Volatile fingerprinting of the plum brandies produced from different fruit varieties

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Abstract Nowadays, fingerprinting of food became one of the most perspective analytical tools to resolve a problem of food quality and authentication, especially in difficult cases like differentiation of fruit varieties. In this work, plum brandies distilled by the same technology from 25 plum cultivars were distinguished by comprehensive two-dimensional gas chromatographic analysis and sensory evaluation. The number of identified compounds in studied samples varied between 91 and 195 depending on the plum variety. Enriched volatile organic compounds (VOC) profile was identified for the samples received from “Chrudimer”, “Cacak Fruitful” and “Hanita” plum varieties, whereas in the case of “Gabrovska”, “Presenta”, Elena” and “President” plum varieties, the VOC profile was significantly reduced. From qualitative point of view, the particular plum brandies showed differences in the presence of unsaturated fusel alcohols (e.g. 3-methyl-3-buten-1-ol, *trans*-3-hexenol), unsaturated aldehydes (2-butenal, 2-nonenal), monoterpene derivatives (e.g. linalool acetate,

geraniol acetate) and lactones, which were mainly detected at the trace level.

Keywords Plum brandy · Plum cultivar · Comprehensive two-dimensional gas chromatography · Sensory analysis · GCxGC–TOF-MS

Introduction

Plum orchards are widely grown worldwide especially in Central Europe and Asian regions, and their areas are ranked on the 2nd place after apple among all pome and stone fruit crops. Nearly over 2000 named varieties of plums have been established with a dozen different species (Gómez-Plaza and Ledbetter 2010). *Prunus salicina* (Japanese plum) and *Prunus domestica* (European plum) are the most common cultivated plum species. At the same time, wild plums are mainly applied as donors to enhance resistance and ecological adaptability of cultivars, for instance *Prunus cerasifera* originated from central Asia, *Prunus americana* and *Prunus nigra* derived from the North America. Various plum cultivars differ significantly in their properties such as climatic adaptation, harvest yield or fruit characteristics, e.g. fruit size, shape, colour, taste and flavour. For example “Italian Prune”, “Hanita” and “Harbella” are considered as good donors for flavour and fine acid content (Hartmann and Neumüller 2009), while cultivars “Katinka”, “Tegera” and “Cacak Beauty” are found as effective parents to improve firmness of the plum fruit.

Prunus domestica plums are commonly consumed fresh but more frequently are used for production of alcoholic beverages and syrups. Alcoholic beverages, particularly plum distillates are known for their

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production traditions and appears under different names depending on geographic region, e.g. rakia (Balkan countries), pálinka (Hungary), Slivovica or Slivovitz in Easter and Central European countries. The quality of received alcoholic beverages mostly depends on fruit conditions, fermentation and distillation technologies. Influence of different yeasts (isolated from plums fruits, plum musts and commercial strains) on the fermentation and chemical composition of plum brandies has been studied by Satora and Tuszyński (2010). In comparison to commercial yeast strains, the lower amounts of higher alcohols were obtained in the samples fermented with indigenous strains. Simultaneously, effect of maturation process and botanic species of wood used for maturation was investigated for these beverages (Pecić et al. 2012). It was found that wood origin mainly defined the composition of phenols, whereas the time of maturation influenced their concentration. In addition, the impact of cultivars on the Volatile Organic Compounds (VOC) composition of alcoholic beverage could be an issue of critical study, because variable chemical profile was shown for several types of fruits, such as apples (Lasekan et al. 2013), pears (Chen et al. 2007), cherries (Serradilla et al. 2012), raspberries (Malowicki et al. 2008), or elderberries (Veberic et al. 2009). For example, in case of apple distillates it was demonstrated that concentration of ethyl octanoate, hexyl 2-methylbutanoate, 1-hexanol, benzaldehyde and furfural was correlated with apple variety (Versini et al. 2009). On the other hand, the content of propanol, 2-methyl-1-propanol and 2-phenylethanol (with pleasant rose flavour) varied in apple wines produced from 3 different apple varieties (Satora et al. 2008). The characteristic VOC profile was identified for Italian distillates produced from wild and three cultivated pears. The main differences were found in content of farnesene isomers, citronellol and methyl and ethyl unsaturated decanoate isomers (Versini et al. 2012). The concentration of amyl alcohols changed significantly in spirits received for black current cultivars and red currant cultivars (Vulić et al. 2012).

