with Impurities

Menthol's dual sensory effect makes both the odor and taste evaluation of menthol a difficult task. The cooling-anesthetic effect interferes greatly with the odor evaluation of menthol for trace impurities; that can be critical in applications where menthol is used by itself and at low concentrations, as, for example, in tobacco products. The impurities are less critical when menthol is combined with other materials such as anethole, methyl salicylate or carvone, as, for example, in oral hygiene products. However, there are cases where even in such products the trace impurities stand out.

Menthol

Mwt 156, C₁₀H₂₀O
CAS 89-80-5
FEMA-GRAS 2265



Classification:

A saturated cyclic-monoterpene alcohol, found in nature mainly in the plants of the *Mentha* species

Additional Names:^{1,2,3}

The name "menthol" commonly refers to the 1-isomer, which is only one of eight antipodes of the molecule 5-methyl-2-(1-methyl-ethyl) cyclohexanol

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

French: Menthol

German: Menthol

Portuguese: Mentol

Spanish: Mentol

Physical Data:^{4,5}

Appearance: l-Menthol U.S.P. grade is a colorless crystal; often found as large crystals with numerous faults that appear as cloudy-white areas. Racemic (d,l) menthol U.S.P. is an amorphous fused colorless-white mass. The U.S.P. lists both products together with their specifications, although they are really two different materials with respect to usage.

Specific Gravity 15°C: 0.890

Refractive Index at 25°C: 1.458

Melting Point: 43-44°C for l-menthol; the U.S.P. allows a melting range of 41-44°C. Racemic menthol displays a congealing point at two levels: 27-28°C and 30.5-32°C.

Boiling Point: 212°C

Flash Point: 93°C (200°F)

Solubility in H₂O at 20°C: 0.04%. Soluble in ethanol, essential oils, esters, alcohols, chlorinated solvents, mineral and edible oils, DEP.

Since all commercially available l-menthol production ends with a crystallization step, small amounts of the mother liquor, with its 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; they can be seen as dislocations in the structure of these strikingly large, beautiful crystals. However, even small crystals contain these inclusions. Thus, each manufacturing process colors the basic menthol impression with impurities generated or present in the system.

For natural menthol, which is crystallized from peppermint oils, the impurities are considered beneficial because they impart a pleasant, fresh peppermint note that has become critical for some applications.

Synthetic menthol crystals will display off-odors reflecting the materials used to produce the product and impurities used in the final production steps. Examples of these materials include citronellal, thymol, methyl benzoate, and solvents such as acetone. These impurities often go undetected if the product is smelled neat from the bottle. However, in the end application, they can cause severe problems, such as nose and throat irritation. Two methods, aside from GLC analysis, will help detect these off-odors. One method is headspace smelling. Another method places diluted samples — usually from

clean ethanol solutions — on a blotter. One should pay special attention to the blotter dry out. Its odor should be clean fresh-floral, not sour-acrid or metallic.

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

Natural Sources

Two essential oils are rich in l-menthol content: cornmint oil *Mentha arvensis* L. f. *piperascens* Malinv. ex. Holmes, syn. *M. canadensis* L. (46-80%) and peppermint oil *Mentha piperita* (50-60%). Menthol is not widely distributed in other available essential oils and is found only in minor or trace amounts in fennel, lemon balm, *Tagetes minuta* and yarrow.^{9,10}

The high cost of *Mentha piperita* and the difficulty of crystallizing significant quantities of menthol from it makes *Mentha piperita* an impractical commercial source. Therefore, the sole source of the world's supply of commercially available natural l-menthol is plantations of numerous subspecies of *Mentha arvensis* plants grown mainly in India and China.

Production of isolated natural l-menthol worldwide is estimated at 9,400 metric tons (Mtons), though slightly more for 1998. The consumption of menthol (both l-menthol and racemic menthol) is presented later in Tables 1 and 2.

History of Menthol

Brazil challenges China: Peppermint and menthol have been known to man since ancient times. Shimoyama reported that menthol was known in Japan more than 2000 years ago. Its first report in European sources was by Flueckinger in 1771.¹¹ Prior to World War II, China and Japan were the only significant commercial sources for natural l-menthol. European and American flavor and fragrance houses of that period produced synthetic l-menthol, usually from citronellal oil-based feed stocks.

