

DETERMINATION OF PEPPERMINT AND ORANGE AROMA COMPOUNDS IN FOOD AND BEVERAGES

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Received 21 March 2001, in revised form 18 April 2001

Abstract. Qualitative and quantitative variation of volatile aroma compounds in different foods and beverages containing peppermint and orange aroma was studied using the simultaneous distillation and extraction micromethod for isolating the aroma fraction and capillary gas chromatography for analysing the extracts. In peppermint aroma 41 constituents and in orange aroma 22 compounds were identified. The yields of aroma fractions from different materials varied from 0.2 up to 24 mg/g (peppermint) and from 0.03 up to 2 mg/g (orange).

Key words: *Mentha piperita*, *Citrus sinensis*, aroma compounds, tea, juice, chewing-gum, sweets, SDE, capillary GC.

Aromas are formed by volatile aromatic compounds, which are biosynthesized during the normal metabolic process in plants and which may be further modified by cooking or other processing. Peppermint and orange essential oils isolated from the peppermint herb or from the orange peel are the most important and most widely used flavouring ingredients in many food and beverage products, cosmetics, tooth-pastes, and other products. Natural orange essence obtained during the concentration of orange juice is also used as an important flavour addition to citrus products and other food and beverage products.

Numerous gas chromatographic (GC) studies have been carried out that deal with the analysis of the essential oils from peppermint leaves [1–7], from confectionery and beverages [8], and from orange juice [9–12], orange peel and leaves [13, 14], and orange essences [15]. Different methods have been used for the isolation of the aroma fraction from herbs, fruits, and food and beverage products, such as steam distillation [3, 4, 10, 14], supercritical fluid extraction [3], solid phase extraction [8, 9], extraction with liquid solvents [11, 12], headspace-GC technique [6, 9, 12], cold pressing [14], etc.

In this work peppermint and orange aroma fractions isolated from various food and beverage products were analysed using simultaneous distillation and extraction (SDE) and capillary GC techniques. The composition and yields of these extracts were compared with natural aromas obtained from peppermint leaves and orange fruit.

EXPERIMENTAL

Materials

For peppermint aroma research (samples 1 to 5): peppermint cultivated in Estonia (dried herb), Pompadour peppermint tea, commercial peppermint essential oil, Orbit peppermint chewing-gum, and peppermint sweets made in the Kalev factory (Estonia).

For orange aroma research (samples 6 to 10): orange fruit (peel and pulp), Fanta soft drink with orange aroma, Gutta natural orange juice (100%), orange aroma containing Chewits sweets.

Isolation of the essential oil

For the isolation of aroma compounds from peppermint and orange samples SDE Marcusson's micro-apparatus with *n*-hexane (500 µL) as solvent and *n*-tetradecane (1 µL) as internal standard was used. The distillation time was 2 h. No further concentration of the extract obtained was required.

Capillary gas chromatography

The aroma extracts (2–10 µL) were analysed with a Chrom-5 gas chromatograph with a flame ionization detector on two fused silica capillary columns (50 m × 0.2 mm) with bonded stationary phases (OV-101, PEG 20M). Helium with a flow rate 1.3–1.5 mL/min was used as the carrier gas with the split ratio of 1–150. The column temperature was programmed from 50 to 250 °C (OV-101) and from 70 to 220 °C (PEG 20M) at 2 °C/min. The injector temperature was regulated at about 200 °C.

The identification of the components of the aroma extracts was based on the comparison of their retention indices on two columns with the corresponding data of authentic compounds or with the components of reference oils. There was no need for GC/MS analysis, because the compositions of orange and peppermint aroma are well known.

The quantitative composition of individual compounds in the extracts was calculated by using peak areas without correction for the relative response factor. The quantitative yields (*Y*) of the aroma fraction in the starting material were calculated using the internal standard by the following formula:

$$Y = A_x \times K_{st}/A_{st},$$

where A_x and A_{st} are total peak areas of aroma compounds and the peak area of internal standard (*n*-tetradecane), respectively, and K_{st} is the content of *n*-tetradecane in the sample, mg/g.

