A Profile: An Aroma Chemical

Carvone

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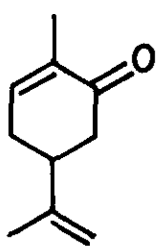
The basic organic chemical structure of the carvones is similar to that of the menthols and menthones. Thus, it is not surprising to discover a *distinct organoleptic impression for each optical antipode*. However, the organoleptic impressions are not similar to menthol or menthone, nor do the carvones display the cooling effect of menthol.

L-carvone—a warm-herbal-spicy-pungent impression. A slightly sweeter tone than d-carvone. L-carvone brings the flavor spearmint to mind.

D-carvone—a warm-herbal-spicy-pungent impression, more dry and hay-like than l-carvone. Both odor and taste recall dill or caraway oil or seed.

Almost all the commercially available l-carvones and d-carvones are synthetic products, produced from limonene via identical chemical reactions. Thus, the secondary off-notes, which may appear in the product from all sources, may be slightly metal-

Carvone



Mwt 150

$C_{10}H_{14}O$

CAS 99-49-0

FEMA-GRAS 2249

Classification

A cyclic, *unsaturated monoterpenoid ketone* found in nature mainly in spearmint (l-carvone) and dill and caraway oils (d-carvone).

Additional names[1-3]

As with other chemicals extracted from natural products, a number of names can be found in the literature. The name for carvone, 2-methyl-5-(1-methyl ethenyl)-2-cyclohexen-1-one, was derived from carum carvi, the Latin name for caraway.

p-mentha-6,8-dien-2-one
1-methyl-4-isopropenyl-Δ^6-cyclohexen-2-one
carvol

French = Carvone
Portugese = Carvona
German = Carvon
Spanish = Carvone

Physical Data

Appearance: mobile, clear, pale-yellow liquid
Specific Gravity: 0.965 (20°C)
Refractive Index: 1,4989 (20°C)
Boiling Point: 230°C
Flash Point: TCC 83°C
Solubility: H_2O (20°C) insoluble. Soluble in ethanol, organic esters, aldehydes, ketones, mineral oil and chlorinated solvents

The US Pharmacopeia does not list specifications for carvone, but instead lists specifications for spearmint oil in its National Formulary, with a *minimum content of 55% carvone* (4).

lic-amine like, sometimes even reminiscent of dilute aniline.

Generally, the commercially available products closely resemble each other and have a clean impression. Small amounts of natural d-carvone (ex-dill oil) and l-carvone (ex-spearmint oil) are available as specialties and both possess more colorful complex character than their synthetic counter part.

Since d-carvone usage is only about 1% of l-carvone, the word "carvone" generally indicates spearmint. These materials are more flavor components than fragrance materials. In flavors, carvone finds little use outside of oral hygiene products, i.e. toothpaste and mouthwash, on a volume consideration. However, the use of small amounts of carvone, d or l, in flavors and fragrances should be explored as the tones they impart may create special effects.

Natural Sources[5]

The carvones are found in nature in more than 100 essential oils, but usually only in trace amounts (.001 to .1%), too small to be used as a source of pure material. The following essential oils contain significant concentrations, thus making them a source of carvone. As a result, their organoleptic impression is basically that of the carvone it contains.

L-carvone:	
Mentha Spicata (garden mint)	55-75%
Mentha Viridis (common spearmint)	55-60%
Mentha Cardiaca (Scotch spearmint)	55-70%
D-carvone:	
Carum Carvi (caraway)	50-76%
Anethum Graveolens (dill)	30-60%
Anethum Sowa (Indian dill)	20-50%

The following oils contain carvone* in trace amounts. Thus, the content of carvone only provides shading of their impression, but does not dominate it. This phenomena indicates that the carvones can be used to shade a basic note, especially in fragrances.

Atremisa fergamensis (d,l)
Bergamot (l)
Cassis (l)
Chamomile Moroccan wild (l)
Clove Oils (l)
Eucalyptyus Globulus (d,l)
Ginger Grass (d,l)
Grapefruit (l)
Juniper berry (l)
Lavender (d,l)
Lemon (l)
Majoram (l)
Mandarin (l)
Mentha Arvensis (d)
Orange (l)
Tagetes (l)

*(l) l-carvone (d) d-carvone
(d,l) racemic carvone

The presence of l-carvone in citrus oils has been found to result from oxidation of limonene upon storage,[6,7] thus causing an off-flavor deemed undesirable for most uses. It may well be that many of the other essential oils containing fair amounts of limonene also contain traces of carvones because of this autoxidation process.

History of Carvone

The availability of pure l- or d-carvone is a recent development (1960s). However, the use of the carvones for flavors, fragrances and medicines goes back before written history in the use of dill and caraway seed and spearmint leaves.