The small differences in VOC profiles were detected among various plum species, e.g. aldehydes were dominant in *P. domestica* and *P. spinosa*, whereas esters were prevailing for *P. salicina*, their hybrids and *P. ussuriensis* (Chai et al. 2012). Moreover, deviations in fermentable sugars (the total of glucose, fructose, and sucrose), sorbitol content, dry matter content and titratable acidity were shown for *Prunus domestica* varieties (Bohačenko et al. 2010). On the contrary, the ratio of the content of 2-methyl-1-propanol and 3-methyl-1-butanol could be a marker of variety recognition used for production of plum brandies (Spaho et al. 2013). At the same

time, volatile fingerprinting is more global approach of food authentication in comparison with the classical techniques (stable isotope analysis, determination of particular markers). This approach could be useful in complicated situations like distinguishing varieties of the same fruit.

The GC–MS is used for determination of VOC profiles, but recently introduced comprehensive two-dimensional gas chromatography (GCxGC) is characterized with enhanced separation efficiency and better resolution power. Thus, it is especially suitable for analysis of volatile organic profile of high-complexity samples such as alcoholic beverages (Vyviurska et al. 2015; Cardeal and Marriott 2009; Villière et al. 2012; Weldegergis et al. 2011; Robinson et al. 2011). This higher efficiency of separation is achieved due to application of two separation columns with different polarity of stationary phases available to resolve structural and geometrical isomers. Simultaneously, high data acquisition rate and a small internal volume of detector used in GCxGC offer increased sensitivity of measurements. In our study, plum brandies produced from 25 *Prunus domestica* plum cultivars were analysed using comprehensive two-dimensional gas chromatography to establish influence of plum variety on the final volatile composition of plum brandies.

Materials and methods

Chemicals

Pentane used for liquid–liquid extraction was obtained from Merck (Darmstadt, Germany), anhydrous NaCl was supplied from Microchem (Pezinok, Slovakia), a mixture for alkanes (C₇–C₃₀) used for calculation of retention indices was purchased from Supelco (Bellefonte, PA, USA). Solution of benzophenone in ethanol with concentration 1.6 mg l^{−1} was applied as an internal standard solution. The standards of chemical listed in Table 2 were obtained from Sigma-Aldrich (St. Louis, USA), Microchem (Pezinok, Slovakia), Merck KGaA (Darmstadt, Germany), SAFC Biosciences (Lenexa, USA).

Samples

The plums of different varieties were obtained from several botanical gardens (Table 1). The all plums were fermented by the same technology under pseudo-anaerobic conditions with addition of 0.5 kg of sucrose to 100 kg of fruits and using the same type of yeast strains. Fermented beverages were distilled by pot still method, and then diluted to final ethanol content 50–52% (v/v). The received brandies were kept for maturation in glass bottles for 2–3 years.

Table 1 Plum fruits

Code	Plum variety	Fruit source
SL1	Chrudimer	Moravský Žižkov, Czech Republic
SL2	Cacak Fruitful	Vilémov, Czech Republic
SL3	Cacak Early	Vilémov, Czech Republic
SL4	Cacak Beauty	Horné Obdokovce, Slovak Republic
SL5	Stanley	Kyjov, Czech Republic
SL6	Tolar	Moravský Žižkov, Czech Republic
SL7	Blue free	Moravský Žižkov, Czech Republic
SL8	Top King	Slup, Czech Republic
SL9	Haganta	Slup, Czech Republic
SL10	Hanita	Kyjov, Czech Republic
SL11	Top Taste	Moravský Žižkov, Czech Republic
SL12	Topper	Veselé pri Piešť'anoch, Slovak Republic
SL13	Tophit	Veselé pri Piešť'anoch, Slovak Republic
SL14	Švestka domácí	Dambořice, Czech Republic
SL15	Durancie	Kyjov, Czech Republic
SL16	Katinka	Veselé pri Piešť'anoch, Slovak Republic
SL17	Gabrovská	Starý Poddvorov, Czech Republic
SL18	Carpatin	Moravský Žižkov, Czech Republic
SL19	Vlaška	Moravský Žižkov, Czech Republic
SL20	Top Gigant	Veselé pri Piešť'anoch, Slovak Republic
SL21	Presenta	Dambořice, Czech Republic
SL22	President	Slup, Czech Republic
SL23	Firense	Moravský Žižkov, Czech Republic
SL24	Amers	Moravský Žižkov, Czech Republic
SL25	Elena	Týn u Pterova, Czech Republic

