An Aroma Chemical Profile

Menthone

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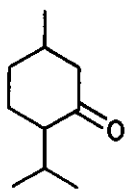
Of the aroma chemicals that make up peppermint oil, the one most closely associated in the mind with the peppermint impression is menthol. Thus, it is surprising to realize that menthone is as essential as menthol or any other of the materials found in that oil. This conclusion is based upon the recent development of a new mint oil—*Mentha spicata Eromenthe,* which contains only menthone and its analogues and almost no menthol, menthyl esters or menthofuran. The analysis of this new mint is presented in Table I.

Menthone, minty-peppermint with a high impact, imparts lift to flavors and fragrances in low or trace amounts. Nature suggests its use at low concentration by its presence at such levels in geranium or rose oil. When used in concentrations over 1% in a formula, menthone's presence makes itself known by a shift to a peppermint impression, thus preventing its use in large amounts in anything but herbal-spice flavors with mint overtones.

Table I. Chemical analysis of *Mentha spicata Eromenthe* oil

α-pinene	0.49%	l-menthone	57.82%
camphene	0.01	menthofuran	0.00
β-pinene	0.66	d-isomenthone	18.20
sabinene	0.34	β-bourbonene	0.32
myrcene	1.53	linalool	0.02
α-terpinene	0.01	linalyl acetate	0.01
heptanal	0.02	menthyl acetate	0.03
l-limonene	1.15	neomenthol	1.29
1,8-cineole	2.51	terpinen-4-ol	0.05
cis-β-ocimene	0.90	β-caryophyllene	2.73
γ-terpinene	0.13	l-menthol	0.08
p-cymene	0.01	pulegone	0.96
terpinolene	0.03	α-terpineol	0.28
3-octanol	0.15	germacrene-D	5.38
1-octen-3-ol	0.05	piperitone	0.78
trans-sabinene hydrate	0.00	viridiflorol	0.01

Menthone



Mwt 154 $C_{10}H_{18}O$
FEMA-GRAS 2667
CAS 14073-97-3

Classification:
A saturated, optically active monocyclic monoterpene ketone. Found in nature throughout the Labiatae family although commonly occurs in the oils of the *Mentha* species where it is generally accompanied by the isomer isomenthone. Commercial grade menthone is generally encountered as a mixture of isomers menthone and isomethone.

Additional Names:[2-4]
l-menthone*
p-menthan-3-one
2-isopropyl-5-methyl cyclohexan-1-one
*d-Menthone also is known and available, but seldom used. It mainly is encountered as its 50-50 mixture with l-menthone in synthetically prepared racemic (d,l) menthone or found in a few natural essential oils.

French: Menthone
German: Menthon
Portuguese: Mentona
Spanish: Mentona

Physical Data:

Appearance:	Mobile, clear, colorless liquid
Specific Gravity:	0.888-0.895 (25°C)
Refractive Index:	1.448-1.453 (20°C)
Boiling Point:	207.2°C at 760 mmHg
Optical Rotation:	–10.0°C minimum*
Flash Point (TCC):	178°F (81.1°C)

* See separate discussion of optical rotation.

