JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Comparison of Isolation Methods for the Determination of Important Aroma Compounds in Black Currant (*Ribes nigrum* L.) Juice, Using Nasal Impact Frequency Profiling

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The influence of isolation method on the determination of important aroma compounds in black currant juice was investigated by surface of nasal impact frequency (SNIF) gas chromatography−olfactometry (GC-O). The applied methods were solvent extraction, static headspace, and purge and trap using 15 and 60 min of purge time. By the four methods, a total of 59 odors were observed, and, of these, 44 corresponded to compounds that could be identified. For the headspace methods increasing purge volumes resulted in recoveries of additional, less volatile compounds. The main compound groups recovered by the headspace methods were esters and terpenes, whereas compounds recovered by solvent extraction were not as dominated by fruity odors. For most compounds there was agreement between the size of the SNIF value obtained by GC-O and the amount of the measurable compound found by gas chromatography−mass spectrometry.

KEYWORDS: GC−olfactometry; NIF; SNIF; aroma isolation method; black currant juice aroma; GC-MS

INTRODUCTION

Most cultivation and usage of black currants occurs in Europe, and the main part of the fruit is processed as frozen berries, juice, syrup, or jam. Black currants are characterized by having high contents of vitamin C, organic acids, and anthocyanins (*1*). The aroma of black currant berries constitutes >150 aroma compounds, of which the major groups are terpenes, esters, and alcohols (*2*). The processing of berries to juice leads to some major changes in the aroma composition (*3*−*6*). Important compounds of black currant berries have been identified by gas chromatography−olfactometry (GC-O) by Latrasse et al. (*7*) and Mikkelsen and Poll (*5*) and those of black currant nectar and juice by Iversen et al. (*3*) and Varming and Poll (*6*). Compounds reported in two or more of these papers include methyl butanoate, ethyl butanoate, ethyl hexanoate, cineole, linalool, 4-terpineol, β-damascenone, 1-octen-3-one, 2-methoxy-3-isopropylpyrazine, and 4-methoxy-2-methyl-2-butanethiol.

Most aroma isolation methods are based on the analysis of either a solvent extract of a food or the headspace above it. During GC analysis of a solvent extract low-boiling compounds can be masked by the solvent front, and the method results mainly in the isolation of intermediate and higher boiling compounds. By static headspace collection, equilibrium between the sample and the headspace above it is obtained and usually a fraction of the headspace is withdrawn for GC analysis. During dynamic headspace collection and purge and trap the sample is purged with a gas stream above or through the sample, respectively, continuously removing the headspace, shifting the sample/air equilibrium. Reviews concerned with the issue of aroma isolation methods have been published (*8*, *9*).

The part of the volatiles present in a food system that is responsible for its odor can be identified by sniffing the GC effluent of an aroma isolate. Combined hedonic aroma response measurement (CHARM) analysis and aroma extract dilution analysis (AEDA) are GC-O methods that have often been used. These methods are based on one or a few assessors sniffing stepwise dilutions of a solvent extract until no odors can be detected. Methods of GC-O have been reviewed by Blank (*10*).

The principle of dilution to detection threshold has been questioned as the method is based on the assumption that slopes of the psychophysical functions for all aroma compounds are equal, which is not the case (*11*). Also, the occurrence of gaps in coincident response for panelists during extract dilution sniffing analysis has been contemplated (*12*), and due to large variances among subjects, more than one or a few assessors are required for reliable GC-O results (*11*−*14*). Some of these problems are overcome by the nasal impact frequency (NIF) method described by Linssen et al. (*15*) and Pollien et al. (*14*). The NIF method uses only one dilution level, but GC-O is repeated by a number of panelists; that is, data treatment is based on detection frequency rather than successive dilutions. For this method a panel of a minimum of 6, optimally 8−10, assessors

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10.1021/jf035133t CCC: $27.50
Published on Web 02/21/2004

are needed for reliable results (*14*), and the method has been found to correlate well with sensory odor intensities (*13*).

