

The Genuineness of Two Mint Essential Oils*

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Essential oils from the genus *Mentha* have been produced for centuries. Collectively these oils are referred to as "mint oils." Mint essential oils are primarily obtained by steam distillation of the fresh overground portion of the mint plant. In the case of peppermint-type oils, two very distinctive varieties are produced commercially on a worldwide basis. These oils are obtained from the following plants:

- *Mentha arvensis* L.
- *Mentha piperita* L.

Several varieties of each of these plants are produced.

The oil obtained from the distillation of *Mentha piperita* is referred to as peppermint oil. In the United States this is the only oil which may be called peppermint oil, because the identity standard for peppermint, according to the Food Chemical Codex III, is "an essential oil obtained by steam distillation from the fresh overground parts of the flowering part of *Mentha piperita* L. (Fam. *Labiatae*); it may be rectified by distillation, but is neither partially nor wholly dementholized. It is a colorless or pale yellow liquid having a strong penetrating odor of peppermint and a pungent taste, followed by a sensation of coldness when air is drawn into the mouth."¹

In contrast, the oil obtained from *Mentha arvensis* must be labeled as *Mentha arvensis* oil if not dementholized, and "cornmint" oil if partially dementholized. The Food Chemical Codex III further states that *Mentha arvensis* oil, partially dementholized (cornmint oil), is "the portion of oil remaining after the partial removal of menthol, by freezing operations only, from the oil of *Mentha arvensis* var. *piperascens* Holmes (forma *piperascens* Malinvaud). It is a colorless to yellow liquid having a characteristic minty odor. It is soluble in most fixed oils, in mineral oil,

and in propylene glycol. It is insoluble in glycerin."¹

In 1995, approximately 4,700 metric tons of *Mentha piperita* were produced in the United States and approximately 4,200 metric tons of cornmint oil were produced worldwide. While the relative quantity of material produced in each case is similar, the relative value is not. Typical prices for peppermint currently are in the \$13.00 to \$20.00/lb. range, while for cornmint they range from \$2.50 to \$5.25/lb. This price differential—along with a distinct adverse quality variation in cornmint—is the driving force behind adulterating peppermint and/or mislabeling cornmint as peppermint. This does not suggest that useful applications for cornmint and peppermint oils do not exist. The issue here is one of awareness and labeling requirements.

The composition of both peppermint and cornmint has been studied quite extensively and some very comprehensive literature reviews exist on both peppermint²⁻⁶ and cornmint.^{2-4, 7, 8}

The issue of determining the presence of cornmint in peppermint also has been the topic of several investigations. Lawrence in 1983 suggested that the "routine" detection of cornmint in peppermint using trans-sabinene hydrate, menthofuran and viridiflorol may no longer be effective because of the presence of other varieties with varying levels of these constituents.⁴ In 1990, S. C. Varshney proposed using a menthone/isomenthone ratio as an easier method of detecting adulteration.⁹ This suggestion was made because, as Lawrence had pointed out, the "routine" procedure was not accurate enough.

The authors of this article are of the opinion that the constituents mentioned thus far provide good indication of the presence of cornmint and are worthy of consideration, but that they are not enough to definitively determine the presence or absence of cornmint oil in peppermint. With this in mind, an effort was made to identify constituents that would more absolutely determine the presence of cornmint.

* Adapted from a paper presented at the Essential Oil Congress, October, 1995, in Istanbul, Turkey

Experimental

The authors performed a gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) study to differentiate between these two essential oils.

Essential oil samples: All samples analyzed in this study were uniform lots of mint oil that represented no less than 10,000 pounds of product. The samples were all natural mint oils that did not go through any distillation other than the initial steam distillation at the field. The samples were supplied by and owned by the A. M. Todd Company and were known to be true-to-type unadulterated samples.

Gas chromatography: All results that are reported as GC area percent were obtained using a Varian^a 6000 gas chromatograph equipped with flame ionization detector (270°C) with nitrogen makeup; fused silica capillary column: 60 m x 0.25 mm x 0.25 μm film Supelcowax10; carrier gas helium with linear velocity of 20 cm/sec; temperature program: 75°C with 8 min hold to 220°C at 4°C/min with 25 min hold; injection port 270°C; split 150:1; data system Varian 402; all samples were injected neat with an injection size of 0.2 μl.

