Mint Oils: Potential for Standardizing Profiles with Natural Flavoring Substances

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The peppermint herb *Mentha piperita,* when grown in different regions and soils, can yield essential oils with varying composition and organoleptic profiles. Some of these oils with specific flavor profiles command a premium value when traded commercially.

Peppermint is a widespread herb, as demonstrated in Lawrence's reviews on its origins and essential oil composition.[1-11] These excellent reviews are the starting point for this study.

Cornmint, or *Mentha arvensis*, is known confusingly in parts of Europe as peppermint. The chemistry of Brazilian, Chinese and Indian *M. arvensis* oils from several years' crops was reported in an excellent review by Boelens.[12]

A GLC method for detecting the addition of cornmint oil to *M. piperita* is based on the higher levels of isopulegol and neo-iso-isopulegol found in cornmint. It clearly indicates mixtures of the oils.[13] This particularly useful method is less likely to be obviated than other GLC methods[14] because the isopulegols are not easily removed from the cornmint by normal fractionation.

The reasons for quality differences of peppermint oils have been reported.[15]

There is no doubt that the enantiomeric distribution of isomers of many of the mint components will be an important area of research in the field of natural product chemistry. In this article, we do not make any claims as to the correctness of any of the enantiomers for the natural isolates listed; rather we point the way for further research by others more competent in this specialist field.

This article explores the potential for adding mint fractions and isolated components from all of the mint species,[16-18] as well as from sources of natural flavoring substances available from alternate routes. These alternate routes include other non-mint natural isolates,[19] natural products made by fermentation and enzyme technology,[20] and the natural flavoring substances made by so-called "soft chemistry" from natural ingredients reacted with catalysts.

Lawrence[21] also has published details of a scheme for characterizing the origin of a peppermint oil by calculating the ratios of selected components and plotting them on a "spider's web" grid pattern. Lawrence plotted more than 50 different production batches for each origin. The normal variations then appeared as shaded eccentric rings, each characteristic of that origin. Using this method, it is possible in most cases to detect as little as 5% of an oil of one origin (such as a lower-priced Indian *M. piperita)* having been added to oils produced in various growing areas in the United States.[22]

Commercial gain is not a valid reason for blending mints. The sole purpose should be to achieve consistency in the commercial supply and availability of mints, no matter what the crop from any one region can yield. Any such blends should be clearly marked as being from an unspecified origin or country, or they should be marked as containing other natural flavorings.

Analysis

Organoleptic profiles are vital to any mint blend standardization. It is for this reason that we have included an odor description of all of the identified mint components that we found. We recognize that all of the components of *Mentha piperita* may not have been identified in this study, but we believe that the important characterizing flavoring substances have been elucidated.

Dual capillary gas-liquid chromatography (GLC) using non-polar DB1 and polar DB wax columns was used with

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Table I. Film, function and measured "G pack" for analysis columns

Film	Function	Measured "G Pack"
DB wax	dual capillary GLC (polar)	1.267
DB1	dual capillary GLC (non-polar)	0.996
DB5	GC/MS	1.005

cross-referenced relative retention indices[23-25] and GC/MS on a DB5 column to ensure correct identification of the components listed. All the identities were in good agreement with most of the average values in the published scientific literature. However, the numerous books and databases listing retention indices show some unacceptable variations for the same components found in different oils.

We believe that this reported spread is caused by the use of uncalibrated columns. All of the Relative Retention Index (RRI) values reported in this paper are on calibrated "G pack" capillary columns[26] standardized using a specially prepared test mixture, the NC mix, which contains components typical of those encountered in essential oil analysis. Such calibration is vital to ensure that meaningful, reliable and reproducible indices are obtained. Component identities reported by other authors using columns that are not supported by polarity calibration should be viewed as only tentative identifications.

The RRI data reported in this paper conforms to the standardized methodology published in a collaborative study by the essential oil subcommittee of the Analytical Methods Committee/Essential Oils (AMC/EO) of the Royal Society of Chemistry. This subcommittee is made up of analysts working for the major essential oil users in the UK and dedicated to commercial oil analysis. The authors of this article have been associated with that subcommittee's work and publications for 26 years.