World War II caused a sudden disruption in the supply of menthol and encouraged Brazilian entrepreneurs to begin planting *Mentha arvensis* mint and producing cornmint oil and menthol in that country. The war brought a perceived urgency to that need, as menthol cigarettes (supplied in the ration kits of the US military) found their way around the world with the US armed forces. Today, mentholated cigarettes are still an American phenomenon, representing about 40% of US domestic menthol usage and smoked in few other places on the globe.

Brazil rapidly replaced both China and Japan in occidental markets as the commercial supplier of menthol. In the 1960s Brazilian production peaked at more than 3000 Mtons per year. Coincidentally, China began supplying menthol, but US foreign policy prohibited sales of Chinese menthol in the US.

In the late 1960s, the severe competition for the menthol markets depressed its price to US\$3.50-4.00/lb. Bra-

zilian producers lost interest in growing cornmint. This price depression eventually led to the menthol shortage of 1974, when prices of up to US\$57.00/kg were extracted by some dealers.

Keep in mind that the menthol market, like the potato market, is inelastic. A 100 Mton shortage of l-menthol, in the world market with a demand of 11,000 Mton, will cause prices to double or triple; on the other hand, even a slight over-supply of 1000 Mtons may cause prices to fall by 50%. The menthol market exhibits one of these pricing cycles

every eight to ten years, as, for example, it did in 1974-1975, 1984-1985, 1988-1989 and 1996-1997.

Commercialization of synthetic l-menthol: During and since the 1960s, increasing consumption of menthol led various chemical companies to investigate the production of synthetic l-menthol.^{12,13} (So dramatic was this increase, in fact, that around 1990, menthol displaced vanillin as the aroma chemical having the highest annual consumption.) By 1974, Glidco-SCM (Millennium), Haarmann & Reimer (H&R) and Takasago had entered the synthetic menthol market. China had expanded its production and Brazil's production was decreasing due to unfavorable economics.

The menthol market received its greatest over-supply shock in 1978 when H&R opened a 1100 Mton synthetic menthol plant in Charleston, SC and China increased its plantings of *Mentha arvensis*—simultaneously. This over-supply led to the depressed prices of 1980-1984 and forced H&R to file a dumping action against Japan and China claiming that their sales of l-menthol in the United States had depressed market prices and, hence, H&R's profit potential. The result was a Pyrrhic victory: the US International Trade Commission decided that the Chinese had dumped menthol (that is, they had sold it at prices below their production costs), but H&R (a subsidiary of Bayer-AG in Germany) had suffered no significant financial loss.

In 1985, Takasago built a new synthetic menthol plant based on pinene as a feed stock. This facility, more versatile than previous facilities, is capable of producing a number of chiral chemicals. Thus, Takasago is not locked into a single-product system.

China cuts back: In the mid-1980s, China began to have supply problems due to socio-political restructuring of its society. (This emerging problem would again raise its head in 1996.) Internal consumer demand began to take precedence over "export for hard currency" policies and Chinese raw materials began to display tightness in supply. China's problems and Brazil's dwindling supplies of available cornmint oil led to another menthol shortage in 1984-1985, when prices reached US\$33.00/kg, dipped back to the US\$13.00/kg level by 1986, but rose again by 1988 to the US\$40.00-42.00/kg level and remained there until late 1989.

The challenge from India: India has emerged as a significant source of natural l-menthol. At the 1989 International Congress of Essential Oils, Fragrances and Flavors in New Delhi, S.C. Varshney, general secretary of the Essential Oil Association of India, announced India's intentions to become the world's dominant supplier of menthol. In throwing down the gauntlet, Varshney said, "Witness the next match between India and the rest of the world."¹⁴

Government policy in India favored private development of a menthol industry. This industry was not so fortunate in some other countries. Governmental policies in Brazil, for instance, have nearly eliminated the growth of *Mentha arvensis* plants in that country (see sidebar).

As Indian menthol started to enter the world's markets in significant quantities, the price of menthol sagged to the US\$20.00/kg level by 1990. The market battle was between China and India, because the synthetic producers were by then sold out of capacity. The pricing of menthol continued to drop and reached a US\$13.00/kg level by 1994, a price that had not been seen since 1988.

China industrializes: As China opened its doors to the outside world, foreign investment began to flow into the market of 1.3 billion potential consumers. The world's major chewing gum, cigarette, flavor and fragrance, and toothpaste manufacturers made investments in new production facilities in China with the aim of satiating China's growing internal consumer demand.