^a Varian Instruments, Walnut Creek, CA

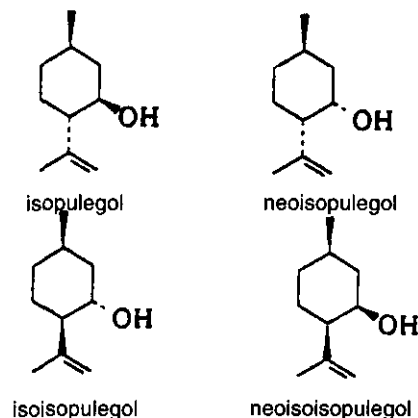
Gas chromatography mass spectroscopy: Mass spectra were obtained via a Varian 3400 gas chromatograph setup as above, except with 100 m Supelcowax10 column that was coupled with a Finnigan^b 800 series ion trap detector (ITD). ITD parameters were: Mass Range 41 to 300 amu; 5 micro scans/sec; transfer line 250°C; mass defect 100 mm/100 amu; Automatic Gain Control on background mass 40 amu; ITD temperature 220°C.

Identification of oil constituents: The compounds were identified using the *Wiley/NBS Registry of Mass Spectral Data*, a terpene library made by Robert P. Adams¹⁰ and supplied by Finnigan, and a user-generated library with the retention times and mass spectra of authentic reference standards supplied by SCM Glidco^c and Aldrich.^d

Mass Spectroscopy Results and Discussion

GC analysis of peppermint oils versus cornmint oils continually showed that on a Supelcowax10 polar capillary column there were two constituents present at elevated levels in the cornmint samples. The first of these constituents eluted immediately after menthyl acetate and the second eluted immediately after β-caryophyllene.

A literature review showed that the most probable identity of these constituents was pulegol related. There did not seem to be much agreement as to the actual identity of these constituents, although in the literature they were all closely related. The possible identity of these constituents is shown below.



Standards for these materials were obtained and the identity was determined. A standard was not available for neoisoisopulegol. The first peak, the one eluting after menthyl acetate, was determined to be isopulegol. Figure 1 shows the total ion chromatogram (TIC) of the standard from Aldrich. Figure 2 shows the mass spectra for this material.

The second peak, the one eluting after β-caryophyllene, was tentatively determined to be neoisopulegol. This tentative identification is based upon both the similarity of the spectra for this material relative to isopulegol and