RESULTS AND DISCUSSION

Peppermint aroma

The peppermint aroma extracts studied (samples 1–5) contained 41 compounds. They included monoterpenic and sesquiterpenic hydrocarbons, terpenic alcohols, ketones, and esters (Table 1). It is well known that monoterpenoids – menthone, isomenthone, menthyl acetate, menthol, and 1,8-cineole – are characteristic aroma components of *Mentha piperita* oil [1–7]. These compounds were the main components also in the peppermint aroma extracts studied in our laboratory. Neomenthol, menthofuran, limonene, piperitone, pulegone, β -caryophyllene, and germacrene D occurred in quantities over 1%.

Table 1. Results of qualitative and quantitative analysis of peppermint aroma samples

Compound	Retention index		Concentration, %				
	OV-101	PEG 20M	1*	2	3	4	5
α -Thujene	921	1029	0.1	0.05	–	–	–
α -Pinene	927	1029	0.8	0.2	0.2	0.2	0.3
Sabinene	964	1125	0.6	0.1	–	0.05	0.2
β -Pinene	968	1116	1.1	0.2	0.1	0.2	0.4
Myrcene	982	1161	0.3	0.05	0.7	0.1	0.1
α -Terpinene	1008	1180	0.4	0.1	–	0.1	0.4
<i>para</i> -Cymene	1011	1273	–	–	–	–	0.2
1,8-Cineole	1018	1211	7.5	1.9	0.7	1.9	4.0
Limonene	1020	1204					
<i>cis</i> - β -Ocimene	1027	1232	0.6	0.05	–	0.3	–
<i>trans</i> - β -Ocimene	1039	1250	0.1	0.5	–	–	0.1
<i>trans</i> -Sabinene hydrate	1055	1461	2.0	0.6	–	–	0.2
Terpinolene	1076	1282	0.2	0.05	0.1	–	0.1
Linalool	1086	1547	0.2	0.3	1.4	–	0.1
α -Thujone	1090	1417	0.1	–	0.3	0.1	0.2
β -Thujone	1094	1435	0.1	–	0.1	–	–
Menthone	1135	1464	19.1	24.3	25.0	12.8	15.3
Isomenthone	1142	1489	2.7	4.1	4.9	15.0	2.8
Menthofuran	1146	1483	3.2	0.3	4.0	1.4	1.4
Neomenthol	1151	1590	3.3	3.1	4.2	–	1.6
Menthol	1163	1637	44.4	45.3	47.3	37.6	58.3
Isomenthol	1171	1660	0.5	0.8	1.3	0.8	0.2
α -Terpineol	1172	1693					
Estragol	1179	1660	0.05	0.2	–	–	–
Carvone	1215	1725	–	–	0.3	–	0.5
Pulegone	1219	1662	1.3	0.8	1.6	0.2	0.7

Table 1 continued

Compound	Retention index		Concentration, %				
	OV-101	PEG 20M	1*	2	3	4	5
Piperitone	1228	1720	0.5	1.1	0.6	0.2	0.3
<i>trans</i> -Anethol	1260	1819	0.1	0.2	0.2	0.3	0.1
Menthyl acetate	1277	1560	1.2	5.9	1.9	21.9	2.7
Carvacrol	1291	2186	0.1	0.2	0.2	0.8	0.1
α -Copaene	1369	1486	0.05	0.1	–	0.3	0.1
γ -Elemene	1377		0.3	0.5	0.4	0.2	0.2
β -Caryophyllene	1411	1589	1.5	2.2	0.8	0.8	1.1
β -Farnesene	1445	1660	0.3	0.2	0.1	0.7	0.2
Allo-aromadendrene	1464	1685	–	–	–	–	0.4
Germacrene D	1470	1700	1.8	1.8	0.2	0.2	1.1
γ -Muurolene							
δ -Cadinene	1509	1749	0.1	0.1	0.1	–	0.1
Germacrene-4-ol	1559	2038	0.05	–	0.1	–	–
Viridiflorol	1576	2255	0.7	0.4	–	0.6	0.1
Farnesol	1654	2255	0.1	0.3	–	–	0.2
Group composition:							
Monoterpenes			14.1	4.0	1.7	2.9	6.3
Oxygenated monoterpenes			77.1	86.6	93.4	91.0	84.4
Sesquiterpenes			4.0	4.8	1.5	2.2	3.1
Oxygenated sesquiterpenes			1.2	1.0	0.4	0.6	0.5
Total			96.4	96.4	97.0	96.7	94.3