Natural Flavoring Substances

Natural flavoring substances are derived primarily via the following techniques:

- Isolation from *Mentha piperita* by physical means, such as fractional distillation and freezing
- Isolation from *Mentha* subspecies by physical means
- Isolation from non-mint species by physical means
- Fermentation technology with subsequent concentration techniques
- Enzyme technology
- So-called "soft chemistry" from natural starting materials. An example is menthyl acetate from natural menthol and natural acetic acid. The naturalness of catalysts for such reactions is the subject of much scientific debate.

Table II. Components of *Mentha piperita* with Relative Retention Index (RRI)

Peak no.	RRI	Component	Area (%)	
			Lot 1	Lot 2
1	790	dimethyl sulphide (odor confirmed by sniff GLC)	0.02	0.04
2	820	isobutanal	0.03	0.04
3	880		0.01	0.02
4	900	3-methylbutanal	0.09	0.12
5	940	2-ethylfuran	0.03	0.03
6	980		<0.001	<0.001
7	990		<0.001	<0.001
8	1002		<0.001	<0.001
9	1015	tricyclene	<0.001	<0.001
10	1020	α-pinene	0.77	0.77
11	1032	α-thujene	0.05	0.05
12	1038	ethyl 2-methylbutyrate	<0.01	<0.01
13	1052	camphene	0.05	0.05
14	1069		<0.01	<0.01
15	1095	β-pinene	1.0	0.95
16	1108	sabinene	0.46	0.44
17	1151	β-myrcene	0.17	0.14
18	1156		< 0.01	< 0.01
19	1161		<0.005	<0.005
20	1173	α-terpinene	0.32	0.36
21	1190		<0.005	<0.005
22	* 1198	l-limonene	1.7	1.2
23	1205	β-phellandrene	0.1	0.1
24	* 1210	1,8-cineole	4.9	3.7
25	1214		0.04	0.04
26	1228	cis-β-ocimene	0.23	0.17
27	1234		< 0.001	< 0.001
28	1239	γ-terpinene	0.51	0.58
29	1243	trans-β-ocimene	0.06	0.03
30	1247	octan-3-one	< 0.01	< 0.01
31	1260	para-cymene	0.14	0.13
32	1268		< 0.005	<0.005
33	1272	terpinolene	0.18	0.18
34	1284	1-octen-3-one	0.10	0.09
35	1289		< 0.005	< 0.005
36	1315	3-methylcyclohexanone	< 0.005	< 0.005
37	1327		< 0.005	< 0.005
38	1345		< 0.005	< 0.005
39	1372		< 0.01	< 0.01
40	1380	cis-3-hexenol	0.05	0.02
41	1388		< 0.01	< 0.01
42	1394	3-octanol	0.30	0.25
43	1408	trans-2-hexenol	0.03	0.01
44	1451	1-octen-3-ol	0.16	0.28
45	1459	l-menthone	17.5	27.5
46	* 1464	trans-sabinene hydrate	1.1	1.0
47	1476	menthofuran	4.6	1.2
48	* 1484	d-isomenthone	2.8	3.3
49	1492		< 0.005	< 0.005
50	1504		< 0.01	< 0.01
51	1511	β-bourbonene	0.32	0.31
52	1523	neo-menthyl acetate	0.20	0.16
53	1535		< 0.01	<0.01
54	1547	linalol	0.31	0.26
55	1558	l-menthyl acetate	5.4	3.9
56	1562		< 0.01	< 0.01
57	* 1567	isopulegol	0.10	0.10
58	1573	isomenthyl acetate	0.3	0.2
59	1581		0.06	0.06
60	* 1587	β-caryophyllene + neo-iso-isopulegol (trace)	1.5	1.4
61	1593	neo-menthol	3.6	3.4
62	1598	terpinen-4-ol	0.90	1.03
63	1623	neo-isomenthol	0.89	0.77
64	1640	l-menthol	44.6	41.0
65	1660	pulegone	0.32	0.37
66	1664	α-humulene	0.24	0.20
67	1668	isomenthol	0.15	0.13
68	1675	trans-piperitol	0.05	0.04
69	1690	α-terpineol	0.14	0.12
70	1699	germacrene D	1.6	1.8
71	* 1716	piperitone	0.47	0.71
72	1722	l-carvone	0.37	0.27
73	1741		0.05	0.05
74	1748		0.08	0.08
75	1751		0.04	0.04
76	1758		< 0.005	< 0.005
77	1765		< 0.01	< 0.01
78	1771		< 0.01	< 0.01
79	1787		< 0.01	< 0.01
80	1798		< 0.005	< 0.005
81	1828		< 0.01	< 0.01
82	1850		< 0.01	< 0.01
83	1882		< 0.01	< 0.01
84	1905		< 0.01	< 0.01
85	1934		< 0.01	< 0.01
86	1968		0.04	0.04
87	1973		0.05	0.03
88	1981		< 0.005	< 0.005
89	1992		< 0.005	< 0.005
90	2008		< 0.005	< 0.005
91	2120	viridiflorol	0.21	0.15
92	2159		< 0.005	< 0.005
93	2181		0.04	0.04
		others	0.47	0.48
Total area			**100.000**	**100.000**