^b Finnigan MAT, San Jose, CA

^c SCM Glidco, Jacksonville, FL

^d Aldrich Fine Chemical, Milwaukee, WI

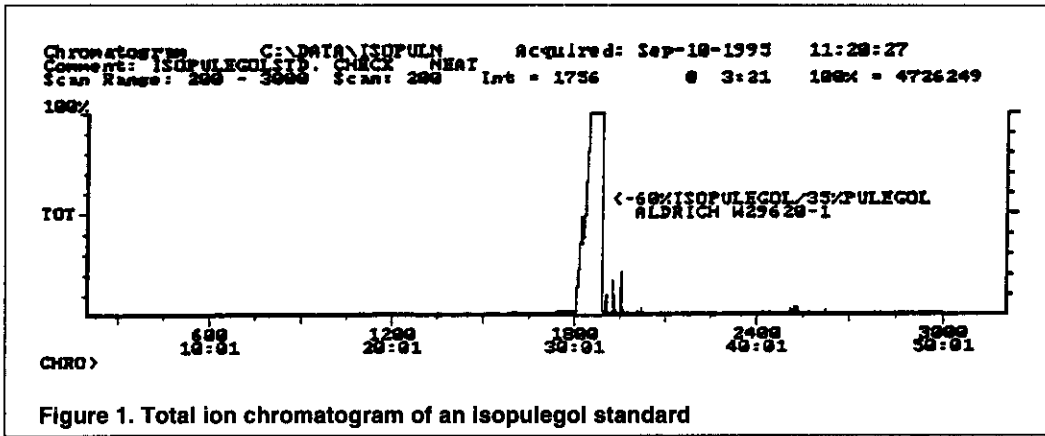


Figure 1. Total ion chromatogram of an isopulegol standard

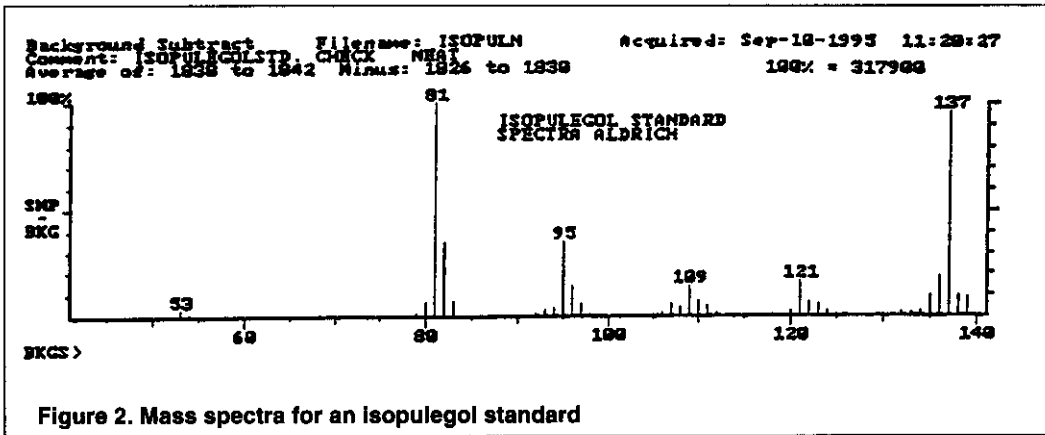


Figure 2. Mass spectra for an isopulegol standard

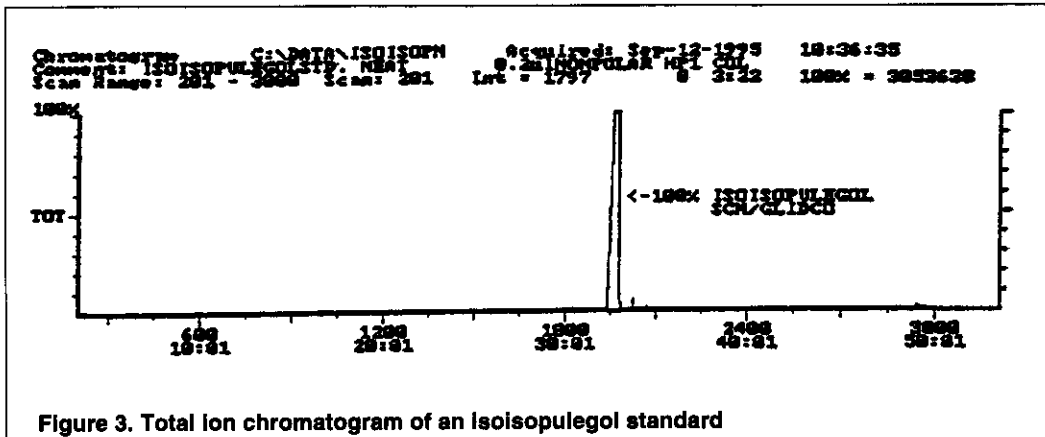


Figure 3. Total ion chromatogram of an isoisopulegol standard

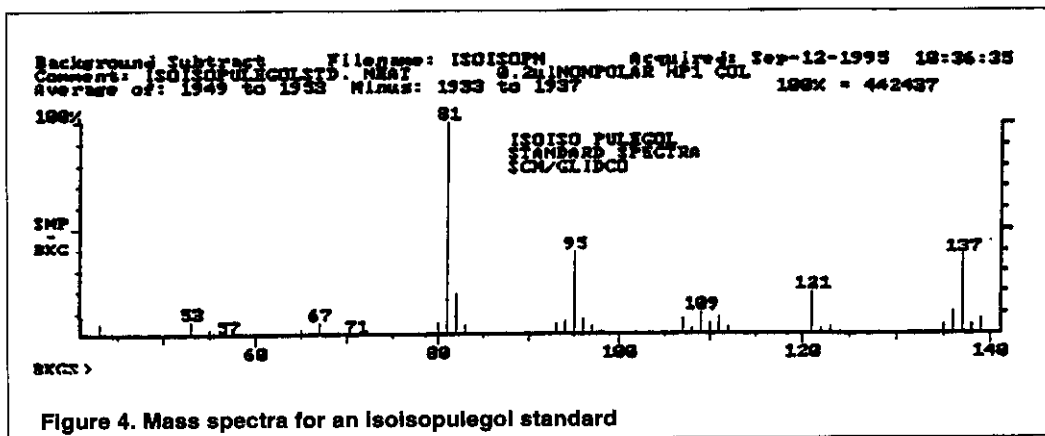


Figure 4. Mass spectra for an isoisopulegol standard

the shorter retention time of the suspect material. Figure 3 shows the TIC for isoisopulegol. Figure 4 shows the mass spectra for isoisopulegol. A more comprehensive ID of the suspect neoisopulegol will be completed when a standard is available.

At this point, samples of three mint oils were run to determine the presence of isopulegol and the suspect neoisopulegol. The samples included a commercial quality American *Mentha piperita* oil, a Chinese *Mentha arvensis* oil and an Indian *Mentha arvensis* oil. The TICs for these three oils are shown in Figures 5, 6 and 7.

The area of interest, from menthyl acetate to β -caryophyllene, was then looked at and the presence or absence of isopulegol and the suspect peak for each oil was determined. A blowup of the TIC for this region for each oil may be seen in Figures 8, 9 and 10.

The mass spectra from each of these ranges confirmed the presence of elevated levels of both isopulegol and tentative neoisopulegol in both the Chinese and the Indian cornmint oils. The mass spectra from the American oil showed that isopulegol is present only at very low levels and, in addition, that there may be low levels of pulegol that are coeluting with the isopulegol. The American oil did not show

neoisopulegol at a level sufficient to resolve on the column used on the MS, but the authors are of the opinion that in the quantitative phase of this study the resolution was sufficient to separate these low levels of neoisopulegol from the β -caryophyllene in American mint oils. This is the reason that neoisopulegol levels are reported as being present in peppermint at this time.