Sensory analysis

Quality of plum brandies aroma was characterized by 7 certified distillate tasters in blind sensory evaluation. Evaluation took place in authorized sensory laboratory under conditions recommended for distillates (30 ml of distillate poured into ISO XL5 wine taster glasses; serving temperature 12 °C). Aroma of each plum brandy sample was evaluated in two repetitions by Quantitative Descriptive Analysis. Tasters have evaluated positive fruity like odours as well as possible off flavours by ten-point scale (0 representing not perceived and 10 representing extreme value of odour descriptor perception). Intensities of following major attributes were evaluated: plum, marzipan, plum jam, stones, spicy flavour, sweetness, green leaves, fusel alcohols, volatile acidity, and solvent. Other variable odour descriptors were evaluated as well: apple, sour cherry, cherry, apricot, banana, pear, citrus, beet, caramel, conifer, and nutmeg. Spider web diagrams characterizing aroma of individual spirits were constructed based on average values of means obtained by the evaluation.

Sample preparation

Liquid–liquid extraction (LLE)

In total, 30 ml of sample previously mixed with NaCl (2 g) and 100 µl benzophenone used as an internal standard solution, was extracted with three 10 ml portions of pentane in a separation funnel. The combined pentane extracts were concentrated using the Kuderna-Danish apparatus at 55 °C to final volume of 1 ml. After then, the extract was removed into a volumetric flask and filled to the final volume of 2 ml with pentane. An amount of 1 µl of the sample was injected into GC in splitless mode.

Solid phase microextraction (SPME)

The HS-SPME procedure was performed using Gerstel multipurpose sampler with SPME fibres coated with 100 µm of polydimethylsiloxane (PDMS), 65 µm of polydimethylsiloxane-divinylbenzene (PDMS/DVB), 85 µm of polyacrylate (PA), 85 µm of (CAR/PDMS), and 50/30 µm of divinylbenzene-carboxene-polydimethylsiloxane (DVB/CAR/PDMS). Both 3 ml of plum brandy and 3 ml of distilled water were combined in a single 20 ml capped glass vial, and 0.5 g of sodium chloride and 20 µl of the internal standard solution were added. The vial with sample was heated at 60 °C for 30 min with stirring at a rate of 400 rpm. The SPME fibre was exposed to the headspace for 30 min, and then transferred to the injector for desorption at 220 °C for 2 min.

Gas chromatography–mass spectrometry analysis

The gas chromatography analysis was performed on Pegasus 4D GCxGC–TOFMS (LECO Corporation, St. Joseph, MI, USA), consisting of Agilent 6890 gas chromatograph (Agilent, Agilent J&W Column, Agilent Technologies, Palo Alto, CA, USA), a dual stage jet cryogenic modulator based on liquid N₂, time of flight mass spectrometer (LECO Corporation, St. Joseph, MI, USA) and Gerstel MPS2 autosampler (Gerstel, Mülheim, Germany). The column setup contained a 30 m × 0.25 mm ID column coated with 0.25 µm film thickness of polyethylene glycol modified by nitroterephthalic acid phase (DB-FFAP from Agilent, Agilent J&W Column, Agilent Technologies, Palo Alto, CA, USA) or HP-5 column (Agilent, Agilent J&W Column, Agilent Technologies, Palo Alto, CA, USA) of 30 m × 0.25 mm ID coated with 0.25 µm film thickness of (5%-phenyl)-methylpolysiloxane stationary phase in the first dimension, and BPX-50 column (SGE Analytical Science, Victoria, Australia) 1.5 m × 0.1 mm ID coated with 0.1 µm film thickness of 50% diphenyl–50% dimethyl polyphenylene-siloxane in the second

Table 2 Compound which identification confirmed with authentic standards in the plum brandies with GCxGC–TOFMS