* Characterizing for the genuineness of *Mentha piperita*

Table III. Sources for natural flavoring substances used to standardize *Mentha piperita*

Peak	Identity	FEMA	Purity (%)	Odor	Source	Method[a]	Occurrence (%)
10	α-pinene	2902	90	light pine	turpentine	c	70
15	β-pinene	2903	80	light pine	lemon terpenes	c	10
			90		turpentine	c	20
16	sabinene	——	50	pepper, herb	*Pinus pinaster* (Pine)	c	15
					nutmeg terpenes	c	30
17	β-myrcene	2762	80	unripe mango	orange terpenes	c	3
					Pimenta racemosa (Bay)	c	20
20	α-terpinene	3558	90	lemon, herb	lime terpenes	c	5
22	l-limonene	——	80	light citrus	*M. arvensis* terpenes	b	40
			90		*M. spicata* terpenes	b	10
			90		*Pinus* spp	c	10
24	1,8-cineole	2465	80	fresh eucalyptus	*M. piperita* terpenes	a	50
			98		*Cinnamomum camphor*	c	35
					Eucalyptus spp	c	80
28	γ-terpinene	3559	50	citrus, herb	lemon terpenes	c	12
			50		lime terpenes	c	15
			80		*Satureja hortensis*	c	50
29	β-ocimene	3539	80	warm, herb	*Ocimum canum*,eugenol	c	10
31	p-cymene	2356	90	light citrus	*Cuminium cyminum*	c	10
			90		*Origanum* spp	c	20
33	terpinolene	3046	80	fresh pine	lime terpenes	c	10
42	3-octanol	3581	80	herb, oily	*M. arvensis* terpenes	b	20
44	1-octen-3-ol	2805	90	mushroom	*Lycopus americanus*	c	35
45	menthone	2667	80	herb, mint	*Agastache mexicana*	c	70
					M. arvensis	b	20
46	trans-sabinene hyd	3239	50	camphor, lime	*Marjorana hortensis*	c	4
47	menthofuran	3235	80	hay, mint	*M. piperita* Stolons	a	46
48	isomenthone	3460	50	herb, mint	*M. arvensis*	b	10
			80		*Agastache rugosa*	c	40
54	linalol	2635	80	lavender	*M. citrata*	b	40
			95		*M. longifolia*	b	80
			90		*Ocimum basil. Linalol*	c	55
			95		Ho leaf oil	c	80
			95		*Aniba rosae* (Rosewood)	c	80
55	l-menthyl acetate	2668	80	herb, mint	*M. dumetorum*	b	20
			80		*M. piperita*, Stolons	a	25
			80		*M.arvensis*,Brazil	b	7
			98		menthol acetylated	d	127
57	isopulegol	2962	80	mint herb	*M. arvensis*, Indian	b	2
60	β-caryophyllene	2252	90	spicy wood	clove terpenes	c	80
			90		Copaiba balsam oil	c	80
60	neo-iso-isopulegol	——	80	mint herb	*M. arvensis*, Indian	b	1
61	neo-menthol	2666	80	cool mint	*M. arvensis*	b	3
			80		*M. sacchalinensis*	b	58
62	terpinen-4-ol	2248	80	musty, pine	*Origanum majorana*	c	30
			80		*Melaleuca alternifolia* (teatree)	c	40
			80		*Eucalyptus dives*	c	4
64	l-menthol	2665	98	cool mint	*M. arvensis*	b	70
65	pulegone	2963	80	herb mint	*Barosma crenulata* (Buchu)	c	25
			80		*Hedeoma pulegioides*	c	70
			95		*M. pulegium*	b	70
			97		*Acinos majoranifolius*	c	70
68	trans-piperitol	——	80	mint	*M. sylvestris*	b	45
69	α-terpineol	3045	95	sweet floral	*Pinus* spp	c	90
70	germacrene D	——	80	mild woody	*Collinsonia canadensis*	c	46
			80		*Acinos arvensis*	c	49
71	piperitone	2910	95	mint camphor	*Eucalyptus dives*	c	45
			90		*M. pulegium*	b	8
72	l-carvone	2249	90	sweet mint	*M. spicata*	b	70
91	viridiflorol	——	90		*Salvia off.* Sage oil	c	5
			50		*Rosemarinus off.*	c	3
			50		*Cistus* labdanum oil	c	5