The purpose of the present study was to determine important aroma compounds in black currant juice using four different isolation methods and to investigate how the relative importance of the aroma compounds is influenced by isolation method. Methods of solvent extraction, static headspace collection, and purge and trap were applied and important aroma compounds determined by NIF using nine assessors.

MATERIALS AND METHODS

Materials. A commercial black currant juice of the variety Ben Lemond was obtained from an industrial plant. The juice preparation included crushing, heating, enzyme treatment (50 °C/maximum 6 h), pressing, pasteurization (98 °C/30 s), clarification (45 °C/maximum 6 h), and filtration. The juice was stored at −18 °C and thawed immediately before use.

Static Headspace Collection. One hundred and fifty grams of black currant juice was weighed into a 500 mL glass flask equipped with a purge head. To maintain static conditions, the gas inlet of the purge head was sealed with a box nut. One milliliter of internal standard (50 μL/L 4-methyl-1-pentanol, Aldrich, Steinheim, Germany) was added to verify that the analysis performed satisfactory. The sample was placed in a water bath at 30 °C and allowed to equilibrate for 60 min. The box nut was then removed from the purge head and replaced with a tube connected to running tap water, slowly displacing (5 min) the headspace (430 mL) above the sample. The volatiles were collected on a trap containing 250 mg of Tenax-GR (mesh size = 60/80, Buchem bv, Apeldoorn, The Netherlands). To detect a possible breakthrough of volatiles, a second identical trap was connected in series with the first trap and subjected to GC-MS analysis.

Purge and Trap. Sample preparation was the same as for static headspace collection. The sample temperature was equilibrated in a 30 °C water bath for 10 min. Under magnetic stirring (200 rpm) the sample was then purged through the liquid with nitrogen (100 mL/min) for either 15 or 60 min, and volatiles were collected into Tenax GR traps. The purge times corresponded to purge volumes of 1.5 and 6.0 L, respectively.

Solvent Extraction. One hundred and fifty grams of black currant juice was weighed into a 500 mL blue-cap flask, and 50 mL of ether/pentane 1:1 and 1.00 mL of internal standard (50 μL/L 4-methyl-1-pentanol, Aldrich) were added. Volatiles were extracted for 30 min under magnetic stirring (100 rpm). The sample was then left for phase separation for 15 min and placed in a freezer, allowing the water phase to freeze and the solvent phase to be decanted. The solvent phase was then dried with Na_2SO_4 and concentrated to 0.20 g under a gentle stream of nitrogen. The extract was stored at −18 °C, and prior to GC analysis, 2.0 μL of the extract was injected into a Tenax-GR trap.

GC-MS. The collected volatiles were thermally desorbed using an automated thermal desorber (ATD 400, Perkin-Elmer). Desorption time from the trap (250 °C) to the cold trap (5 °C) was 15 min, with a helium flow of 60 mL/min. Volatiles were desorbed from the cold trap to the GC column by flash heating from 5 to 300 °C. Using a split ratio of 1:10, separation and identification of aroma compounds was carried out on a Hewlett-Packard (Palo Alto, CA) G1800A S GC-MS system equipped with a J&W Scientific DB-Wax column (30 m × 0.25 mm × 0.25 μm) using helium as carrier gas (1 mL/min). The column temperature was kept at 40 °C for 10 min, increased with 6 °C/min to 240 °C, and kept isothermal for 25 min. For analysis of solvent extracts, a solvent delay of 3 min was used. The mass selective detector used the electron ionization mode, and the mass/charge (*m*/*z*) range between 20 and 425 was scanned. Samples were analyzed in triplicate. Identifications were carried out by probability-based matching with mass spectra in the G1035A Wiley library (Hewlett-Packard) and comparisons with mass spectra and retention indices (RI) of authentic reference standards analyzed under identical conditions. Aroma standards (numbers referr to **Table 1**) were obtained from **1**, **3**, **6-1**, **10**, **12**, **13**, **16**, **19**, **21**, **23**, **25**, **27**, **29**, **31**−**33**, **35**, **36**, **40**, **50**, **51**, and **58** (Sigma-Aldrich, Copenhagen, Denmark), **2**, **4**, **5-2**, **7**, **8**, **14**, **49**, and **57** (Merck, Darmstadt, Germany), **5-1**, **6-2**, **20**, and **30** (Fluka, Buchs, Switzerland), **55** (Supelco, Bellefonte, PA), **34** (Roth, Karlsruhe, Germany), **17** (Lancaster, Morecambe, U.K.), 15 (K&K Laboratories, Plainview, NY), and **46** (Firmenich, La Plaine, Switzerland). When authentic reference standards could not be obtained, tentative identifications were based on matching with mass spectra in the Wiley library and comparisons of RI and odor properties reported in the literature. Linear retention indices were calculated after analysis under the same conditions of an *n*-alkane series (C9−C24). The amounts of the measurable identified aroma compounds were calculated on the basis of single ions.