The internal demand for aroma chemicals and essential oils for both domestic consumption and export of finished products in China rose dramatically over the period 1985-1996. This added demand was given preference over the export of raw materials, because it satisfied internal consumer demands and lessened political pressures. Moreover, the export of finished flavors and fragrances resulted in more favorable foreign currency yields than did the export of simple raw materials.

The industrialization of China resulted in new factories being built on the limited farmland available in a country where only 15% of the land is arable. The result has been a decrease in the supply of both cornmint oil and menthol from China to the outside world and an increase in prices during the 1995-1997 period. China's almost total withdrawal from the menthol market in 1996 resulted in menthol prices skyrocketing to the US\$100.00/kg level and remaining there into the first six months of 1997.

***Mentha arvensis* and Menthol in India**

An imported species: The *Mentha* species is not native to India, but was introduced there only recently.¹⁵ *Mentha piperita* was imported from Great Britain in the 1800s and grown thereafter in India as a garden plant. *Mentha arvensis* was brought into India from Japan in 1954 by the regional research laboratory Jammu & Kashmir.

India had a fairly large internal requirement for l-menthol in the 1950s and all of it was satisfied by imports at great foreign exchange cost. Thus, the government was interested in developing a domestic industry for any prod-

uct that was being imported, and also in setting up domestic industries that could export locally produced products. Cornmint oil and l-menthol fit both sides of this equation.

The first *Mentha arvensis* clone: In 1958, the Jammu & Kashmir laboratory introduced the initial clone of *Mentha arvensis* to local farmers in order to induce a domestic cornmint-menthol industry. Without strong local technical support, the initial clone was multiplied and divided over and over again, rapidly and indiscriminately. The result was a deterioration of the plant over a 20-year period, to the point that by 1978, it yielded oil with an l-menthol content so low that no l-menthol crystals could be obtained from it by cooling.

The decision was then made to develop new strains of *Mentha arvensis* better suited to the climate of northern India. This research on new agricultural products was sponsored by the Indian government through the Indian Council of Agricultural Research, which supports projects in the various growing areas of India. The result of these efforts was the development of two new hybrid species of *Mentha arvensis* that proved disease-resistant and gave superior yields of oil with a high l-menthol content (>85%).

By 1989, India's cornmint-menthol industry had become so firmly established that India began to eye the world market and aspired to become the dominant supplier of these products to the world.

The Shivalik-88 *Mentha arvensis* clone: The production of *M. arvensis* oil in India had grown from 400 Mtons in 1980¹⁶ to 1,000 Mtons by 1989.¹⁷ This sudden surge of production was due mainly to the introduction of one new *Mentha arvensis* clone: CIMAP MAS-1, more commonly known as Shivalik-88. Shivalik-88 was released to the Indian farmers in 1985.

A second factor contributing to the surge of production was an improvement in crop procedures. Inter-cropping of mint with other food crops encouraged the production of mint oil. It was discovered that much higher yields of *Mentha arvensis* plant could be obtained if the crop was removed from the soil and rotated in a three-crop per year system using *Mentha arvensis*, followed by potatoes and then followed by one of several other crops.

Since 1989, India has propelled itself into the forefront of the l-menthol trade using the oil produced from Shivalik-88. In 1998, India will produce 14,000 Mtons of Shivalik-88-based *Mentha arvensis* oil and isolate from this oil about 6,000 Mtons of natural l-menthol.¹⁸ This clearly places India as the world's dominant supplier of both l-menthol and of *Mentha arvensis* oil.

Changing demand for *Mentha arvensis* oil: The oil of *Mentha arvensis*, like its cousin *Mentha piperita*, has also found increased worldwide demand. With it, natural l-menthol has increased in availability and now accounts for over 80% of the world's supply. The resurgence of natural menthol is due to higher prices and a change in demand. At one time, menthol was the only saleable product from cornmint essential oil and dementholized cornmint oil was of no value. Today, world consumption of dementholized cornmint oil for toothpaste and chewing gum has resulted in growing demand.

World Consumption and Pricing

Consumption: Estimates of the world consumption of menthol can vary for several reasons. For instance, do the estimates include natural or synthetic l-menthol or both? Do they also include racemic menthol? Does the definition of consumption include only what is internalized by humans or does it also include what humans are exposed to during normal usage of menthol-containing products? Tables 1 and 2 provide a "total usage" estimate that includes what goes up in smoke, evaporates from the skin, is spit out of the mouth, imbibed directly or absorbed through the skin.