RT	DBFFAPxBPX-50	RI	HP-5xBPX-50 RI	Compounds	Area (%) ^f												
					SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9	SL10	SL11	SL12	SL13
ID (min)	2D (s)																
9.6	1.54	984	596	2,3-Butanedione ^a			0.28	0.24	0.42	0.56	0.21	0.05			0.08	0.66	0.58
11.8667	1.46	1085	591	2-Butanol ^{a,e}		0.66	0.21	5.70					0.03				
12.4	2.89	1028	804	Ethyl butanoate ^{a,e}	0.31	0.92	0.47	0.30	0.49	0.54	0.31	0.57	0.10	0.84	0.90	0.78	0.17
13.0667	3.37	1051	851	Ethyl 2-methylbutanoate ^{a,e}	0.09		0.04	0.32	0.04	0.20		0.03		0.02			
13.6	1.39	1038	581	1-Propanol ^{b,e}	9.10	8.25	13.51	8.04	17.44	13.53	9.37	16.10	1.21	16.65	13.95	11.33	26.33
13.7333	1.91	1063	697	2,3-Pentanedione ^{a,e}	0.06	0.02	0.02	0.06		0.08			0.03			0.13	0.04
14.2667	2.83	1074	816	Butyl acetate ^{c,e}	1.59		0.33	0.04				0.01				0.61	
16.8	1.48	1091	669	2-Methyl-1-propanol ^{a,e}	2.31	11.95	17.94	22.34	14.79	23.52	10.93	10.38	22.13	3.32	17.15	12.84	16.18
16.9333	3.27	1122	880	3-Methylbutyl acetate ^{d,e}	10.28	9.47	12.08	9.32	1.79	9.63	3.32	7.33	1.37	7.37	3.83	11.55	3.06
17.6	3.62	1133	906	Ethyl pentanoate ^{a,e}	0.04	0.03								0.03		0.03	
17.6	3.63	1133	854	Ethyl 3-methylbutanoate ^{a,e}			0.03	0.60	0.06	0.05		0.03					
17.7333	1.62	1108	701	3-Pentanol ^a								0.03					
18.6667	4.65	1160	992	Myrcene ^a	0.03												
19.0667	1.58	1122	701	2-Pentanol ^{a,e}	0.20	0.12	0.01	0.13				0.01	0.13			0.11	
20.8	3.47	1178	925	Methyl hexoate ^{a,e}	0.08	0.12	0.15	0.04	0.04	0.05	0.08	0.10	0.11		0.10	> 0.01	> 0.01
21.0667	3.07	1176	891	2-Heptanone ^a												> 0.01	
21.3333	1.46	1157	678	1-Penten-3-ol ^a			0.11	0.10	0.04	0.11	0.10		0.05		0.09	0.10	0.05
23.8667	1.61	1200	732	2-Methyl-1-butanol ^{a,e}	1.45	7.77	8.61	4.47	9.86		0.12	6.58	8.82	6.49	3.40		
24.1333	4.14	1224	1000	Ethyl hexoate ^{a,e}	1.42	3.05	2.73	0.89	1.33	2.77	2.30	3.10	2.70	3.16	4.27	3.76	1.32
24.2667	1.73	1201	730	3-Methyl-1-butanol ^{a,e}	15.39	15.01	1.43	13.45	4.51	8.20	36.29	15.61	3.19	8.15	13.62	14.88	10.06
24.9333	1.4	1202	640	2-Methyl-2-propen-1-ol													
25.0667	1.74	1215	802	2-Hexanol ^{a,e}	0.07									0.02			
26	2.77	1248	892	Styrene ^{d,e}		0.32	0.03	0.11	0.08	0.02	0.04	0.36	0.10	0.10	0.06	0.05	
26.2667	4.56	1258	1059	3-Methylbutyl butanoate ^{a,e}	0.02												
26.9333	1.62	1243	766	1-Pentanol ^{a,e}	0.98	0.18	0.25	0.20	0.33	0.40	0.24	0.29	0.14	0.29	0.16	0.31	0.18
26.9333	1.53	1241	727	3-Methyl-3-buten-1-ol ^a	0.31	0.09	0.10	0.04	0.17	0.04	0.09	0.07	0.04	0.05	0.04	0.08	0.05
30.9333	1.68	1305	840	4-Methyl-1-pentanol ^{a,e}	0.02	0.02	0.02	0.01	0.01	0.05	0.02	0.02	0.06	0.02	0.03	0.03	0.03
31.3333	1.91	1313	903	2-Heptanol ^{a,e}	0.17	0.03	0.07	0.08	0.03	0.03	0.05	0.27	0.08	0.13	0.04	0.12	
31.3333	4.2	1324	1102	Ethyl heptanoate ^{a,e}	0.09	0.03	0.04	0.03	0.03	0.06	0.02	0.03		0.06	0.05	0.02	0.01
32.4	4.35	1339	1111	cis-Rose oxide ^{a,e}	0.01												
32.9333	1.67	1335	813	Ethyl 2-hydroxypropanoate ^{a,e}	0.59	1.71	0.57	0.52	1.04			1.35	1.73	1.83	1.28		1.51
33.4667	1.8	1343	870	1-Hexanol ^{b,e}	2.87	1.17	4.23	0.55	1.32	1.49	0.49	2.01	0.94	2.08	0.73	2.52	0.97
34.1333	3.79	1366	1115	Heptyl acetate ^{a,e}	0.07												