GC-O. GC-O and GC−flame ionization detection (FID) were carried out on a Hewlett-Packard 5890 GC equipped with an SGE olfactory detector outlet ODO-1. The volatiles were thermally desorbed from the traps using a short-path thermal desorber model TD-4 (Scientific Instrument Services, Inc., Ringoes, NJ). Dry purge time was 20 min, and desorption time was 3 min. The column type and GC settings were the same as for GC-MS. For GC-O the column was detached from the FID and led directly to the sniffing port, where the effluent was mixed with humidified air (150 mL/min). Nine people between 25 and 61 years of age were recruited among staff and students of the department. The panelists, who all were familiar with GC-O, were instructed to note starting and ending time of the odors and to give free choice descriptions of the odor qualities. One sniffing session continued for 40 min, and each panelist participated once in the sniffing of each of the four isolates, performed in random order. The nine individual profiles were summed to one NIF profile, but odors detected by only one or two judges were considered to be noise (*13*). Peak heights (number of judges) of the profiles are termed nasal impact frequency (NIF), and peak areas are termed surface of nasal impact frequency (SNIF) (number of judges × min).

Pollien et al. (*14*) estimated a least significant difference (LSD) between SNIF values for a given peak found in two different samples. The LSD was calculated from the standard deviation (SD), based on between- and within-panel variation, and Student's constant (*t*), which takes into account the number of degrees of freedom:

$$\mathrm{LSD} = t(\sqrt{2})\mathrm{SD} \quad (1)$$

We used this approach, as an approximation, to estimate the LSD between SNIF values of the four isolation methods of a given peak. With the number of peaks in our study, *t* approaches 2, and the SD is based on an average relative standard deviation of 18% (*18*) of the SNIF mean value for a given peak:

$$\mathrm{LSD} = 2(\sqrt{2})18/100 \times \bar{x} \quad (2)$$

GC-O/FID retention times were correlated to GC-MS retention times using a standard mixture of potent aroma compounds in the relevant retention time span, analyzed under the same conditions.

RESULTS AND DISCUSSION

Odors Observed and Compounds Identified by the Four Methods. A total of 59 contributors to the aroma were detected by GC-O by three or more judges. Of these, 44 corresponded to compounds that could be identified either fully or tentatively (**Table 1**). The remaining 15 compounds were present in concentrations below the GC-MS detection limit but above the sensory threshold of GC-O, and they were all in the medium- to low-volatility area. The main groups of compounds identified were esters and oxygenated terpenes. Compared to earlier studies of important compounds of black currant berry or juice, the total number of odors observed in this study was much higher. This is explained by (1) the application of four methods covering a broad spectrum of compounds, (2) a purge time of 60 min with a flow of 100 mL/min, which allowed a considerable concentration of aroma compounds, and (3) participation of nine assessors, which increased the sensitivity of GC-O. Compounds identified in this study that were previously reported by two or

Table 1. Odor Descriptors of Black Currant Juice Aroma Compounds As Determined by Each of the Four Isolation Methods