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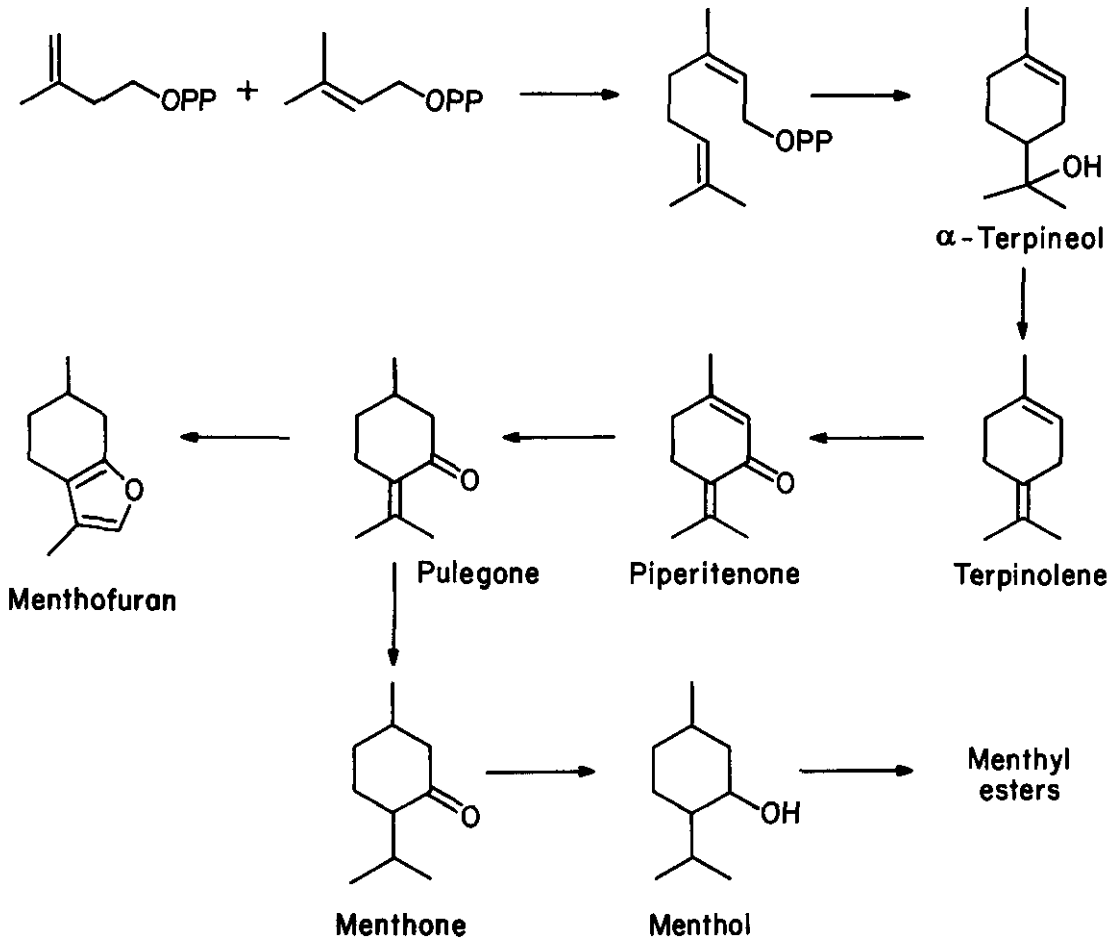


Figure 1. Biosynthesis of menthone.

Menthone's Optical Rotation

Commercially available menthone always contains *significant quantities of isomenthone.* These two isomeric ketones are easily chemically interconvertible and can be separated into their pure forms. However, they will immediately begin to isomerize (epimerization) at a very low rate back to an equilibrium mixture of menthone-isomenthone, which has been estimated at 70%:30% ratio.[5] The rate of isomerization is dependent upon the catalysts employed or found as impurities in the product or introduced into the ketone from the containers used to store the product.

The isomerization is catalyzed by light, acids, bases and metal salts. Sufficient base can be found in the walls of some glass containers to catalyze this interconversion of isomers, as will traces of organic acids found in essential oils. Thus, essential oils containing menthone or isomenthone, which the plant produced in a pure isomeric form, will show increasing amounts of the other isomer as the oil ages. Clean, neutral storage containers, absence of light and a cool storage temperature will slow down—but not prevent—the interconversion of one isomer into the other.

The isomers (epimers) of menthone have been isolated as pure entities and their physical properties are shown in Table II.[6] The isomerization of l-menthone results in d-isomenthone as the two materials are structurally related despite their opposing signs of rotation.

The reader should note the optical rotational values of l-menthone (-28.1°) and pure d-isomenthone (est. +90°). The interconversion of these products results in a drift of the observed optical rotation as l-menthone is converted into d-isomenthone. d-Menthone is similarly converted into l-isomenthone. Since the epimer of the menthone has the opposite sign of rotation, the mixture under consideration can be observed to drift from ±28° to ±ca. 7.5° for pure menthone or from 90° to 7.5° for isomenthone. l-Menthone's optical rotation will actually *decrease* to 0° and then change the sign of rotation as it reaches the equilibrium value of +7.5.

Table II. Optical rotation of menthone isomers

Substance	Purity	Optical Rotation
l-menthone	100 %	-29.1°
d-menthone	98.8	+27.2°
l-isomenthone	99.4	-91.3°
d-isomenthone	99.0	+89.6°
d,l-menthone	99 +	0°
d,l-isomenthone	99 +	0°

Natural Sources

Menthone is not widely distributed in the plant kingdom and is found in high concentrations in only a few species of plants with the species *Mentha* predominating. Menthone appears to arise from neryl pyrophosphate via the biosynthetic route shown in Figure 1.[1] When used in flavor or fragrance compounds at low or trace concentrations, menthone or isomenthone often will not stand out; yet, trace amounts (a spike of menthone) can lend unique effects to a composition.