Table 2 continued

RT	DBFFAPxBPX-50	RI	HP-5xBPX-50 RI	Compounds	Area (%) ^f												
					SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9	SL10	SL11	SL12	SL13
ID (min)	2D (s)																
34.1333	1.69	1355	852	<i>trans</i> -3-Hexen-1-ol ^a	0.04												
35.2	3.5	1381	1094	2-Nonanone ^{a,e}	0.10			> 0.01			0.02	0.02				0.02	
35.2	3.85	1378	1126	Methyl octanoate ^{a,e}	0.19	0.43	0.44	0.12	0.18	0.12	0.33	0.28	0.42	0.50	0.28	0.17	0.13
35.3333	1.68	1375	859	<i>cis</i> -3-Hexen-1-ol ^{a,e}	0.22			0.03	0.05	0.08	0.04	0.09		0.04	0.04	0.07	0.04
36	2.16	1385	997	3-Octanol ^{a,e}	0.04	0.01	0.03	0.01	0.01	0.01	0.01	0.02		0.03		0.01	0.01
36.9333	1.63	1398	871	<i>trans</i> -2-Hexen-1-ol ^d	0.02	0.01	0.01					0.01					
37.4667	1.63	1407	867	<i>cis</i> -2-Hexen-1-ol ^d	0.06		0.02					0.04				0.01	
37.7333	2.08	1413	1003	2-Octanol ^a	1.62	0.42	2.99	2.77	6.33	6.85	7.92	3.02	10.32	9.31	6.85	6.56	4.95
38.1333	4.42	1426	1198	Ethyl octanoate ^{a,e}													
38.2667	3.39	1426	1090	α , <i>p</i> -Dimethylstyrene ^d										0.01			
38.8	2.69	1428	1072	Linalool oxide ^{a,e}	0.17	0.11	0.20	0.01	0.03		> 0.01	0.06	0.03	0.02	0.01	0.02	0.02
39.6	1.9	1443	981	1-Octen-3-ol ^{a,e}	0.14	0.05	0.14	0.03	0.02	0.03	0.04	0.07	0.02	0.08	0.02	0.04	0.01
40	1.88	1449	974	1-Heptanol ^{a,e}	0.31	0.09	0.28	0.06	0.07	0.15	0.07	0.10	0.04	0.17	0.11	0.09	0.06
40.2667	1.14	1443	685	Acetic acid ^{a,e}	4.07	3.11	2.25	0.57	4.93	1.53	0.26	2.91	2.48	2.27	2.50	0.69	2.17
40.5333	1.96	1455	989	6-Methyl-5-hepten-2-ol ^d	0.01		> 0.01							> 0.01			
40.9333	1.68	1461	832	Furfural ^{a,e}	0.77	1.15	1.24	1.15	2.05	0.09	1.00	0.62	1.55	0.92	1.53	1.42	1.32
42.2667	3.76	1487	1206	Decanal ^{a,e}	0.04	0.02	0.01		0.02	0.03	0.03	0.02		0.02			
43.3333	1.87	1497	914	2-Acetylfuran ^a	0.01	0.01	> 0.01	> 0.01	0.01			0.01	0.01	0.01	0.01		0.01
43.8667	2.26	1510	1104	2-Nonanol ^{a,e}	0.18	0.01	> 0.08	0.04	0.03		0.03	0.67	0.05	0.25		0.02	
44	2.26	1513	959	Benzaldehyde ^{a,e}	6.77	2.92	4.57	6.40	7.48	1.91	4.31	3.39	6.30	2.39	2.13	2.03	0.74
44.5333	4.46	1527	1296	Ethyl nonylate ^{a,e}	0.62	0.58	0.77	0.33	0.59	0.53	0.15	0.45	0.18	0.80	0.52	0.17	0.34
44.5333	3.07	1524	1161	<i>trans</i> -2-Nonenal ^{d,e}	0.01		> 0.01	0.01									
45.6	1.16	1527	694	Propanoic acid ^a	0.03	0.02	0.02	0.01	0.01			0.02	0.02	0.01	0.02	0.01	0.02
45.6	2.22	1539	1100	Linalool ^{a,e}	0.17	0.01	0.22	0.06	0.05	0.03	0.03	0.12	0.09	0.01	0.13	0.12	0.04
45.8667	3.6	1546	1258	Linalool acetate ^a	0.03												
46.1333	2.02	1548	1072	1-Octanol ^{a,e}	0.31	0.20	0.21	0.10	0.11	0.16	0.09	0.28	0.13	0.16	0.13	0.19	0.12
46.6667	4.49	1562	1293	Bornyl acetate ^d	0.13												
47.2	6.46	1575	1426	Caryophyllene ^{d,e}	0.10												
47.6	1.94	1568	963,6	5-Methyl furfural ^a		> 0.01							0.01				> 0.01
48.1333	4.11	1581	1326	Methyl decanoate ^{a,e}	0.25	0.62	0.75	0.10	0.32	0.08	0.34	0.29	0.72	0.70	0.30	0.11	0.16
48.4	2.87	1588	1179	4-Terpinenol ^{a,e}	0.09	> 0.01						0.02		0.02		0.02	
48.9333	2.07	1593	985	Benzonitrile ^a	0.01												
50.2667	2.38	1618	1147	β -Terpineol ^a												0.01	