It is estimated that about 22,230 Mtons of menthol of all types (both natural and synthetic) will be used by the populations of the world in 1998. This estimate is based upon the known production volume of synthetic menthol and on the known concentrations of menthol in natural products. Menthol is present in very low concentrations in other than mint plant products being used by humans, those sources are not included in this estimate. One way to estimate how much of the menthol used is consumed internally and how much never enters the body is to assume the products marketed containing menthol were used as intended. That's the assumption here. In other words, we

ignore the fact that little Arthur ate the tube of toothpaste or that Aunt Inge used it to polish the silverware. A rough estimate of just how the world's people consume the available menthol is presented in Table 1.

Consumption in 1998 of both natural l-menthol and synthetic l-menthol in the flavor, fragrance, pharmaceutical, tobacco and oral-hygiene industries is estimated at 11,800 Mtons (26,000,000 lbs) worldwide. Regional consumption figures are estimated as shown in Table 2.

Pricing: Figure 1 illustrates the problem that cyclically appears when an agricultural commodity suffers from under-pricing over a number of years. Because the demand for menthol is inelastic, very slight reductions or surpluses of supply result in sudden rises in price or very low prices. The steep rise raises the farmer's hopes and always results in overproduction and low prices. It is interesting that the market-price highs experienced in 1974, 1983, 1988 and 1997 all occurred when significant synthetic volume was available to the market.

Supply of Menthol

Of the 11,800 Mtons of pure menthol consumed in the world in 1998, the majority will be natural menthol (9,400 Mtons), while synthetic menthol producers will furnish 2,400 Mtons.

Natural l-menthol: Natural l-menthol suppliers have the advantage of a decentralized supply system. Both crop acreage and oil production are from small, local farms and stills. This system is based upon a low-capital investment and the potential for rapid expansion of output, as can be seen by India's rapid growth. Even the factories to crystallize menthol from the commint 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

Table 1. Estimated world usage of all menthols from all sources in 1998

	Usage (Mtons)	Percentage (%)
Internal usage	12,540	58
Oral hygiene	3,600	17
Topical applications	3,220	15
Tobacco products	2,350	10
Other uses	520	0.4
Total	22,230	100.4

Table 2. Estimated regional usage (In Mtons) of isolated pure menthols by product category in 1998

Product category	1	2	3	4	5
Tobacco	650	200	1,800*	150	200
Oral hygiene	500	800	1,500	500	400
Pharmaceuticals	250	600	1,500	200	200
Confectioneries	110	300	400	200	200
Shaving products	70	150	300	100	100
Miscellaneous	70	100	100	50	100
Total	1,650	2,150	5,600	1,200	1,200

* 1000 Mtons smoking tobacco, 800 Mtons chewing tobacco
 1 = North America (including Canada and Mexico)
 2 = Europe (including Eastern Europe)
 3 = Asia (including China, India, Indonesia, Japan and the Philippines)
 4 = South and Central America
 5 = Others (including Near East, Africa, Australia and New Zealand)

L-MENTHOL Prices 1960-1998

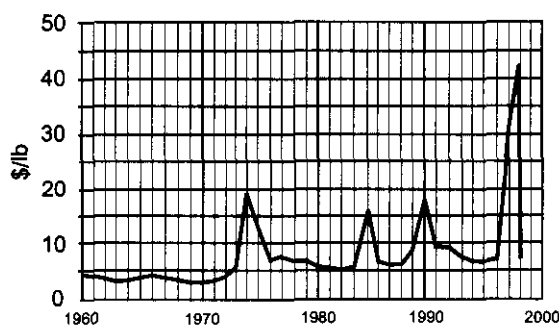


Figure 1. l-Menthol prices 1960-1998

and the establishment of permanent plantations. Land available for growing mint is more than enough to meet the needs, especially in India, where farmers can plant *Mentha arvensis* crops on small plots without government intervention in the form of quotas or price regulation.

Synthetic menthol: 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 and public environmental concerns. Another problem is the expense of tailor-made, sophisticated equipment needed to produce l-menthol.

The 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 replacing aging equipment. Some of these synthetic plants are more than 20 years old and will require extensive capital to replace worn-out equipment in the future.

Prediction: The future for the supply of menthol will see expanded production of natural menthol in India. China, after a few years of adjustment, will return as a stable and reliable — though minor — player in the l-menthol market. Synthetic producers will remain in the market for the near future, especially those manufacturing

menthol from natural feed stocks that allow more flexible production with less capital investment than those using racemic intermediates.