Essential Oils

The following essential oils show high concentrations of total menthone-isomenthone.

Mentha spicata Eromenthe	70-80%
Buchu leaf	40
Mentha arvensis (dementholized)	26
Mentha piperita	16-20
Mentha pulegium (Pennyroyal)	11-18
Pelargonium sp. (Geranium Bourbon)	6-13

These essential oils show low concentrations or trace amounts of total menthone-isomenthone.

Mentha spicata (Native type)	0-0.9%
Mentha gracilis	1-2
Artemisia annua	0.2-0.3
Andropogon fragrans	trace
Barosma pulchellum	trace
Cassis	trace
Eucalyptus citriodora	trace
Micomeria abissinica Benth.	trace
Nepeta japonica	trace

History

There is some question as to who first reported menthone as a pure chemical compound. The fact that menthol was recognized as a pure substance and categorized as such and as an isolate of *Mentha arvensis* oil by Dumas in 1832 leads one to believe that menthone must have been recognized as a chemical before its first report[7] by Moriya in 1881. The year after Moriya's report, Atkinson and Yoshida[8] reported the isolation of menthone as a pure entity.

Outside of academia, there was really little use for menthone except to produce l-menthol, which did not become a practical route until 1903. The usage as an additive in flavors and fragrances was very limited until the recent interest in artificial peppermint flavors and reconstituted essential oils.

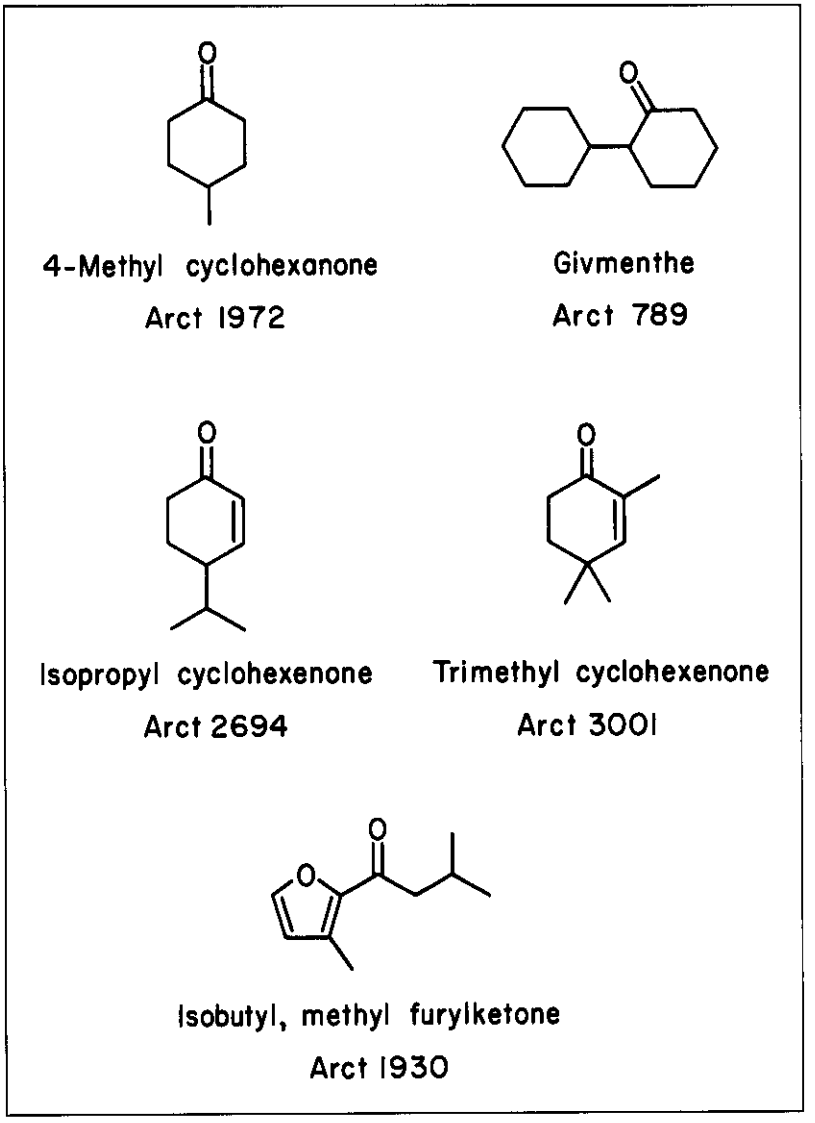
By the mid-1920s, menthone had become a standard lesser aroma chemical in the flavor and fragrance industry via its isolation from Chinese and Japanese peppermint oil. Multiple tons of menthone-isomenthone mixtures were often available and little direct use for them was found. The Bouveault-Blanc sodium metal reduction method was usually employed to hydrogenate the ketone mixture to menthol. The resulting synthetic menthol was sold on the world

markets as a natural product. Such material was available from Asian-based firms until about 1970.