Gas Chromatography Quantitation

The next step was to quantify the amount of isopulegol and neoisopulegol present in various mint oils. The authors also tracked several other constituents reported to be relevant in determining cornmint in peppermint. These included limonene, 1,8-cineole, sabinene hydrate, D-isomenthone and piperitone.

Because the thrust of this project was to determine a method of detecting cornmint in American peppermint, it was important to evaluate the presence of these constituents in oils from all five of the primary American mint oil-producing regions. These five primary areas are referred to as the Midwest (Indiana, Wisconsin, Michigan), Willamette (Oregon), Madras (Oregon), Idaho (including eastern Oregon) and Kennewick (Washington). To adequately establish the typical variation for these compounds, an evaluation of peppermint samples for each of these areas representing a five-year time period (1989-1993) was compiled. The results of this analysis expressed as GC area percent can be seen in Tables I-V.

As can be seen by the data presented in Tables I-V, a small amount of variation does exist between the individual producing regions. This would be expected, since each region produces a unique quality of oil. When

comparing the data between years, it also becomes apparent that, as would be expected, the levels of these various constituents fluctuate with seasonal variation expressed as crop year. In looking at all of the data, the authors felt that it would be beneficial to have a baseline generic value for all of these constituents for an "American Type Peppermint Oil." For this reason, Table VI takes an average of each crop year's average. This row of data marked "Five Year Average" should be considered representative of a typical American peppermint oil. In addition to this, typical values for Indian and Chinese oils are shown directly below the American values. The cornmint values were obtained through the