				SNIF[c] values					
no.	RI[a]	compound	odor descriptors[b]	static headspace	P&T 15	P&T 60	solvent extraction	LSD[d]	lit.[e]
1	844	dimethyl sulfide[f]	vegetable soup, cabbage, moldy	1.9	1.4	0	m[g]	0.6	
2	864	methyl acetate[f]	fruit, solvent, black currant juice	2.3	2.3	1.0	m	1.0	
3	916	methyl 2-methylpropanoate[f]	fruit	0	0	0.4	m	0.1	
4	947	ethyl propanoate[f]	solvent, acetone, fruit	1.2	2.6	2.4	m	1.1	
5	965	2,3-butanedione[f]	caramel, dirty socks, fruit, spirit, pineapple	3.5	4.2	5.9	1.4	1.9	*7*
	989	methyl butanoate[fh]							*3*, *5*, *6*
	1004	methyl 2-methylbutanoate[f]	fruit, spirit, solvent, chewing gum	2.9	2.9	2.2	0.8	1.1	
6		*and/or*							
	1007	2-methylpropyl acetate[f]							
7	1030	ethyl butanoate[f]	fruit, pineapple, acetone, caramel	4.8	4.3	5.6	3.9	2.4	*3*, *5*–*7*
8	1055	ethyl 3-methylbutanoate[f]	black currant, sweet, acidulous fruit	0	0	0.9	0	0.1	
9	1094	methyl *trans*-2-butenoate[j]	black currant, fruit	0	0	1.5	0	0.0	
10	1115	mixture of 2- and 3-methylbutyl acetates[f]	banana, chewing gum	0	0	0.9	0	0.1	*6*
11	1171	isocineole[i]	solvent, sweet, flower	0.8	0.8	1.3	0	0.4	
12	1194	cineole[f]	liquorices, menthol, pine, cat urine	0.8	1.9	3.0	0	0.6	*5*–*7*
13	1206	mixture of 2- and 3-methyl-1-butanols[f]	sweat, green, acidulous, fruit	0	1.4	2.8	1.5	0.7	*5*, *7*
14	1229	ethyl hexanoate[f]	fruit, wine gum, sweets	2.1	2.1	1.6	0.3	0.8	*3*, *5*, *6*
15	1267	hexyl acetate[f]	tobacco, acidulous, citrus, green, herbs	0	0	1.1	0.3	0.2	
16	1278	octanal[f]	flower, fruit, orange	0	0	1.0	0	0.1	
17	1289	1-octen-3-one[f]	mushroom	0.7	1.5	1.4	0.8	0.6	*3*, *5*
18	1305	2-methyl-3-furanthiol[j]	vitamin, bouillon, cooked meat	0.3	1.9	3.4	2.4	1.0	
19	1313	6-methyl-5-hepten-2-one[f]	black currant, boiled fruit, "bitter"	0	0	1.3	0	0.2	
20	1332	*cis*-rose oxide[f]	paper, flower, greenish	0.4	0.4	1.6	0	0.3	*5*
	1361	methyl-2-hydroxy butyrate[k]	flower, yeasty, deep frying fat,	1.6	2.1	1.7	1.2	0.8	*6*
21		*and/or*	spoiled fruit						
	1372	*cis*-3-hexen-1-ol[f]							
22	1378	methyl octanoate[f]	green	0	0	0.4	0	0.1	*3*
23	1380	nonanal[f]	library, flower, citrus	0.7	0.7	0.7	0	0.3	*3*
24	1398	unknown	mushroom, sour dishcloth	0	0	0.4	0.7	0.1	
25	1419	2-methoxy-3-isopropylpyrazine[f]	pea, dry, pea pod, grass, bell pepper	1.2	1.2	1.8	1.2	0.7	*5*, *7*
26	1429	acetic acid[f]	acetic acid	0	0	0	0.7	0.1	