[a] Method: a = ex *Piperita*, b = ex *Mentha*, c = ex non-mint naturals, d = by "soft chemistry"
(*Note:* Fermentation technology and enzyme technology are potential methods. The author knows of no instances of their use.)

It is quite clear that the blending of natural flavoring substances from the last four techniques (non-mint isolation, fermentation, enzyme technology and "soft chemistry") will give a WONF (With Other Natural Flavors) peppermint oil. We believe that the technique of isolation from *Mentha* subspecies also gives a WONF oil, provided the *Mentha* oil is **not** *piperita*. When the *Mentha* oil **is** *piperita*, as is the case in the first technique mentioned, the result is the true natural.

Sources

The essential oils used in this study were from mint herb grown in the Yakima Valley in the far western United States and steam distilled there on commercial equipment. Oil that we have designated "lot 1" was from a first cutting of herb; "lot 2" was from a so-called double-cut herb, which is a second crop. We believe both oils used in this study were totally pure, genuine and unblended with any other source oils.

Results

The three columns used in our analysis were capillary columns 30 m by 0.248 mm with a 0.25 μm film thickness.[27] Table I shows the film, function and measured "G pack" for each column. These are well within the ranges of standardized values recommended by the AMC/EO committee, and the GLC conditions used were as published by them.[26]

Table II lists the components in elution order on a polar DB wax capillary GLC column.

The components found at greater than 0.1% were identified. They totaled in excess of 99%. Peaks marked "*" have been reported[13] as characterizing for the genuineness of *piperita*. We were unable to resolve β-caryophyllene from neo-iso-isopulegol on a 30 m or a 50 m capillary DB wax column, although it reportedly has been resolved on a 60 m column.[13]

Of these 93 components, those listed in Table III are available as natural flavoring substances, without being specific as to their enantiomers. In an attempt to clarify the legislative status of these substances, Table III gives the derivation technique for each. Table III also gives the sources for these natural flavoring substances.

The data presented show the potential of available ingredients for the standardization of peppermint profiles. There are specific components responsible for the differences in the flavor profiles of the oils from different origins. This was demonstrated by Lawrence[21] in his "spider's web" profiling of the characterizing components.

Conclusion

The natural flavoring substances suitable for the standardization of peppermint oil profiles are commercially available. The potential exists to use these natural flavorings in commercial blended mint oils.

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