* Sample 1 – peppermint leaves, 2 – peppermint tea, 3 – peppermint essential oil, 4 – peppermint sweets, 5 – peppermint chewing-gum;
– not detected.

The peppermint aroma extracts isolated from different materials showed different quantitative composition (Table 1, Fig. 1). The aroma fraction from dried peppermint leaves (sample 1) contained a larger number of components than the other samples. The monoterpene fraction was the largest (14%) in this oil. Compared with the other samples, the content of limonene (3%) and 1,8-cineole (5%) was higher and the content of menthyl acetate (1%) was lower in this sample. In the aroma fraction of peppermint tea (sample 2) from Germany, prepared also from dried peppermint leaves, the monoterpene fraction was smaller (4%) and the content of menthyl acetate higher (6%) than in Estonian peppermint. These differences may be caused by different origins of peppermint plants or changes in the oil during the preparation of tea.

Menthone and menthol isomers, which possess peppermint-like aroma, were present in high concentrations (>90%) in the commercial peppermint oil (sample 3). This oil did not contain much mono- and sesquiterpenic hydrocarbons (total 3%).

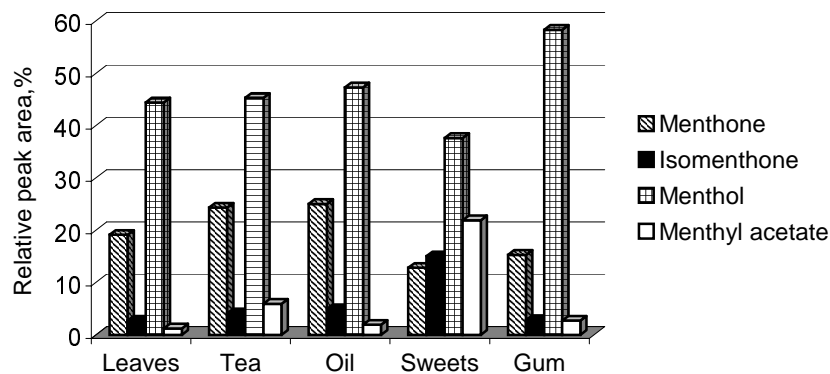


Fig. 1. Variation in the concentrations of the main components of peppermint aroma isolated from different materials.

Comparison of the aroma composition of samples 4 and 5 with sample 3 showed that peppermint oil had been added to the chewing-gum and to sweets as an aroma admixture. It is interesting to note that the aroma of peppermint sweets contained more menthyl acetate (22%) and isomenthone (15%) than the other samples. These compounds may be formed during the preparation of sweets.

The dried peppermint leaves (sample 1) gave the highest yield of aroma compounds (24 mg/g) as comparison of the yields of the aroma fractions from different samples (Fig. 2) reveals. The yields of aroma from the tea and from the chewing-gum (samples 2 and 4) were similar (10 mg/g), but the yield of oil from the sweets (sample 5) was very small (0.2 mg/g).

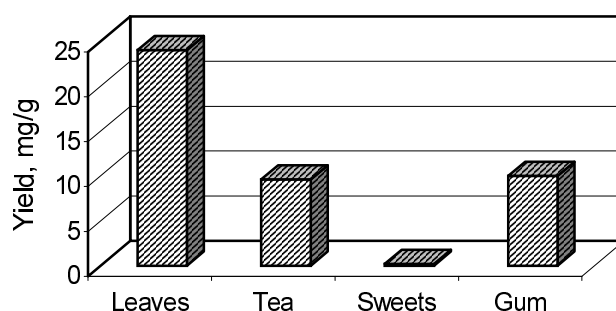


Fig 2. Variation in the yield of peppermint aroma isolated from different materials.