The spearmint plant (Mentha spicata), sometimes called Garden Mint, has been used in folk medicine as a carminative, in oil to flavor condiments, and the leaves to make herbal teas. Both dill and caraway seeds have been used as spices in food stuffs for centuries. Today, dill is the key to the flavor of dill pickles and caraway is usually recognized as the flavor of certain liquors.

Small amounts of carvone were produced prior to the 1940s by various synthetic processes. The methods employed were uneconomical. Most of the l-carvone or d-carvone was obtained by distillation of spearmint oil or dill oil, respectively, and was a natural product rather than synthetic.

By the early 1960s a number of firms developed methods to commercially produce l- and d-carvone synthetically, using limonene as the feed stock.[8] The first commercial production in the United States was carried out by Norda at their Boonton, New Jersey factory.

The availability of synthetic l-carvone provided US toothpaste manufacturers an economic alternative to spearmint oil. This provided a check on the frequent price fluctuations in spearmint oil, that resulted from crop variations because of weather conditions and/or decreases and increases in acreage planted. Such swings in the price of spearmint oil resulted in 1980 in the USDA setting up a Far West spearmint marketing order to regulate the sale of spearmint oil and prevent wild fluctuations in price and supply. This system of regulations places limits on the price for carvone, as it is the basis of synthetic spearmint oils.

By 1980, Norda had moved its carvone production to a subsidiary in Mexico, thus leaving the US without a domestic producer. Frutaroma (Israel) and Shiono (Japan) were producing material, and a new supplier, Formosa Perfumery, began operations in Brazil. All of the present four producers of l-carvone in the world have based their production on d-limonene, which is obtained from orange oil. The chemistry presently in use by all the producers is the reaction of nitrosyl chloride with limonene, as shown below.

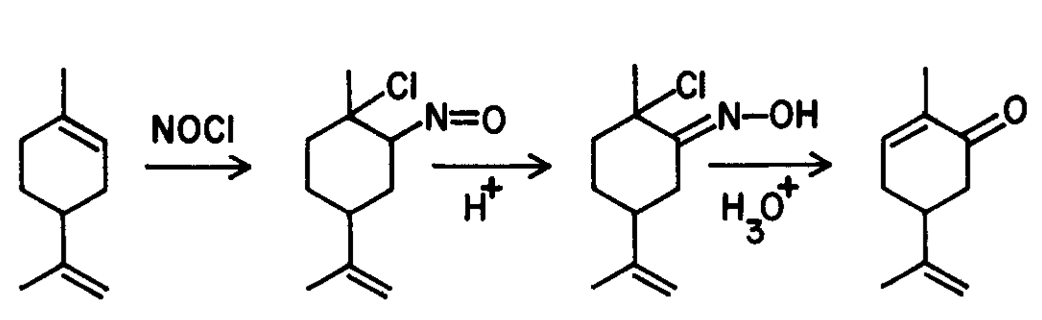
In this reaction d-limonene yields l-carvone, while l-limonene yields d-carvone. The yields of carvone based upon limonene are fairly low (30-35%), thus the cost of limonene is reflected strongly in the production cost of carvone.

The low yields of carvone have been and continue to be a complication in the production process, as about 60% of the d-limonene charged is converted to useless by-products. The intermediate oxine is converted through the Beckman rearrangement and similar side reactions into organic wastes which are a disposal problem. Moreover, the large amounts of water required in the multi-step process result is a waste water disposal problem. Thus, the confines of the process used to produce carvone have caused the manufacturers to seek production locations where abundant water supplies are available and where the organic wastes can be readily disposed of by burning or other means. Consequently, the production of carvone has moved geographically since 1960 to areas where raw material is plentiful, water is abundant, and pollution controls are minimal. The future will see further changes as the pollution problem weighs more heavily on those manufacturers operating in densely populated areas and where process water is a problem.

World Consumption

Worldwide annual consumption of carvone (both d- and l-carvone, and as natural and synthetic material) is estimated at 1826 M tons. This figure includes consumption via major essential oils and breaks down as follows:

l-carvone, synthetic	800 M tons
d-carvone, synthetic	10 M tons
l-carvone, natural	940 M tons
d-carvone, natural	76 M tons
Total all carvone sources:	1826 M tons



It is estimated that 1552 M tons or 85% of all carvone consumption is l-carvone for use in oral hygiene products (toothpaste and mouthwash), while l-carvone consumption in chewing gum is estimated at 180 M tons or 10% of tota usage. The remaining 5% or 91 M tons is consumed as mainly d-carvone in food stuffs (80 M tons), while fragrance applications consume the remaining 11 M tons.