27	1433	methional[l]	boiled potato, deep frying fat	1.0	1.2	2.0	2.0	0.8	
28	1469	unknown	unpleasant flower, deep frying fat	0	0	0.7	0	0.1	
29	1476	decanal[f]	sweetish, orange, flower	0	0	0.7	0	0.1	
	1498	camphor[f]	green, dry, green house, leaf	0	0.8	1.3	0.5	0.3	
30		*and/or*							
	1504	1,4-dimethyl-3-cyclohexenylmethyl ketone[k]							
31	1512	3-methoxy-2-isobutylpyrazine[f]	dry, green, leaf, spicy, green pepper	0.7	1.3	1.6	0.6	0.5	
32	1530	(*E*)-2-nonenal[l]	library, cucumber salad	0	0.4	1.1	0.2	0.2	*5*
33	1540	linalool[f]	althea, flower, sweet candy, fruit	0	0.5	1.2	0	0.2	*6*, *7*
34	1595	4-terpineol[f]	green, licorices, moldy	0	0	1.4	0	0.2	*5*, *6*
35	1613	butanoic acid[f]	parmesan cheese, vomit, butanoic acid	0	0	0	2.1	0.3	
36	1655	mixture of 2- and 3-methylbutyric acids[f]	dirty socks, vomit, butanoic acid	0	0	0	1.4	0.2	
37	1658	3-mercapto-3-methyl-1-butanol[i]	bouillon, vitamin, cooked meat	0.7	1.1	1.1	0	0.4	
38	1668	unknown	sour, flower, pearl onion	0	0	0.5	0	0.1	
39	1679	unknown	spoiled food	0	0	0.7	0	0.1	
40	1688	α-terpineol[f]	rice, green, flower, washing up liquid	0	0.2	0.4	0.6	0.2	
41	1710	phellandral[k]	rice, licorices, flower	0	1.1	2.8	1.4	0.7	
42	1716	unknown	liver pate, onion	0	0	0	0.9	0.1	
43	1754	unknown	green, cucumber, acid, dry	0	0	0.6	0	0.1	
44	1785	unknown	rice, greenish, moldy, tobacco	0	0	0.4	0.5	0.1	
45	1801	unknown	boiled fruit, alcoholic fruit, flower	0	0	1.0	0	0.1	
46	1813	β-damascenone[f]	black currant juice, boiled fruit, flower	0.9	1.0	1.3	1.1	0.5	*5*–*7*
47	1838	unknown	tobacco, woody, rubber	0	0	1.2	0.6	0.2	
48	1860	unknown	baked oats, fruit juice	0	0.4	0	0	0.1	
49	1866	benzyl alcohol[f]	perfume, flower, fruit	0	0	0.4	0	0.1	
50	1902	2-phenylethanol[f]	flower, rose	0	0	1.0	0.9	0.2	
51	1936	β-ionone[f]	flower, rose, menthol, berries, violet	0	0.6	0.5	0	0.1	
52	1991	unknown	curry, licorices	0	0	0	0.5	0.1	
53	2004	unknown	flower	0	0	0.5	0	0.1	
54	2027	unknown	clove, cake, spices	0	0	1.0	0.7	0.2	
55	2068	4-methylphenol[f]	bad smell, horse manure, leather	0	0	0.9	0.8	0.2	
56	2131	unknown	fruit, flower, scent eraser	0.7	1.2	1.5	1.4	0.6	
57	2153	eugenol[f]	Christmas, dentist, eugenol	0	0	1.7	1.0	0.3	*5*
58	2181	4-vinyl-2-methoxyphenol[f]	dentist	0	0	0	0.6	0.1	
59	2220	unknown	coconut, mandarin, dill, perfume	0	0	0.8	2.7	0.4	