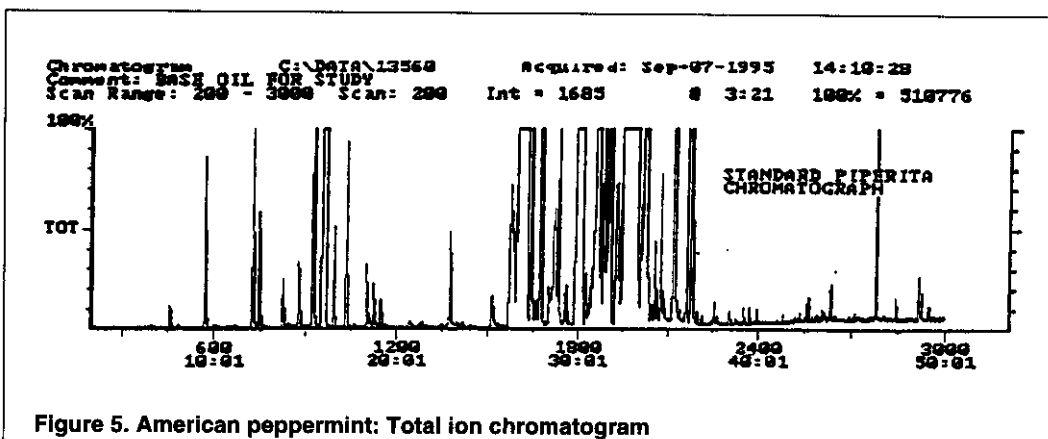


Figure 5. American peppermint: Total ion chromatogram

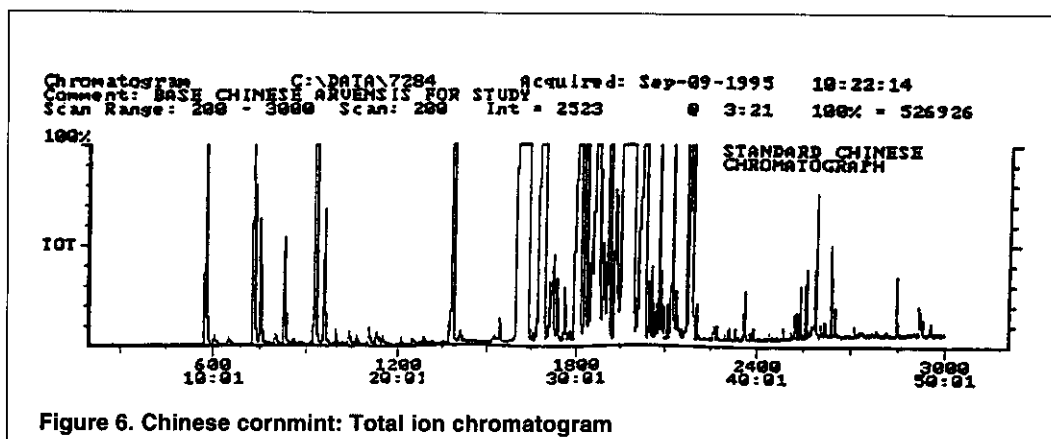


Figure 6. Chinese cornmint: Total ion chromatogram