Table 2 continued

RT	ID (min)	2D (s)	Compounds	HP-5xBPX-50 RI	Area (%) ^f												
					SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9	SL10	SL11	SL12	SL13
50.5333	1.88	1620	916	Butyrolactone ^a	0.02	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01		0.01	0.01	> 0.01	0.01	> 0.01	> 0.01
50.5333	1.2	1620	812	Butanoic acid ^a	0.01	0.05	0.03		0.02		> 0.01	0.03	0.04	0.02			0.04
50.6667	4.74	1625	1397	Ethyl decanoate ^{a,e}	5.44	0.66	0.67	3.13	3.50	5.13		3.12	12.86	6.92	3.24	5.50	8.86
50.9333	3.19	1631	1264	<i>trans</i> -2-Decenal ^{d,e}	0.02	0.01	> 0.02		0.02	0.01		0.01			0.01	> 0.01	
51.2	2.22	1633	1044	Benzeneacetaldehyde ^{a,e}	0.08	0.02	0.05	0.02	0.02								
51.6	2.34	1640	1067	Acetophenone ^{a,e}	0.02	0.02	0.02	0.01	0.01	0.01		0.01	0.02	0.01		0.01	0.01
52	3.81	1652	1355	Citronellyl acetate ^{a,e}	0.03												
52.1333	2.17	1653	1175	1-Nonanol ^{a,e}	0.79	0.37	0.69	0.39	0.29	0.82		0.13	0.18	0.44	0.31	0.37	0.71
52.5333	1.36	1656	857	2-Furanmethanol ^a	0.01	> 0.01	> 0.01	> 0.01	0.02	0.01		0.01	0.02	0.01	0.02	0.01	0.01
53.0667	4.17	1661	1413	Decyl acetate ^{a,e}	0.02	0.05	0.02					0.01		0.01			
53.0667	2.63	1671	1152	p-Vinylanisole ^{a,e}	0.30	1.34		0.50	0.11	0.01		0.52	0.84	0.41	0.10	0.53	0.01
53.2	2.55	1670	1181	Diethyl butanedioate ^{a,e}	0.56	0.08	0.11	0.03	0.14	0.05		0.31	1.30	0.12	2.08	0.05	0.32
54	2.46	1669	1192	α -Terpineol ^{a,e}	0.05	0.08	0.08	0.02		0.01		0.01		0.17	0.03	0.12	0.03
54.4	2.62	1692	1216	<i>trans,trans</i> -2,4-Nonadienal ^a				> 0.01									
54.5333	2.17	1691	1054	γ -Hexalactone ^a		> 0.01	> 0.01						> 0.01				
55.8667	2.51	1719	1165	Phenylmethyl acetate ^{a,e}	0.88	0.01	0.05	0.03	0.04	0.01		0.01	0.04	0.01	0.01	0.01	> 0.01
57.3333	3.53	1748	1384	Geraniol acetate ^e	0.04												
57.6	2.51	1751	1180	Methyl benzeneacetate ^a	0.01												
57.7333	1.62	1749	915	2(5H)-Furanone ^a	0.01	> 0.01	> 0.01	0.02	0.02	0.03		0.01	0.02	0.04	0.02	0.01	0.02
57.7333	2.06	1725	1177	Epoxylinalol ^e	0.01	> 0.01	> 0.01						> 0.01				
57.7333	2.28	1754	1273	1-Decanol ^{a,e}	0.06	0.03	0.03	0.01	0.02	0.03		0.01	0.06	0.03	0.02	0.02	0.01
58	2.13	1758	1229	β -Citronellol ^{a,e}	0.09	> 0.01	> 0.01		0.01	> 0.01			0.02	0.01	0.01	0.01	0.01
58.2667	2.5	1766	1197	Methyl salicylate ^{a,e}	0.03	0.09	0.13	> 0.01	0.14	0.10		0.01	0.06	0.01	0.07	0.02	0.09
58.8	3.83	1776	1396	α -Damascone ^a	0.01												
59.4667	2.2	1787	1262	<i>cis</i> -4-Decen-1-ol ^{a,e}	0.01		0.08					0.01	0.02	0.01		> 0.01	
59.6	4.52	1790	1530	Citronellyl butyrate ^a	0.02												
59.7333	2.1	1790	1229	Nerol ^{a,e}	0.06	0.01	0.03						0.03	0.01	0.01		
59.7333	4.34	1787	1526	Methyl dodecanoate ^{a,e}	0.24	0.31	0.40	0.04	0.16	0.04		0.20	0.16	0.54	0.15	0.09	0.14
60	2.77	1798	1273	Ethyl salicylate ^{a,e}	0.24	0.07	0.17	0.03	0.19	0.13		0.03	0.10	0.04	0.04	0.03	0.09
60.4	3.57	1805	1388	β -Damascone ^{a,e}	0.10	0.04	0.04	0.01	0.03	0.01		0.02	0.02	0.05	0.02	0.05	0.03
60.5333	1.72	1808	1075	1-Phenylethanol ^{a,e}	> 0.01												
61.8667	4.86	1829	1595	Ethyl dodecanoate ^{a,e}	2.15	10.03	1.38	1.52	5.24	2.92		1.51	1.16	4.11	6.10	1.50	7.61
62.2667	2.07	1838	1256	Geraniol ^{a,e}	0.11	0.05		> 0.01	0.04	0.01		0.01			0.01	0.01	0.01

