Chemical Characterization of Cornmint Oils

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The chemical composition of cornmint oils from Brazil, China and India was studied during the period 1986-1991. In this paper, we list the main constituents and their concentrations, we give a detailed analysis of one of the Indian oils, and we discuss the isolation of L-menthol from the oils by slow crystallization.

Botanical Origin

Cornmint oil is the steam-distilled oil from the aromatic plants of *Mentha arvensis* L., variety *piperascens* Malinv. from the family of the *Lamiaceae*, formerly called the Labiateae. Reviews have been written by Lawrence[1] and Maarse et al.[2] about the chemical composition of cornmint oil. Some specific genotypes or chemotypes have been mentioned in literature. For example, Donalisio et al.[4] published about a Brazilian genotype with 40% menthofuran. Lawrence[5] also mentioned an oil from wild growing plants in Brazil, containing 74% menthone. Vorobeva et al.[6] investigated a Russian oil, which contained about 40% acyclic monoterpenoids.

Production

Cornmint oil is one of the most important essential oils, both with respect to its worldwide production of up to 10,000 tons per year, and with respect to its economic value of about $100 million per year. Cornmint oil is important for the isolation of natural menthol. Moreover, dementholized cornmint oil is used to reconstitute *Mentha piperita* oil.

Figures about the world production of cornmint oils during the last decade have been published by Lawrence[7] and Clark[8]. These figures and the estimated world production in 1992 are shown in Table I. Nantong's production[9] of 1700 tons is said to be 30% of China's total production and 10% of the world's production.

Table I. World production of cornmint oil during 1984-1992

	(7) 1984 Tons	(8) 1988 Tons	(9) 1992 Tons
China	2800	4000	5000
Brazil	800	2000	2500
India	200	1000	1500
Others	400	1000	1000
Total	**4200**	**8000**	**10000**

Chemical Composition

Over 40 publications[4-6,10-47] have appeared about the qualitative composition of cornmint oil and the quantitative composition of dementholized oil. Most of these publications have been reviewed by Lawrence[1] and Maarse et al.[2] Most work on the quantitative composition of cornmint has been carried out with dementholized oil, which is often used for the reconstitution of peppermint oil.

Little is known about the quantitative chemical composition of genuine cornmint oils. However, the composition

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of the genuine oil is of considerable importance for the yield and the organoleptic quality of the isolated L-menthol. (A possible biosynthetic pathway for the formation of L-menthol in peppermint was proposed by Croteau[3] to proceed as follows: geranyl pyrophosphate, terpinolene, piperitenone, D-pulegone, L-menthone, L-menthol. The conversion of geranyl pyrophosphate via terpinolene into piperitenone in this pathway is speculative.) The number of constituents so far found in cornmint oil is shown in Table II and the constituents are identified in Table III.

In 1985 and 1986 Werkhoff et al.[10,11] published their results of a thorough investigation on the isolation and gas chromatographic separation of menthol and menthone enantiomers from natural peppermint oils, such as cornmint oil.

Moreover they determined the enantiomeric excesses (so-called E.E. values) in the natural products, which were over 99%.

In our experiment during the period 1986-1991, the concentrations of the main constituents of 33 samples of cornmint oils from Brazil, China and India were investigated. The chemical composition of cornmint oil was studied as a quality control for the contents of menthol, menthone and their isomers. This quality control was carried out by Destilaciones Bordas Chinchurreta, one of Europe's largest producers of natural menthol from cornmint oil.

GC analyses were carried out using a Carlo Erba MEGA HRGC 5300, equipped with a fused-silica column 0.32 mm i.d. x 50 m coated with SE 54 (Hewlett Packard HP-5; high performance cross linked 5% phenyl silicone gum phase), film thickness 1.05 μ. Oven temperature programmed, 40-280°C at 4°C/min; injector and FID: 220°C; carrier gas helium, 120 kPa head pressure. Inlet split 50 ml/min. GC/MS data were obtained on a Finnigan TSQ70 mass spectrometer directly coupled with a Hewlett Packard 5890 gas chromatograph. Columns used and gas chromatographic conditions as above.

Table II. Number of constituents in cornmint oils according to published data[4-6,10-47]

Hydrocarbons	21
Alcohols	24
Aldehydes	6
Ketones	12
Acids	7
Esters	21
N-compounds	3
S-compounds	1
Ethers/epoxides	9
Phenols	1

Each of the 33 samples represented 2-10 tons of oil. The average concentrations of menthol, menthone and their isomers are given in Table IV, where also the concentration ranges are shown. A difference in the concentration of menthol and menthone present in the oils from various parts of the world can be noticed. A high menthol-concentration always corresponds with a low menthone concentration and vice versa. The sum, however, of the menthol and menthone concentration in the oils from various countries is 80-82%.