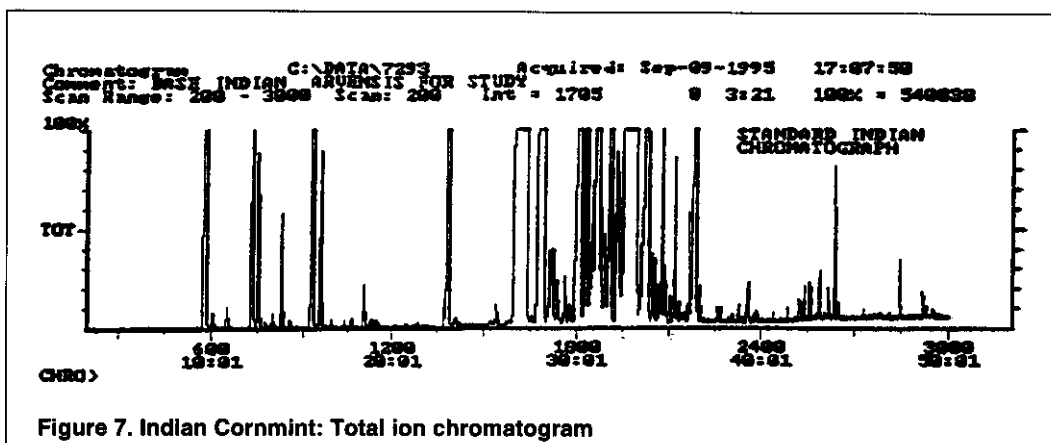
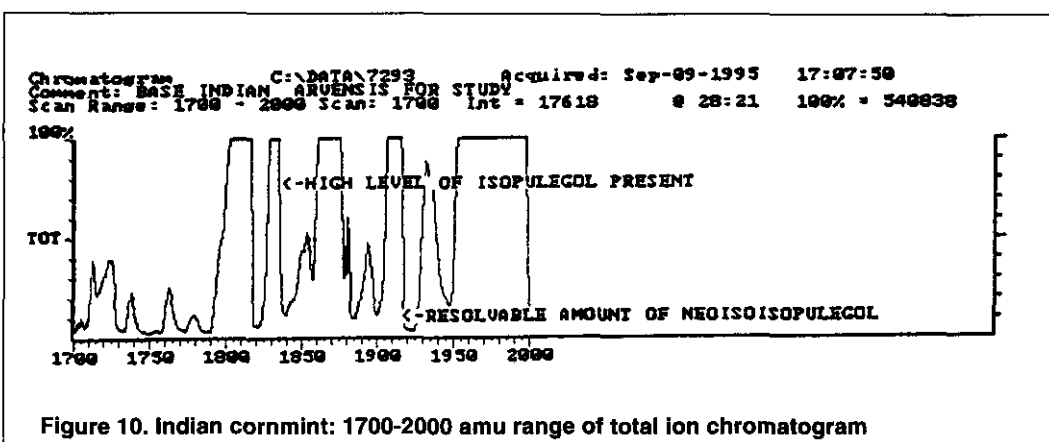
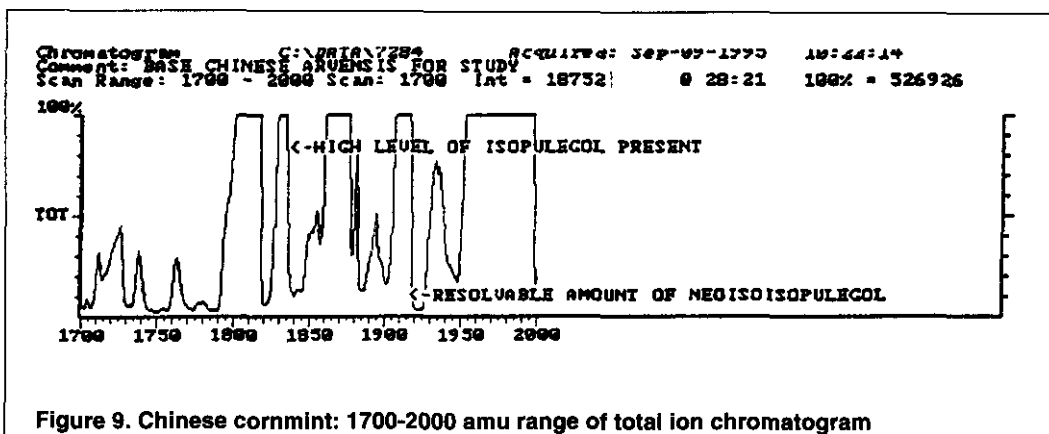
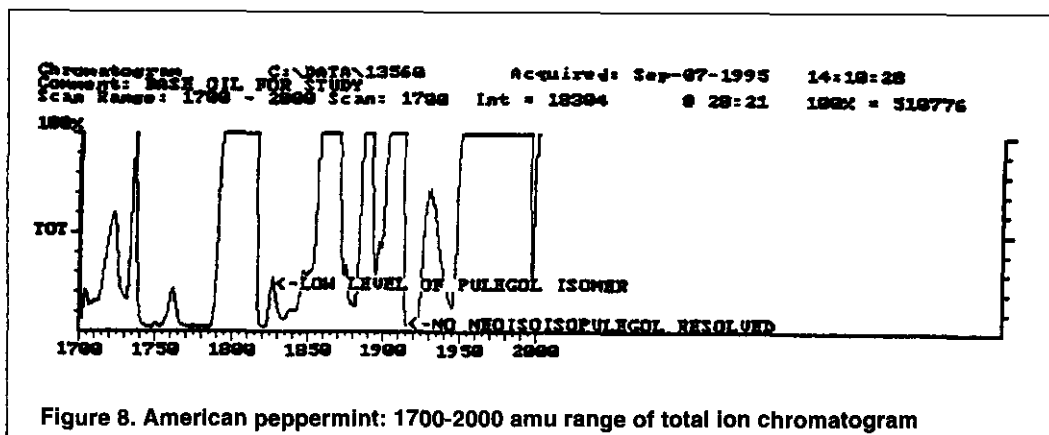