[a] Retention indices calculated from GC-MS data. [b] Most frequent odor quality perceived during GC-O. [c] Peak areas of individual odors detected by three to nine assessors. [d] Estimated from eq 2. [e] Compounds previously reported as being important in black currant berry or juice. [f] Mass spectra and RI agreed with authentic standards. [g] Sniffing started at RI 950 due to the solvent peak. [h] Odor descriptions matching methyl butanoate were only recorded for P&T 60 and were here mixed in the descriptions of 2,3-butanedione. [i] Mass spectra agreed with the Wiley library and RI agreed with literature values. [j] No interpretable MS signal; RI and aroma properties agreed with the literature. [k] Mass spectra agreed with the Wiley library. [l] No interpretable MS signal; RI and aroma properties agreed with authentic standards.

Table 2. Top Five Most Potent Compounds of Black Currant Juice Aroma As Determined by Each of the Four Isolation Methods

static headspace		P&T 15		P&T 60		solvent extraction	
SNIF[a]	compound	SNIF	compound	SNIF	compound	SNIF	compound
4.8	ethyl butanoate (**6**)[b]	4.3	ethyl butanoate (**6**)	5.9	2,3-butanedione (**5**) methyl butanoate	3.9	ethyl butanoate (**6**)
3.5	2,3-butanedione (**5**)	4.2	2,3-butanedione (**5**)	5.6	ethyl butanoate (**6**)	2.7	unknown (**59**)
2.9	methyl 2-methylbutanoate 2-methylpropyl acetate (**6**)	2.9	methyl 2-methylbutanoate 2-methylpropyl acetate (**6**)	3.4	2-methyl-3-furanthiol (**18**)	2.4	2-methyl-3-furanthiol (**18**)
2.3	methyl acetate (**2**)	2.6	ethyl propanoate (**4**)	3.0	cineole (**12**)	2.1	butanoic acid (**35**)
2.1	ethyl hexanoate (**14**)	2.3	methyl acetate (**2**)	2.8	2/3-methyl-1-butanol (**13**)	2.0	methional (**27**)

[a] SNIF = peak areas of individual odors. [b] Numbers in parentheses correspond to compounds in **Table 1**.

more papers, by GC-O, as important for black currant berry or juice are methyl butanoate, ethyl butanoate, cineole, 3-methyl-1-butanol, ethyl hexanoate, 1-octen-3-one, 2-methoxy-3-isopropylpyrazine, linalool, 4-terpineol, and β-damascenone. Other compounds previously reported as being important for black currant aroma were, however, not found to be important in the present study (*3*, *5*−*7*). This could be due to different isolation and GC-O methods being used, as well as berry variety and degree of processing influences on the aroma profile (*4*−*6*, *16*). Some of the compounds identified by GC-MS in this study have not previously been reported in either black currant berry or juice. With varying certainty of identification these compounds were methyl 2-methylpropanoate, ethyl propanoate, 2-methyl-3-furanthiol, 6-methyl-5-hepten-2-one, methional, 3-methoxy-2-isobutylpyrazine, 3-mercapto-3-methyl-1-butanol, and 4-vinyl-2-methoxyphenol.

The most odors were observed by P&T 60 (51) followed by solvent extraction (32), P&T 15 (28), and static headspace (20). This was expected because P&T 15 results in collection of 3.5 times the headspace volume of static headspace, and P&T 60 results in collection of 4 times the headspace volume of P&T 15. P&T 60 and solvent extraction led to relatively more odors with high retention indices than static headspace and P&T 15. For most odors, P&T 60 resulted in the same or higher SNIF values than the other methods. Exceptions from this were compounds with retention indices below 900, where smaller SNIF values were observed by P&T 60 due to breakthrough on the Tenax GR traps. When solvent extracts were analyzed, only a fraction of the extract could be injected; therefore, SNIF values of this method were sometimes smaller than for P&T 15 and P&T 60.

Six odors corresponding to less volatile compounds were observed only by solvent extraction, namely, the three acids, 4-vinyl-2-methoxyphenol, and two unknowns. Sixteen odors were observed by P&T 60 only, namely, five esters, three carbonyls, one alcohol, one terpene, and six unknowns. Comparing the headspace methods, all odors perceived by static headspace collection were also observed by P&T 15, and all odors observed by P&T 15 were also observed by P&T 60. The only exceptions were dimethyl sulfide, due to breakthrough of the traps, and an unknown (**48**). Static headspace collection and P&T 15 differed from P&T 60 particularly in that a lower number of esters and aldehydes, and no phenolics, were observed. The relative number of esters and terpenes observed by solvent extraction was lower than for the headspace methods.