Producers of Natural Menthol

South America: Brasway is the largest producer in Brazil. It has the capacity to crystallize 3,500 Mtons/year of menthol and produce 4,000 Mtons/year of dementholized cornmint oil. Recent actual production has been estimated at 200-300 Mtons of l-menthol produced by re-crystallizing Chinese or Indian menthol.

Yah Sheng Chong is the last of more than 20 small crystallizers that were active in Brazil 20 years ago. It has an estimated production of 100 Mtons/year of menthol produced from either imported cornmint oil or Chinese or Indian l-menthol.

The Paraguayan firm Amigo & Arditi produces l-menthol from the limited supply of locally grown corn mint oil. Production has been about 100 Mtons/year over the past few years.

India: Jindal Drugs Ltd. is currently the largest producer of l-menthol, either natural or synthetic, in the world. Capacity is estimated at more than 2,000 Mtons/year of natural l-menthol crystallized from locally produced Indian *Mentha arvensis* oil. Jindal also produces more than 2,000 Mtons/year of dementholized and triple-

rectified cornmint oils. This leader in the Indian mint industry also produces over 1,000 Mtons/year of *Mentha piperita* and *Mentha spicata* oils and other essential oils.

Mentha and Allied Products Ltd. has an estimated capacity of 200 Mtons/year of l-menthol crystallized from locally produced Indian *Mentha arvensis* oil.

Many small producers operate in India. Their collective capacity is approximately 3,000 Mtons/year, but the individual production capacity of each is difficult to gauge. Capacity estimates are made more difficult due to the practice of these smaller producers of pooling their capacity to meet a large order obtained by any one of them. The following are among those that could be identified; Anamica Enterprises, Bhagat, Dee Kay Exports, Ghaziabad Aromatics, Hindustan Chemicals & Allied Industries, Khushboo Essential Oil, Rupangi Impex Ltd., Sharp Menthol India PVT Ltd., Siva Essential Oils and Chemicals, Som Extracts Ltd., Surya Aromatics & Allied Chemicals, Vaishali and Virat Expors Pvt. Ltd.

China: The capacity of each crystallizer is difficult to estimate, although China in total is estimated to produce more than 2,000 Mtons/year of l-menthol. The largest factory is in Beijing and was built before World War II. This factory is estimated to produce 1,000 Mtons/year of l-menthol. At least six other smaller plants produce l-menthol in other areas.

Far East: Dayspring Co. Ltd. in Taiwan has a capacity rated at about 300 Mtons/year of l-menthol, produced from imported crude Indian *Mentha arvensis* oil.

Production by Nagaoka & Co. Ltd. in Japan is estimated at 300 Mtons/year of l-menthol using imported crude *Mentha arvensis* from India.

Small amounts of l-menthol and cornmint oil are produced from locally grown *Mentha arvensis* oil in North Korea and Thailand.

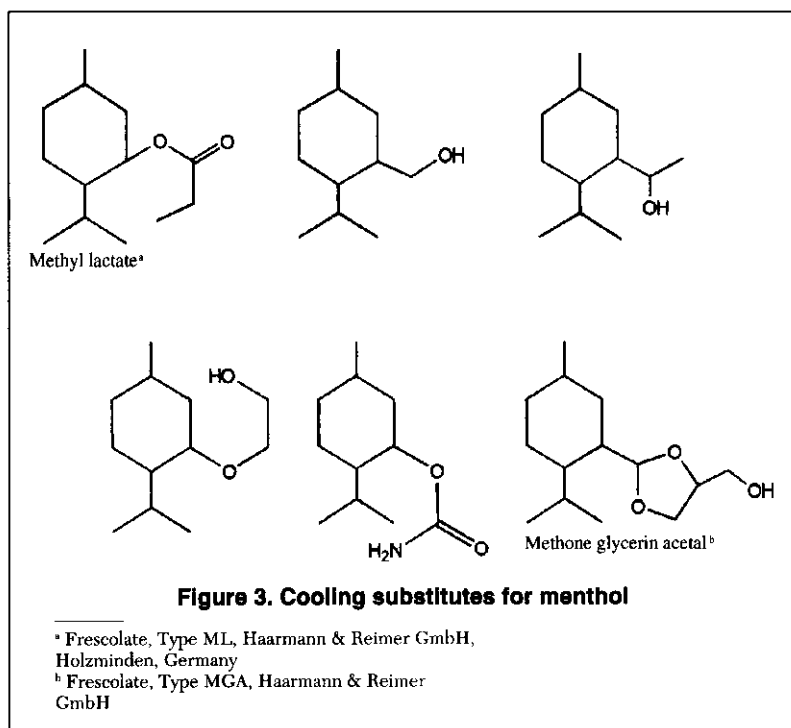
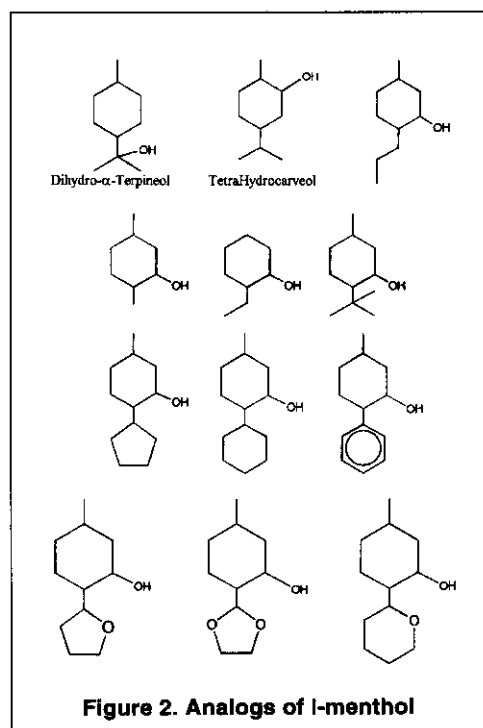
Producers of Synthetic Menthol