Figure 7. Indian Cornmint: Total ion chromatogram



Limonene: Limonene has low utility because there is not a large difference in peppermint vs. cornmint, the material is readily available on the market at a low price and the values are easily modified through conventional distillation techniques.

1,8-Cineole: In crude oils, 1,8-cineole has a medium utility due to the large differential in values, but the material is available in purified form and is also easily modified by conventional distillation techniques.

Sabinene hydrate: This material has a low-to-medium utility because it has lower values in cornmint, but it is readily available in other essential oils as well as in purified form, and the material may break down into monoterpenes if exposed to slightly acidic distillation conditions, which could give a false positive.

D-Isomenthone: This material has a medium utility because the large range allows for easy detection of gross adulteration, but because this material is present in peppermint at a significant

level, it is a poor indicator at lower levels of addition.

same methodology as the peppermint, but with a much more limited data set that does not represent near the volume of material that the peppermint does. The authors do feel comfortable that the cited typical values are representative of cornmint oils available in the trade.

Looking at the individual values in Table VI for the typical oils, one would initially think that many, if not all, of them would be good indicators for the presence of cornmint in peppermint. The authors feel that all of the information presented is valuable, but the best indicator for cornmint presence is isopulegol. A discussion of each constituent explains why.

level, it is a poor indicator at lower levels of addition.

Neoisopulegol: This material has a high utility and should be used as an indicator, but the authors feel that in routine analysis there is a very great potential not to have adequate resolution and have the material coelute with β -caryophyllene.

Piperitone: This material has a low-to-medium utility because it is present in both materials at significant levels, which suggests its use for detecting gross adulteration, but it is also easily removed by means of conventional distillation techniques.

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Table I. 1993 *Mentha piperita* crop: constituent data summary (GC area %)

Region	Number of samples	Limonene	1,8-Cineole	Sabinene hydrate	D-isomenthone	Isopulegol	Neoisoisopulegol	Piperitone
Midwest	39	1.402	5.897	0.921	2.990	0.112	0.035	0.429
Willamette	55	1.330	4.682	0.901	2.733	0.070	0.031	0.518
Madras	46	1.585	4.415	1.105	2.343	0.060	0.031	0.500
Idaho	38	1.464	4.685	1.120	2.501	0.078	0.030	0.467
Kennewick	59	1.496	4.909	1.224	2.070	0.059	0.030	0.333
Final average		1.455	4.918	1.054	2.527	0.076	0.031	0.449

Table II. 1992 *Mentha piperita* crop: constituent data summary (GC area %)

Region	Number of samples	Limonene	1,8-Cineole	Sabinene hydrate	D-isomenthone	Isopulegol	Neoisoisopulegol	Piperitone
Midwest	55	1.465	5.549	0.794	2.862	0.072	0.040	0.408
Willamette	96	1.321	4.856	0.823	2.805	0.065	0.025	0.475
Madras	55	1.641	4.705	1.096	2.621	0.069	0.032	0.490
Idaho	47	1.622	4.576	1.039	2.833	0.074	0.028	0.478
Kennewick	77	1.586	4.766	1.092	2.519	0.072	0.032	0.435
Final average		1.527	4.890	0.969	2.728	0.070	0.031	0.457

Table III. 1991 *Mentha piperita* crop: constituent data summary (GC area %)