Orange aroma

Table 2 gives a list of the compounds identified, their retention indices measured in two columns, their concentration and component group concentrations of the orange aroma fractions (samples 6–10) isolated from orange fruit,

orange juice, Fanta orange drink, and orange chewing-gum sweets. In these samples 22 components were identified, accounting for more than 90% of the oil fractions.

Table 2. Results of qualitative and quantitative analysis of orange aroma samples

Compound	Retention index		Concentration, %				
	OV-101	PEG 20M	6	7	8	9	10
α -Pinene	927	1029	0.4	0.4	0.3	0.1	0.5
Sabinene	964	1125	0.5	0.1	0.05	0.3	0.2
β -Pinene	968	1116	0.05	–	–	–	0.2
Myrcene	983	1161	2.1	1.4	1.7	1.4	1.8
Octanal	985						
3-Carene	1003	1148	0.1	–	0.2	0.4	0.1
Limonene	1020	1204	93.4	91.0	91.0	83.1	92.0
γ -Terpinene	1048	1246	0.05	–	0.1	0.2	0.2
Fenchone	1064	1397	0.1	0.1	–	–	–
Terpinolene	1076	1282	0.05	–	0.2	–	–
Linalool	1086	1547	1.4	0.6	0.3	1.4	0.3
Nonanal	1086						
Camphor	1120	1511	0.1	0.1	–	–	–
Citronellal	1132	1480	0.1	0.6	0.2	0.5	–
Terpinen-4-ol	1159	1593	0.05	0.5	0.1	–	–
α -Terpineol	1173	1693	0.2	0.4	0.7	3.7	0.1
Decanal	1186	–	0.1	0.1	0.3	1.0	0.2
Neral	1216	1677	0.2	–	–	–	–
Geranial	1249	1728	0.1	–	–	–	–
α -Humulene	1441	1660	0.1	–	–	–	–
Valencene	1482	1737	0.4	0.8	0.8	0.4	0.1
δ -Cadinene	1508	1749	–	–	0.3	0.2	–
Group composition:							
Monoterpenes			96.7	93.0	93.6	85.5	95.0
Oxygenated monoterpenes			2.3	2.3	1.6	6.6	0.6
Sesquiterpenes			0.5	0.8	1.1	0.6	0.1
Total			99.5	96.1	96.3	92.7	95.7

* Sample 6 – orange peel, 7 – orange pulp, 8 – orange juice, 9 – Fanta orange drink, 10 – orange chewing-gum sweets;
– not detected.

The content of monoterpenes was very high (86–97%) in orange aroma fractions, the principal component being limonene (83–93%), which is in agreement with reference data [7–15]. Myrcene content was found to be 1–2% and the content of other monoterpenes lower than 1% in these oils. Monoterpenic oxygen compounds accounted for 1–7%. The concentration of linalool and α -terpineol was over 1% (Fig. 3) and that of sesquiterpenes was rather small (0.1–1%).