The supply of menthone-isomenthone still continues to exceed demand, although in recent years (ca. 1970 to now), the development of artificial peppermint flavors has been an outlet for some of the natural menthone available from peppermint oil, as well as for synthetic menthone.

The introduction of the gas chromatograph with the resulting analysis of essential oils down to trace ingredients in parts per billion has resulted in new, albeit low volume usages for menthone and isomenthone in the reconstitution of essential oils and as a touch additive to flavor and fragrance compositions.

In the mid-1970s, Haarmann & Reimer introduced the first truly synthetic l-menthol to the flavor and fragrance market. Previously, all the l-menthol available was of natural origin, one way or another.



World Consumption

As a deliberate flavor and fragrance additive, the menthones are relegated to a minor aroma chemical status. However, when one considers the consumption via essential oils (i.e., mainly the *Mentha* species), human worldwide consumption becomes significant (Table III). The amount of synthetic menthones consumed is a relatively minor contribution to overall usage.

Pricing

Prices for l-menthone vary considerably with quality and source. The purer the material as received, the higher the price. In general, natural l-menthone is available in the $8.00-10.00/lb price range, while synthetic pricing is in the $16.00-26.00/lb range.

Supply/Suppliers

The current supply of menthone is in excess of demand, as most of the product offered is produced from *Mentha arvensis* oil fractions. As the current pricing of natural menthol from Chinese and Indian sources is in the $4.00-5.00/lb range, there is little incentive to convert l-menthone into l-menthol. Thus, selling the by-product at $8.00/lb is more desirable. As menthone's actual demand for compounded flavors and fragrances is estimated at about 50 MTons worldwide, the market is in over-supply and will be for the foreseeable future.

Natural menthone at $8.00/lb has suppressed the potential of synthetic l-menthone which, due to higher cost processes, must command about twice the price to make its supply viable.

Table III. Worldwide consumption of menthone-isomenthone in 1993

Source	MTons
Menthone-ex *Mentha arvensis* oils	742
Menthone-ex *Mentha piperita* oils	508
Synthetic	30
Other natural sources	50
Total	1330

Current Producers

All the menthone in use commercially today is l-menthone except for a very small volume of racemic and d-menthone which finds captive use. Manufacturers of l-menthone fall into two groups: synthetic and natural suppliers. This distinction is fairly easy to make as no l-menthone today is being produced by a process that could be considered "natural."