It is general knowledge that natural cis-3-hexenol and its esters are of great importance for natural flavor compounding. cis-3-Hexenol and at least six of its esters (such as the formate, acetate, isovalerate, hexanoate, benzoate and salicylate) occur in peppermint oils. Distillation heads of the oil or so-called peppermint terpenes are used to isolate cis-3-hexenol. However this chemical occurs for only a maximum of 0.05% in the original oils or perhaps 1.0% in the 20 times concentrated heads. The total content of cis-3-hexenyl esters in the oil can be ten times higher, say 0.5% in the

Table III. Chemical composition (%) of cornmint oils according to published data[4-6,10-47]

Hydrocarbons	
cis-β-ocimene	0.0-0.7
β-phellandrene	t
γ-terpinene	0.0-0.1
terpinolene	t
α-pinene	0.2-1.6
santene	t
α-thujene	t
p-cymene	0.0-0.1
β-farnesene	0.2-1.0
β-caryophyllene	0.1-4.0
β-bourbonene	0.0-0.7
myrcene	0.2-1.0
α-terpinene	0.0-0.01
δ-terpinene	t
limonene	1.0-14.4
β-pinene	0.2-1.1
camphene	0.1-1.5
sabinene	0.2-1.0
germacrene D	0.2-1.5
γ-caryophyllene	t
δ-cadinene	t
Alcohols	
ethanol	t
3-methylbutanol	t
3-octanol	0.2-4.0
citronellol	p
nerol	p
menthol	65.0-85.0
isomenthol	0.1-1.0
α-terpineol	0.0-0.3
isopulegol	0.0-1.0
cis-carveol	0.0-0.3
p-menthan-2,5-diol	t
isocaryophyllenol	t
butanol	t
(Z)-3-hexenol	0.0-0.1
2,6-nonadienol	t
geraniol	p
linalool	p
neomenthol	1.0-10.0
neoisomenthol	0.0-0.3
terpinen-4-ol	0.0-1.0
neoiso(iso)pulegol	t
trans-carveol	0.0-1.1
borneol	t
viridiflorol	0.0-0.1
Aldehydes	
acetaldehyde	t
3-methylbutanal	t
geranial	p
2-methylpropanal	t
2,6-nonadienal	t
neral	p
Ketones	
acetone	t
2-heptanone	t
2-isopropylcyclopentanone	t
3-methylcyclohexanone	t
menthone	4.0-20.0
piperitone	0.1-2.0
carvone	t
2-butanone	t
methylheptenone	t
cis-jasmone	0.0-0.2
carvomenthone	t
isomenthone	2.4-7.0
pulegone	0.5-1.5
Acids	
formic acid	t
3-methylbutanoic acid	t
hexanoic acid	t
nonanoic acid	t
acetic acid	t
pentanoic acid	t
octanoic acid	t
Esters	
(Z)-3-hexenyl formate	t
menthyl formate	t
(E)-2-hexenyl acetate	t
(Z)-3-hexenyl acetate	t
1-octen-3-yl acetate	t
geranyl acetate	p
linalyl acetate	p
menthyl acetate	0.4-6.4
isomenthyl acetate	0.1-0.2
neomenthyl acetate	0.0-0.1
neoisomenthyl acetate	t
dihydrocarvyl acetate	0.0-0.15
(Z)-3-hexenyl 3-methylbutanoate	t
menthyl 3-methylbutanoate	t
menthyl pentanoate	t
(Z)-3-hexenyl hexanoate	t
menthyl hexanoate	t
(Z)-3-hexenyl 2-hydroxybenzoate	t
(E)-2-hexenyl phenylacetate	t
(Z)-3-hexenyl phenylacetate	t
menthyl phenylacetate	t
Nitrogen compounds	
3-phenylpyridine	t
3-phenyl-4-propylpyridine	t
2-phenyl-5-propylpyridine	t
Sulfur compounds	
mintsulfide	t
Ethers/epoxides	
menthofuran	0.0-1.6
menthofurolactone	t
1,8-cineole	0.1-0.3
trans-2,5-diethylfuran	t
3-(5,5-dimethyltetrahydro-2-furyl)-(Z)-2-butenol-1	t
piperitone oxide	t
β-caryophyllene oxide	0.0-0.1
Phenols	
2-isopropyl-5-methylphenol (thymol)	t

p = present; t = trace

Table IV. Concentration of main constituents in cornmint oils from Brazil, China and India (in percent)

	Brazilian oils[a]		Chinese oils[b]		Indian oils[c]	
	average	range	average	range	average	range
Monoterpene hydrocarbons	6.84	5.59-8.74	5.50	4.10-7.34	6.00	4.31-7.62
Menthone	14.80	12.33-17.99	11.13	6.42-16.75	6.05	4.03-10.81
Isomenthone	4.14	3.53-5.22	3.97	3.11-5.17	2.71	1.65-3.50
Menthyl acetate	2.35	1.15-3.99	0.77	0.43-1.42	1.96	0.22-3.38
Neomenthol	2.60	2.15-3.90	2.61	0.78-3.51	2.82	2.31-3.35
Menthol	65.08	61.62-67.85	72.10	63.47-76.03	75.52	72.20-78.62
Isomenthol	0.40	0.14-0.71	0.77	0.44-1.02	0.75	0.36-0.97
Piperitone	1.89	1.41-2.98	0.90	0.40-1.80	1.10	0.34-1.80
Pulegone	1.19	1.06-1.35	0.90	0.65-1.15	0.50	0.35-0.70

[a] 12 samples during 1986-1991; [b] 5 samples during 1986-1991; [c] 16 samples during 1988-1991

original oil. It might be worthwhile to hydrolyze in a natural (enzymatic) way the dementholized cornmint oil to increase the cis-3-hexenol content and, as a by-product, also the menthol content from the acetate.