Region	Number of samples	Limonene	1,8-Cineole	Sabinene hydrate	D-isomenthone	Isopulegol	Neoisoisopulegol	Piperitone
Midwest	48	1.716	5.783	0.700	2.998	0.067	0.026	0.472
Willamette	79	1.270	4.766	0.817	2.785	0.067	0.025	0.582
Madras	67	1.465	4.768	0.963	2.429	0.061	0.032	0.549
Idaho	42	1.577	4.700	0.993	2.904	0.073	0.027	0.513
Kennewick	43	1.510	4.832	0.984	2.577	0.073	0.030	0.479
Final average		1.508	4.970	0.891	2.739	0.068	0.028	0.519

Table IV. 1990 *Mentha piperita* crop: Constituent data summary (GC area %)

Region	Number of samples	Limonene	1,8-Cineole	Sabinene hydrate	D-isomenthone	Isopulegol	Neoisoisopulegol	Piperitone
Midwest	35	1.194	5.649	0.837	2.989	0.080	0.038	0.517
Willamette	88	1.355	4.615	0.816	2.789	0.077	0.032	0.587
Madras	58	1.463	4.573	1.031	2.525	0.076	0.040	0.517
Idaho	19	1.561	4.551	1.005	2.931	0.084	0.033	0.541
Kennewick	43	1.559	4.788	1.079	2.435	0.082	0.038	0.457
Final average		1.426	4.835	0.954	2.734	0.080	0.036	0.524

Table V. 1989 *Mentha piperita* crop: constituent data summary (GC area %)

Region	Number of samples	Limonene	1,8-Cineole	Sabinene hydrate	D-isomenthone	Isopulegol	Neoisoisopulegol	Piperitone
Midwest	42	1.164	5.938	0.741	2.956	0.055	0.003	0.302
Willamette	78	1.193	5.135	1.019	2.522	0.054	0.013	0.330
Madras	58	1.417	5.169	1.096	2.301	0.051	0.029	0.353
Idaho	43	1.527	5.094	1.043	2.766	0.058	0.022	0.339
Kennewick	42	1.411	5.350	1.151	2.307	0.059	0.026	0.357
Final average		1.342	5.337	1.010	2.570	0.055	0.019	0.336

Table VI. 1989-1993 *Mentha piperita* crops: combined data summary (GC area %)

Crop Year	Number of samples	Limonene	1,8-Cineole	Sabinene hydrate	D-isomenthone	Isopulegol	Neoisopulegol	Piperitone
1989	263	1.342	5.337	1.010	2.570	0.055	0.019	0.336
1990	243	1.426	4.835	0.954	2.734	0.080	0.036	0.524
1991	279	1.508	4.970	0.891	2.739	0.068	0.028	0.519
1992	330	1.527	4.890	0.969	2.728	0.070	0.031	0.457
1993	237	1.455	4.918	1.054	2.527	0.076	0.031	0.449
Five-year average		1.452	4.990	0.976	2.660	0.070	0.029	0.457
Typical Indian <i>arvensis</i>		2.200	0.500	0.005	10.270	2.020	1.800	1.080
Typical Chinese <i>arvensis</i>		2.875	0.440	0.022	9.200	1.218	1.030	1.406

Isopulegol: Isopulegol has a very high utility. It is consistently present at low levels in peppermint and in relatively high levels in cornmint. The material is easily resolved on conventional GC columns. The authors are not aware of a method of removal that would not cause very significant product loss or else adversely affect the levels of other important oxygenated terpenes present in the oil. The levels that are present in peppermint enable it to function as a sensitive method for detecting low levels of addition. Finally, its presence in peppermint is at a level that is significantly different from the level of its presence in cornmint:

- Peppermint—0.070 GC area %
- Typical Chinese cornmint—1.218 GC area %
- Typical Indian cornmint—2.020 GC area %

Summary

The authors demonstrated that the isopulegol levels present in mint oils, along with the levels of the compound tentatively identified as neoisopulegol, are presently the best indicators of the presence of cornmint in peppermint. This method offers a good detection threshold and is easily performed through standard GC techniques.

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