Table 2 continued

DBFFAPxBPX-50		RI	HP-5xBPX-50 RI	Compounds	Area (%) ^f												
RT					SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9	SL10	SL11	SL12	SL13
ID (min)	2D (s)																
62.6667	4.27	1883	1539	Geraniol butyrate ^a	> 0.01												
63.7333	1.59	1869	1034	Benzyl alcohol ^{a,e}	0.47	0.12	0.19	0.07	0.13	0.02	0.16	0.09	0.18	0.08	0.07	0.01	0.08
65.4667	1.76	1901	1124	2-Phenylethanol ^{a,e}	0.26	0.29	0.21	0.03	0.07	0.11	0.12	0.13	0.29	0.15	0.20	0.02	0.32
65.6	2.41	1905	1260	γ-Octalactone ^{a,e}	0.01	> 0.01	> 0.01							> 0.01			
67.3333	1.4	1941	1159	2-Ethylhexoic acid ^a	0.01	0.01	> 0.01					0.01	0.01		0.01		
69.8667	2.88	1991	1567	Nerolidol ^{a,e}	0.01	0.01	0.01	0.01	0.01			> 0.01	0.01	0.01	0.01	0.01	> 0.01
70.1333	4.56	1994	1727	Methyl tetradecanoate ^{a,e}	0.05	0.03	0.04	0.03	0.02	0.01	0.02	0.02	0.06	0.03	0.02	0.04	0.03
71.0667	2.51	2017	1368	γ-Nonanolactone ^{a,e}	0.02	> 0.01											
71.3333	1.95	2024	1287	4-Ethylguaiacol ^{a,e}				> 0.01									0.01
72.1333	4.97	2035	1796	Ethyl tetradecanoate ^{a,e}	1.10	0.81	0.92	0.33	0.49	0.60	0.56	0.55	0.97	0.79	0.61	0.97	0.71
72.6667	1.4	2051	1174	Octanoic acid ^{a,e}	0.21	0.17	0.22	0.03	0.04	0.02	0.01	0.13	0.21	0.07	0.11	0.03	
73.4667	2.51	2068	1390	Methyl cinnamate ^a	0.20	> 0.01						> 0.01					
73.4667	2.61	2069	1287	δ-Nonalactone ^a	> 0.01												
75.0667	4.65	2097	1829	Methyl pentadecanoate ^{a,e}	0.01												
75.8667	2.71	2120	1468	Ethyl cinnamate ^{a,e}	0.47	0.23	0.02	0.01	0.06	0.02	0.05	0.09	0.08	0.03	0.07	0.01	0.01
76.4	2.61	2133	1474	γ-Decalactone ^{a,e}	0.03	0.01	0.02				0.02	> 0.01		0.01			
77.6	1.98	2159	1362	Eugenol ^{a,e}	0.06	0.04	0.03	> 0.01	0.01		> 0.01	0.01	0.01	> 0.01	> 0.01		0.01
79.7333	4.77	2202	1929	Methyl hexanoate ^{a,e}	0.14	0.04	0.03	0.03	0.05	0.06	0.04	0.04	0.05	0.04	0.06	0.03	0.04
81.3333	5.21	2241	1997	Ethyl hexanoate ^{a,e}	1.62	0.72	0.51	0.36	0.67	1.16	0.55	0.54	0.61	0.59	1.05	0.47	0.58
81.4667	2.72	2248	1578	γ-Undecanolactone ^a	0.02												
82.2667	1.51	2267	1392	Decanoic acid ^{a,e}	0.19	0.08	0.09	0.02	0.03	0.02	0.01	0.06	0.09	0.03	0.06	0.02	0.05
85.6	2.63	2338	1724	Farnesol ^a		0.01			0.01				0.01	0.01	0.01		0.01
86.2667	2.82	2364	1682	γ-Dodecalactone ^{a,e}	0.02	0.01	> 0.01				0.01			0.02			
89.8667	5.33	2447	2195	Ethyl octadecanoate ^{a,e}	0.01	0.01				0.01							
94.1333	1.67	2557	1401	Vanillin ^{a,e}	> 0.01	> 0.01	0.01					> 0.01					
DBFFAPxBPX-50					Area (%) ^f												
DBFFAPxBPX-50		RI	HP-5xBPX-50	Compounds													
RT			RI		SL14	SL15	SL16	SL17	SL18	SL19	SL20	SL21	SL22	SL23	SL24	SL25	
ID (min)	2D (s)																
9.6	1.54	984	596	2,3-Butanedione ^a	0.38	0.10	0.10	0.28		0.03	0.43	0.01	0.70		0.46	0.08	
11.8667	1.46	1085	591	2-Butanol ^{a,e}			8.34	14.79	6.46						0.08	29.00	
12.4	2.89	1028	804	Ethyl butanoate ^{a,e}	0.37	0.06	0.77	0.72	0.56	0.50	1.01	0.22	0.92	0.42			