Regional consumption of d- and l-carvone (both a synthetic and natural material) is estimated as follows:

North America
l-Carvone 478 M Tons
d-Carvone 30 M Tons

Europe
l-Carvone 485 M Tons
d-Carvone 30 M Tons

Asia (including China, Indonesia, the Phillippines, Japan and India)
l-Carvone 415 M Tons
d-Carvone 18 M Tons

South and Central America
l-Carvone 270 M Tons
d-Carvone 5 M Tons

Others (includes the Near-East, Africa, Australia and New Zealand)
l-Carvone 178 M Tons
d-Carvone 3 M Tons

The relatively high usage of d-carvone in North America and Europe is largely the result of consumption of dill and caraway oils as food flavors (pickles) and alcoholic beverages.

Pricing

Synthetic d-carvone prices are currently about $40.00/lb. This price reflects the low level of usage and not the potential should significant demand arise.

L-carvone prices are illustrated in Figure 1, as well as prices for d-limonene and US native spearmint.[9] The period 1980-1982 reflects the market adjustments to the USDA spearmint marketing order as well as crop variations of spearmint oil and the competitive forces created upon the entry of Formosa perfume into market as a new supplier. From 1983 to 1987, l-carvone prices remained relatively flat as did d-limonene pricing, while native spearmint oil varied significantly. However, beginning in 1987 d-limonene prices began to rise because of poor orange crops in Brazil and new uses for d-limonene. Increased demand for d-limonene and reduced supply caused prices to more than triple from 1986 to date, placing pressure on carvone producers to raise prices. The increase in native spearmint prices, the alternative to synthetic carvone, has forced l-carvone prices upward, a direct reflection of the increase in production costs because of d-limonene prices. Limonene prices will remain firm or even rise until either Florida or Brazil has a bumper crop, which will not occur until mid-1989 at the earliest. Thus, carvone prices will remain in the $10.00/lb. area until limonene prices fall.

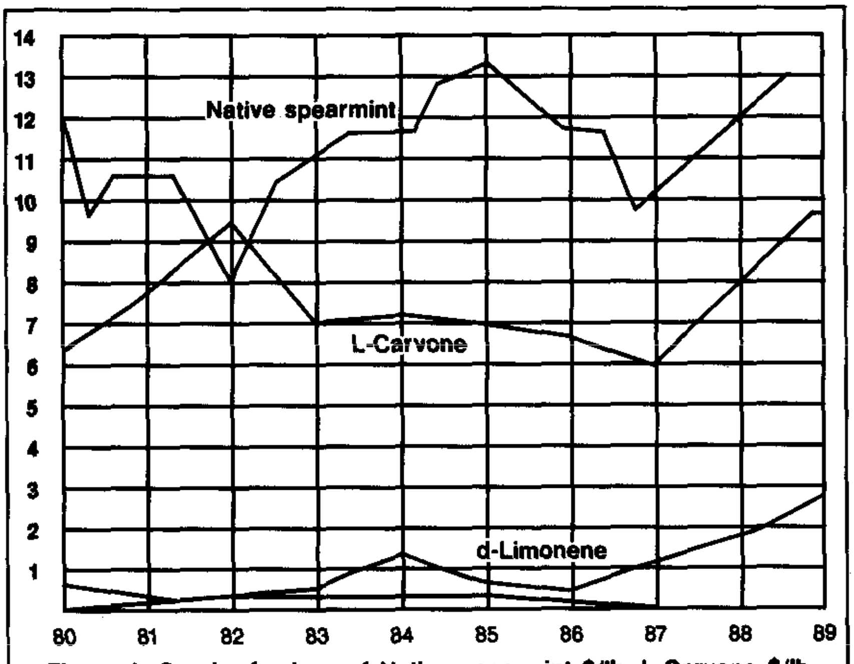


Figure 1. Graph of prices of Native spearmint $/lb, L-Carvone $/lb and d-Lomonene $/Kg.

Carvone

Supply

The 1960 M Tons of carvone consumed as an aroma chemical (not via a natural essential oil) will all be of synthetic origin. The currently active four producers of synthetic carvone have sufficient capacity to supply the needs of the global market for the foreseeable future. The market changes since 1980 have shown that the lowest cost producers must maintain operations where plentiful supplies of d-limonene are locally available, process water is sufficient and waste disposal and pollution controls are not a restrictive hinderance. These considerations will produce changes in the supply of carvone in the future as manufacturing in countries with high population densities and prohibitive controls lose production to firms in more favorable global locations.

Synthetic Producers

Formosa Perfume Ind. e Com Ltda., Brazil—This producer of synthetic carvones began manufacturing in 1980 in the area of Laranjal Paulista in the state of Sao Paulo. This area is the center of orange production in Brazil where d-limonene is available locally in bulk shipments. Annual capacity is estimated at 450 M Tons.