Cornmint Oil from Shivalik

A representative sample of Indian cornmint oil, isolated from the subvariety Shivalik, was analyzed in more detail. The gas chromatogram shows 65 peaks, of which about 50 were identified by mass spectrometry and quantified. These 50 constituents comprise over 99% of the oil. (See Table V.)

At least seven chemical compounds which are new constituents for cornmint oil were found in the Shivalik oil. They include: 3-methyl-2-cyclopenten-1-one, 3-methylcyclohexanol, methyl octyl ether, 1-nonanol, 3-nonanol, myrtenol and myrtenal. Additional new constituents were tentatively identified (Table V).

Isolation of L-Menthol

The L-menthol was isolated from cornmint oil by slow crystallization. The oil was cooled from 35°C to 5°C during 15 days, with the temperature decreasing 2° every 24 hours. The crystallized menthol was centrifuged and sieved. It was found that the analytically and organoleptically best quality of L-menthol was obtained from the cornmint oil with the lowest grade of menthol. Severe problems were sometimes met during crystallization on an industrial scale. These problems occurred with raw material of high menthol content (>75%), and consisted of coagulation of the menthol instead of crystallization.

Although all the reasons for the problems are not exactly known, all known possible causes were checked carefully. It could be that the physical isolation procedure on a technical scale was not completely reproducible. However, all crystallizations were carried out in the same cooling chambers under exactly the same circumstances. Another reason might be that the menthol in the oil was a mixture of enantiomers. Rotations were checked after every crystallization, so this reason should be rejected—a conclusion supported by the literature.[10,11]

It may be possible that the concentration of L-menthol in the oil was too high. After crystallization of about 50% of the product a mother liquor remains, containing 30-50% of L-menthol, depending on the starting oil's menthol con-

Table V. Chemical composition of an Indian cornmint oil (subvariety Shivalik)

Retention Index (SE-54)	Compound	%	Retention Index (SE-54)	Compound	%
559.1	acetic acid	0.02	1176.1	isomenthone	4.59
728.9	3-methylbutanol	0.08	1185.4	menthol	74.51
848.0	3-methyl-2-cyclopenten-1-one	0.02	1189.6	isomenthol	0.05
853.8	(Z)-3-hexenol	0.03	1193.2	p-cymen-8-ol	0.03
940.9	α-pinene	0.15	1196.2	neomenthol	0.12
unknown	3-methylcyclohexanol	t	1200.9	α-terpineol	0.07
unknown	3-methylcyclohexanone	t	1210.2	octyl acetate	0.11
980.1	sabinene	0.06	1211.8	myrtenal + myrtenol	0.04
985.9	β-pinene + 3-octanone	0.24	1224.6	verbenone	0.03
994.9	3-octanol	0.96	1229.6	β-citronellol	0.10
1006.2	(Z)-3-hexenyl acetate	0.04	1237.6	(Z)-3-hexenyl 3-methylbutanoate	0.28
1011.3	α-phellandrene	0.02	1242.2	hexyl 3-methylbutanoate	0.03
1027.0	methyl octyl ether	0.02	1249.8	isomenthyl acetate	0.23
1031.2	p-cymene	0.02	1253.5	pulegone	0.13
1035.8	limonene	0.39	1256.8	carvone	0.05
1039.9	1,8-cineole	0.25	1268.6	piperitone	0.45
1069.2	octanol	0.06	1272.3	decanol	0.03
1074.8	sabinene hydrate	0.02	1283.8	neoisomenthyl acetate	0.16
1095.8	3-nonanol	0.04	1283.8	menthyl acetate	6.11
1101.8	linalool	0.03	1320.9	neomenthyl acetate	0.12
1105.7	3-methylbutyl 3-methylbutanoate	0.03	1344.6	p-menth-8-en-1,2-diol	0.03
1122.5	3-octyl acetate	0.04	1350.5	α-terpinyl acetate*	0.06
1153.1	β-terpineol	0.01	1367.2	terpine hydrate	0.06
1156.6	isopulegol*	0.25	1409.0	methyl eugenol*	0.15
1165.2	menthone	8.30	1572.6	nerolidol	0.02
1171.9	nonanol	0.09	1618.2	caryophyllene oxide	0.29

t = trace
* = tentative identification

tent, such as 65-75%. The menthol concentration in the original oil indeed is the main influence on the ease of crystallization. Finally there could be impurities in the oil, and these impurities could disturb the crystallization of the oil. This factor may also have an important influence. The impurities can be known (e.g., isomenthol) or unknown. Thus one must draw the conclusion that there exist several reasons for crystallization problems.

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