Synthetic Producers
Glidco Organics
Haarmann & Reimer

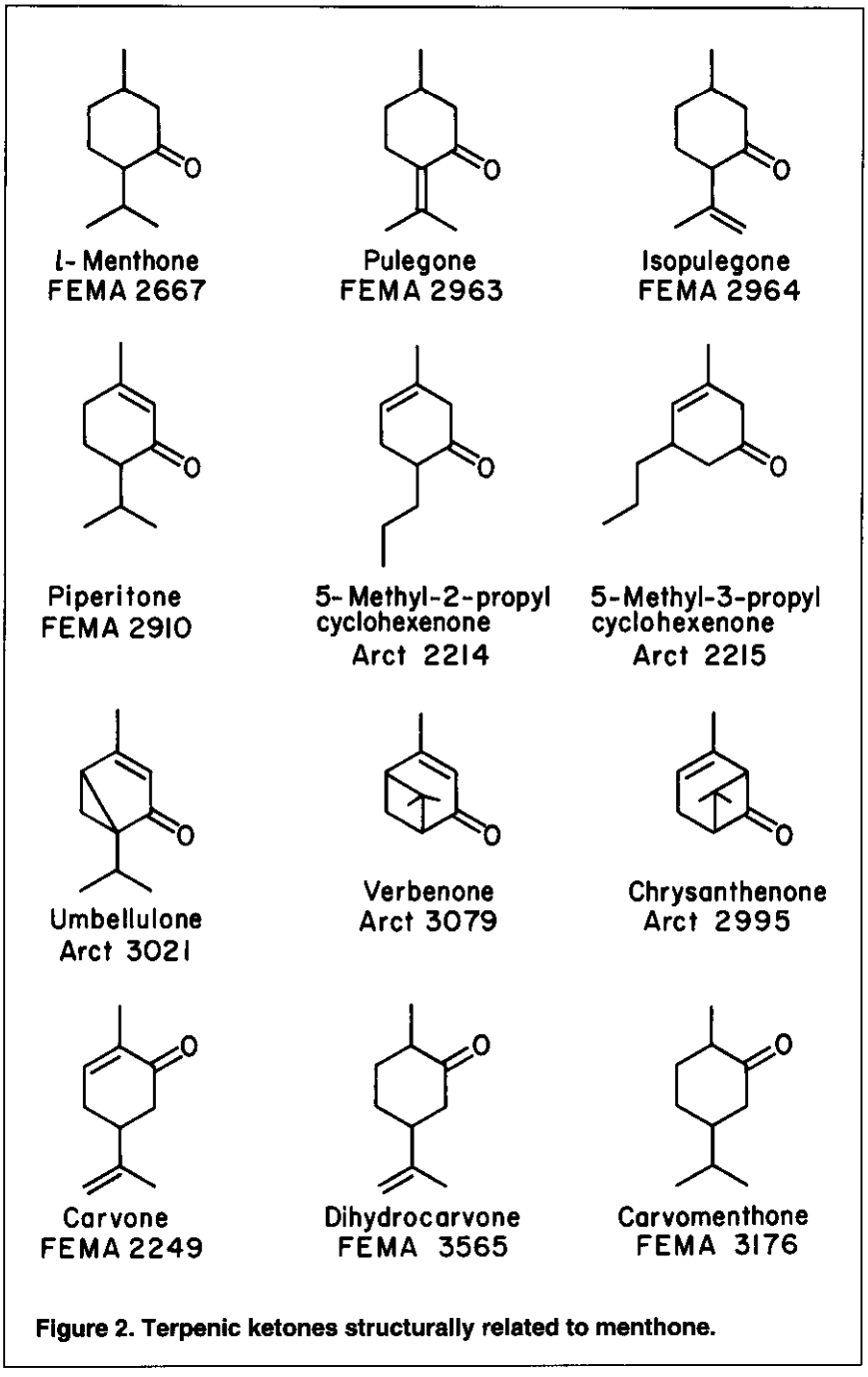
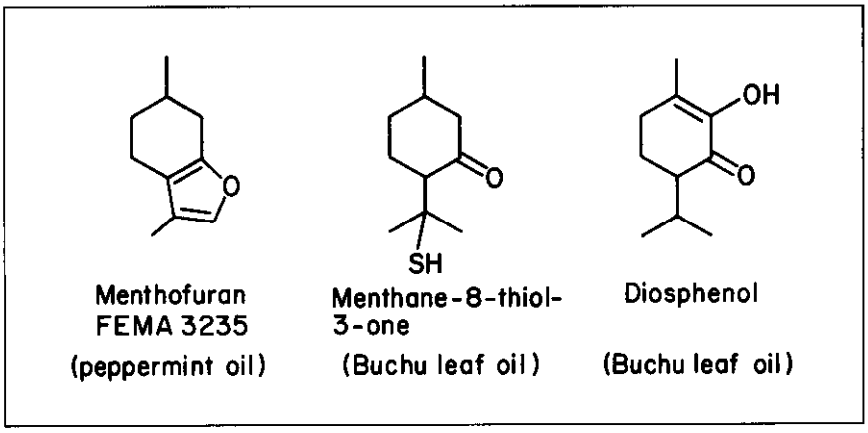


Figure 2. Terpenic ketones structurally related to menthone.



Natural Producers

The following producers offer l-menthone derived from isolation from various peppermint oils, mainly of the *Mentha arvensis* type. The crude menthone fractions are fractionally distilled to yield a product of 95+% purity.

Givaudan-Roure
China
Acedesa
Bhagat Fine Chemicals
Som Extracts, Ltd.

Substitutes

l-Menthone's organoleptic profile is too unique to allow a substitute in flavors. Some minty impact cyclohexanones can provide a menthone-like impression in fragrance compositions.

Analogs and Isomers

The structurally related terpenic ketones in Figure 2 are presented as food for thought.

Derivatives

The most common derivative encountered is menthol and its esters.[9] The following menthone-related aroma chemicals are all found in nature.

References

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