A ranking of compounds within each method according to their SNIF values (based on **Table 1**) is shown in **Table 2**. Ethyl butanoate was the only compound ranked in the top five by all methods. 2,3-Butanedione was represented by the three headspace methods, and static headspace and P&T 15 further ranked three esters in the top five, of which two were the same. According to P&T 60 and solvent extraction no additional esters were in top five, but both ranked 2-methyl-3-furanthiol in the five most important. One terpene and one alcohol were further ranked by P&T 60. When compared to the other headspace methods P&T 60 ranked some less volatile compounds in the top five. Compounds additionally ranked by solvent extraction were butanoic acid, methional, and an unknown. Relative to the headspace methods solvent extraction was dominated by fewer compounds representing fruity odors.

Partially confirmatory results have been reported for the GC-O analysis of cooked seafood products. Purge and trap and static headspace were found to give similar results for the more volatile compounds, whereas AEDA of solvent extraction methods was characterized by identification of mainly intermediate- and low-volatility compounds (*17*, *18*). In a study concerning tea powder, the majority of the compounds identified by static headspace were also identified by AEDA, but by AEDA several additional compounds were identified (*19*).

Relative Concentrations of Compounds Identified by the Four Methods. The relative concentrations of measurable odorous compounds are shown in **Table 3**. Results are based on MS peak areas of single ions, where the highest concentration measured of each compound is set to 100. Some of the compounds listed for static headspace, P&T 15, and solvent extraction were present in very low concentrations; hence, identification was only possible using P&T 60. P&T 60 gave the best results in terms of aroma recovery, followed by P&T 15, but for some of the less volatile compounds the largest amounts were recovered by solvent extraction. The observation by GC-O (**Table 1**) that P&T 60 was subject to breakthrough of the traps for dimethyl sulfide and methyl acetate, and P&T 15 for dimethyl sulfide, was verified by GC-MS. By GC-O, 10 known compounds were detected only using P&T 60 (**Table 1**), whereas by GC-MS decanal and phellandral were the only two compounds detected solely by P&T 60, meaning that the concentrations obtained by the other methods for the remaining eight compounds must have been lower than their odor thresholds.

Generally SNIF values (**Table 1**) corresponded to GC-MS peak areas. The few deviations from this can be due to assessors being less sensitive to changes in concentration than GC-MS or the concentration level having reached the assessor's response plateau. In addition, broader and more overlapping peaks were found by GC-O of P&T 60 than by the other headspace methods; hence, SNIF values of the involved coeluting aroma compounds may be uncertain. In a study by Pollien et al. (*20*) some, but not high, correlations between SNIF values and concentrations of a standard aroma solution were found.

Determination of the isolation method resulting in the GC-O profile closest to the situation during eating can, for example, be established by comparison with sensory evaluation data.

Table 3. Relative Concentrations of the Important Aroma Compounds of Black Currant Juice As Determined by GC-MS for Each of the Four Isolation Methods