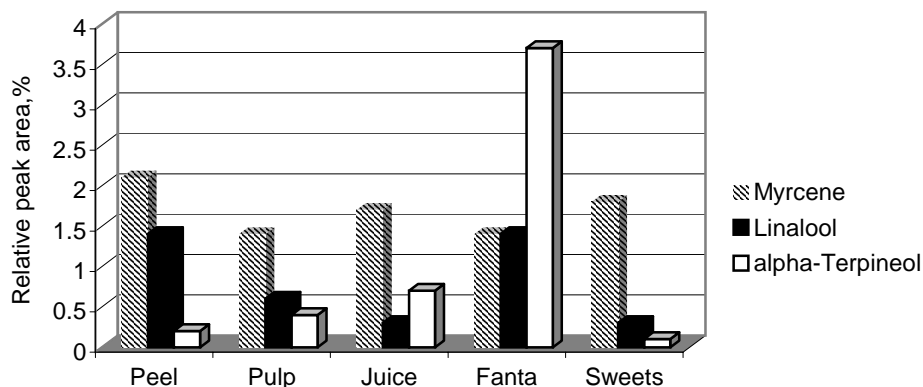


Fig. 3. Variation in the concentrations of myrcene, linalool, and α -terpineol in orange aroma isolated from different materials.

The small quantitative differences in the composition of orange peel oil (sample 6) compared with reference data [13, 14] may be due to different origins or different growing conditions of orange trees. The aroma fraction from the orange pulp (sample 7) contained less limonene and more citronellal, terpinen-4-ol, and α -terpineol than the orange peel oil. The aroma fraction from the orange juice (sample 8) was quite similar to that of the orange pulp as the juice was obtained from orange pulp. The aroma fraction from the chewing-gum sweets (sample 9) contained only two peaks with concentrations over 1%: limonene and myrcene. In addition there were some unidentified compounds that are not characteristic of orange aroma. Fanta orange drink (sample 10) showed a somewhat different aroma fraction composition than the other samples. The content of limonene was lower (83%), that of α -terpineol was higher (4%), and there were more (up to 7%) uncharacteristic peaks of orange aroma than in the other samples.

The yield of aroma fractions from five orange samples is shown in Fig. 4. The greatest amount (2 mg/g) of aroma components was isolated from the orange peel (sample 6) and the lowest (0.03 mg/g) from Fanta (sample 9). The yield of aroma from the sweets (sample 10) was 1 mg/g and from the orange pulp and juice (samples 7 and 8) 0.1 mg/g.

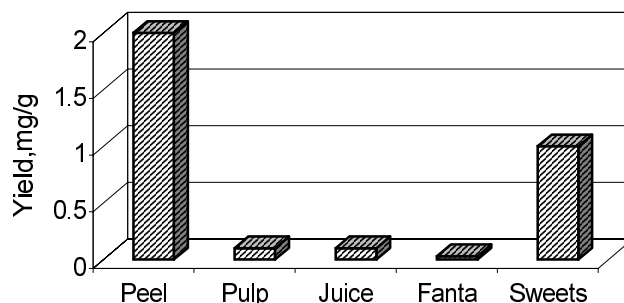


Fig. 4. Variation in the yields of orange aroma isolated from different materials.

CONCLUSIONS

Comparison of the peppermint and orange aroma composition of the natural herb and fruit with the same aroma isolated from various foods and beverages showed that natural aroma had been used in these products. The only exception was the Fanta orange drink where the limonene concentration was much lower than in the other orange samples and which had up to 7% uncharacteristic peaks for orange aroma. The results of this work demonstrate that the capillary GC method can be successfully used for the quality control of foods and beverages.

ACKNOWLEDGEMENT

Financial support for the work reported here was provided by the Estonian Science Foundation (grant No. 4028).

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PIPARMÜNDI- JA APELSINIAROOMI MÄÄRAMINE TOIDUAINETES JA JOOKIDES

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Piparmündi- ja apelsiniaroom eraldati proovidest samaaegse destillatsiooni ja ekstraktsiooni mikromeetodil ning analüüsiti neid kapillaargaasikromatograafiliselt kahe kolonni (OV-101, PEG 20M) abil. Võrreldi toiduainetest (tee, mahl, närimiskumm, kompvekid) eraldatud aroomide koostisi looduslikust materjalist (taimed, puuviljad) eraldatud aroomide ja tööstuslike eeterlike õlide omadega ning kirjandusandmetega. Erinevast materjalist eraldatud aroomifraktsioonide saagised jäid apelsiniaroomi puhul vahemikku 0,03–2 mg/g ja piparmündiaroomi puhul vahemikku 0,2–24 mg/g.