Haarmann & Reimer (H&R) and Takasago are the only major manufacturers currently producing synthetic menthol. Keith Harris of Australia and Camphor and Allied of India are two minor producers. A few Indian synthetic manufacturers produce menthol from menthone-rich *Mentha arvensis* oil fractions.

Haarmann & Reimer: Estimated menthol capacity worldwide is 1,520 Mtons/year, of which 1,100 Mtons/year are produced in the US and the rest is produced in Germany. H&R also supplies racemic menthol U.S.P. and liquid menthol.

The H&R process begins with by-product meta-cresol, produced by Bayer-AG at their Uedingen/Germany works, which supplies H&R plants in Germany and the US. The cresol is alkylated to thymol and then hydrogenated to a racemic mixture of menthol isomers (hexahydrothymol) at Uedingen and most recently in the Czech Republic. Racemic menthol is separated from the isomers by high-plate distillation and the isomers are recycled. It is interesting that the alkylation of meta-cresol 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 resolved 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 Mtons/year at Takasago's one production facility in Japan. The company 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 b-pinene, which is converted to myrcene, and then further converted to d-citronellal and subsequently to l-menthol. Because their feed stock is optically active, there is no need to resolve a racemic mixture, as is required in the H&R process.

Camphor and Allied: Capacity at this Indian company is estimated at less than 200 Mtons/year. Little of their production has been seen outside of India. The process uses δ -carene, which is found in Indian turpentine oil, through a multi-step process involving pyrolysis, addition of hydrogen chloride and subsequent generation of cis-pulegol, from which l-menthol is derived.

Keith Harris: Capacity at Keith Harris is estimated at 30 Mtons/year of l-menthol and levo-racemic menthol

generated from l-piperitone found in native Australian eucalyptus dives oil.

Bordas: Bordas' capacity is estimated at 20 Mtons/year of l-menthol and racemic menthol. Their feed stock is d-pulegone, obtained from Spanish pennyroyal oil. This source has apparently ceased production.

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 few reported analogs (1-methyl-4-isopropyl cyclohexanols) with the hydroxy function in the branches or on the 1- or 4- positions (such as dihydro-a-terpineol) show no cooling effect. The presence of n-propyl methyl cyclohexanols in H&R's feed stocks has not been explored, however, I predict that optically active analogs of l-menthol should show varying and possibly surprising cooling-effect phenomena. In particular, the products in Figure 2 should be of interest because the presence of the 2-hydroxy group next to the alkyl grouping of varying bulks is thought to be the key determinant of the cooling effect.

Substitutes

The materials in Figure 3 have been offered or suggested as substitutes for menthol in the literature⁶ and were known in the industry as the "Wilkinson Sword chemicals." Haarmann & Reimer now offers two of these materials under their trademarked Frescolate label.

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, menthyl salicylate has been used as a sun-screen agent. In Europe, menthyl valerate was previously used as a mild sedative (Validol, Merck Index 5667).

References

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