		amount of compounds[b]			
no.[a]	compound	static headspace	P&T 15	P&T 60	solvent extraction
1	dimethyl sulfide	100 a	35 b	2 b	m [c]
2	methyl acetate	100 a	97 a	20 b	m
3	methyl 2-methylpropanoate	22 b	89 a	100 a	m
4	ethyl propaonate	7 c	35 b	100 a	m
5	2,3-butanedione	12 c	55 b	100 a	21 c
5	methyl butanoate	10 c	40 b	100 a	2 c
6	methyl 2-methylbutanoate	11 c	49 b	100 a	0 c
6	2-methylpropyl acetate	10 c	39 b	100 a	2 c
7	ethyl butanoate	9 c	36 b	100 a	1 c
8	ethyl 3-methylbutanoate	12 c	44 b	100 a	0 c
9	methyl-*trans*-2-butenoate	5 c	27 b	100 a	2 c
10	2- and 3-methylbutyl acetate	8 c	35 b	100 a	1 c
11	isocineole	6 c	30 b	100 a	1 c
12	cineole	6 c	30 b	100 a	2 c
13	mixture of 2- and 3-methyl-1-butanols	6 c	35 b	100 a	12 c
14	ethyl hexanoate	6 c	35 b	100 a	1 c
15	hexyl acetate	3 c	33 b	100 a	20 b
16	octanal	0 b	27 b	100 a	0 b
19	6-methyl-5-hepten-2-one	0 c	25 b	100 a	1 c
20	*cis*-rose oxide	0 c	22 b	100 a	0 c
21	methyl 2-hydroxybutyrate	3 d	21 c	100 a	58 b
21	*cis*-3-hexen-1-ol	3 c	23 b	100 a	15 b
22	methyl octanoate	0 c	32 b	100 a	0 c
23	nonanal	0 b	24 b	100 a	5 b
25	2-methoxy-3-isopropylpyrazine	0 c	27 b	100 a	10 bc
26	acetic acid	2 b	3 b	6 b	100 a
29	decanal	0 b	0 b	100 a	0 b
30	camphor	0 c	31 b	100 a	0 c
30	1,4-dimethyl-3-cyclohexenylmethyl ketone	0 c	25 b	100 a	0 c
31	3-methoxy-2-isobutylpyrazine	0 b	7 b	100 a	0 b
33	linalool	2 b	14 b	100 a	10 b
34	4-terpineol	2 c	17 b	100 a	17 b
35	butanoic acid	1 b	2 b	7 b	100 a
36	2- and 3-methylbutyric acid	0 b	0 b	0 b	100 a
40	α-terpineol	0 c	12 c	100 a	43 b
41	phellandral	0 b	0 b	100 a	0 b
46	β-damascenone	0 c	20 b	100 a	7 bc
49	benzyl alcohol	0 c	2 c	17 b	100 a
50	2-phenylethanol	0 c	2 c	13 b	100 a
55	4-methylphenol	2 d	22 c	100 a	46 b
57	eugenol	0 b	0 b	0 b	100 a
58	4-vinyl-2-methoxyphenol	0 b	0 b	0 b	100 a

[a] Numbers correspond to compounds in **Table 1**. Only compounds of high enough concentrations to be quantified are included. The highest concentration of each compound based on single ions is set to 100; the other concentrations corresponding to this value. [b] Letters a–d are used to compare mean values ($n = 3$) within each row, indicating significantly different results by Duncan's multiple-range test. [c] Detection started at RI 950 due to the solvent peak.

However, sensorial comparison of isolates of headspace methods with solvent extracts is not straightforward. Van Ruth et al. (*21*) investigated flavor release of rehydrated vegetables and found that dynamic headspace with mastication did not differ significantly from direct oral vapor release in the mouth, whereas purge and trap without mastication gave higher and dynamic headspace collection lower GC chromatogram peak areas.

The static headspace approach simulates the odor of the headspace in a food package as it is experienced by orthonasal perception. By purge and trap, on the other hand, some components are more enriched than others, and the composition does not reflect the gas phase at equilibrium, as perceived by the nose. Nevertheless, the detection limit of purge and trap is lower than that of static headspace. A solvent extract does to an even less extent reflect the sensory impression of a food, but it facilitates the identification of some low-volatility components. Depending on the purpose of the investigation, a solution could be to select both a method reflecting the sensory perception and a low detection limit method.

ABBREVIATIONS USED

NIF, nasal impact frequency; SNIF, surface of nasal impact frequency; GC-O, gas chromatography−olfactometry; GC-MS, gas chromatography−mass spectrometry; CHARM, combined hedonic aroma response measurement; AEDA, aroma extract dilution analysis; RI, retention index; FID, flame ionization detector; P&T, purge and trap; SD, standard deviation; LSD, least significant difference.

ACKNOWLEDGMENT

We thank Karina A. Fife and Mehdi D. Farahani for technical assistance and Morten Friis, Vallø Saft A/S, for providing black currant juice.

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Received for review October 3, 2003. Revised manuscript received January 16, 2004. Accepted January 25, 2004. This work was financially supported by the Ministry of Food, Agriculture and Fisheries via the Danish Vertical Fruit and Vegetable Network.

JF035133T