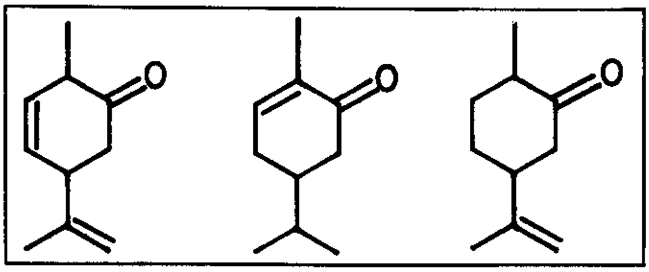
Quest, Mexico—This production site originally was started by Norda in the 1970s to produce l-carvone and phenyl ethyl alcohol. Norda subsequently ceased production of l-carvone at their Boonton, New Jersey site. As limited amounts of d-limonene are available from Mexican sources, Quest imports their feed stocks from Florida and Brazil. Annual capacity is estimated at 300 M Tons.

Shiono Koryo Kaisha, Ltd., Japan—The manufacturing site is located in Osaka in a densely populated industrial area. As no native d-limonene is available, Shiono is reliant solely on imported feed stock. Annual capacity is estimated at 300 M Tons.

Frutarom, Ltd., Israel—This manufacturer of d- and l-carvone is also a producer of other citrus oil derivatives. Annual capacity for l-carvone is estimated at 100 M Tons.

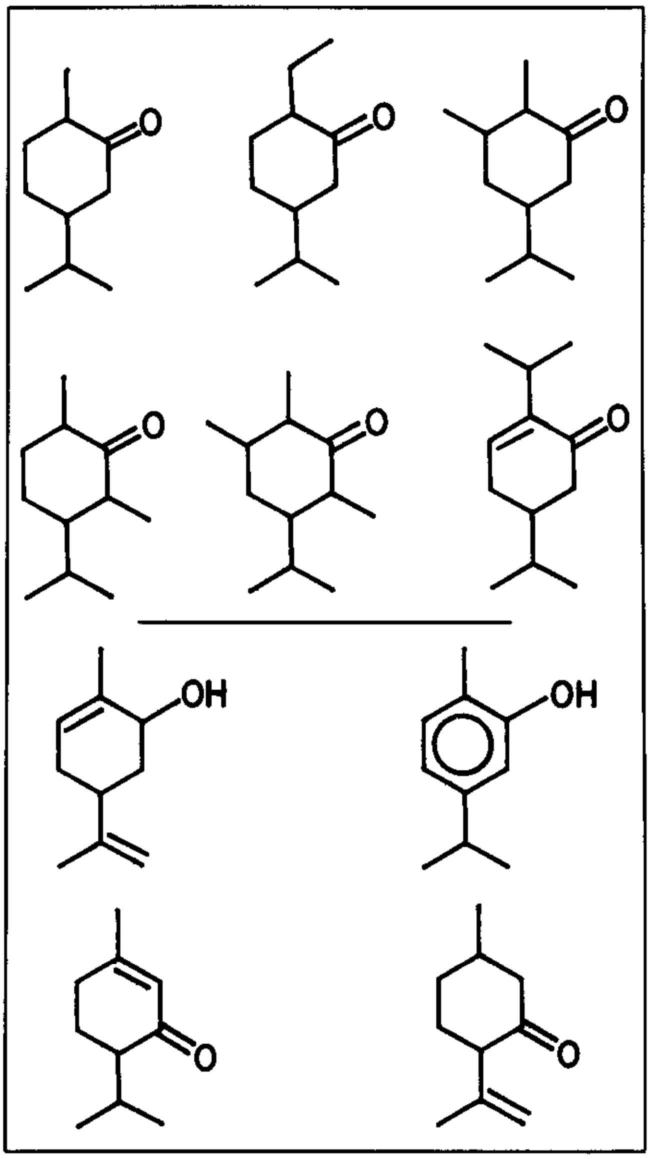
Substitutes

Exact substitutes for either d- or l-carvone obviously don't exist. However, a few materials (all related in chemical structure) display organoleptic impression in the general area. One material, l-spicatone, was previously offered by Glidden some twenty years ago but is unavailable today.



Analogs

A brief review of the literature reveals that no apparent work has been done in the area of analogs of either d- or l-carvone. As in the case of the menthols, minor variations in chemical structure may result in very interesting organoleptic effects. The following structures should provide insight into just what features of the molecule are responsible for the spearmint effect and would be a fruitful area for synthetic chemical research.



Derivatives

Few derivatives of carvone are available commercially. The following are offered by a number of suppliers:

l-Carvyl acetate	GRAS-FEMA Nr.: 2250
l-Carvyl propionate	GRAS-FEMA Nr.: 2251

References

Address correspondence to George S. Clark, Commodity Services Int'l, Inc., P.O. Box 1876, Easton, MD 21601.

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