Table 2 continued

DBFFAPxBPX-50		RI	HP-5xBPX-50	Compounds	Area (%) ^f												
RRT		RI			SL14	SL15	SL16	SL17	SL18	SL19	SL20	SL21	SL22	SL23	SL24	SL25	
IID (min)		2D (s)															
13.0667	3.37	1051	851	Ethyl 2-methylbutanoate ^{a,e}	0.19	0.09	0.02	0.19		0.050							
13.6	1.39	1038	581	1-Propanol ^{b,e}	16.75	9.62	11.65	14.97	12.14	22.23	18.17	22.59	15.99	20.02	20.03	23.00	
13.7333	1.91	1063	697	2,3-Pentanedione ^{a,e}	0.11			0.01	0.01		0.03				0.11		
14.2667	2.83	1074	816	Butyl acetate ^{c,e}			0.01	1.47	0.55	0.06							
16.8	1.48	1091	669	2-Methyl-1-propanol ^{a,e}	12.40	11.26	11.45	14.17	13.47	11.69	15.15	17.00	15.26	4.28	13.39	9.27	
16.9333	3.27	1122	880	3-Methylbutyl acetate ^{d,e}	3.10	1.12	5.28	1.73	1.13	7.94	4.05	0.50	2.40	2.76	9.30	0.09	
17.6	3.62	1133	906	Ethyl pentanoate ^{a,e}	0.06		0.03	0.05	0.01	0.02		0.04		0.01			
17.6	3.63	1133	854	Ethyl 3-methylbutanoate ^{a,e}		0.04	0.01	0.19	0.03								
17.7333	1.62	1108	701	3-Pentanol ^a													
18.6667	4.65	1160	992	Myrcene ^a													
19.0667	1.58	1122	701	2-Pentanol ^{a,e}	0.01	0.01	0.20	0.23		0.01				0.03		0.02	
20.8	3.47	1178	925	Methyl hexoate ^{a,e}	0.01		0.15	0.05	0.08	0.07	0.19	0.02	0.03	0.14	0.05		
21.0667	3.07	1176	891	2-Heptanone ^a			0.05										
21.3333	1.46	1157	678	1-Penten-3-ol ^a	0.04	0.09		0.08	0.06	0.06			0.03	0.05	0.03	0.03	
23.8667	1.61	1200	732	2-Methyl-1-butanol ^{a,e}	10.39	10.58	10.60	0.02	1.36	3.39	0.53		7.12	25.80	3.89	0.05	
24.1333	4.14	1224	1000	Ethyl hexoate ^{a,e}	1.10	0.58	3.71	1.32	3.23	3.77	8.16	1.01	1.20	6.34	2.64	0.18	
24.2667	1.73	1201	730	3-Methyl-1-butanol ^{a,e}	5.39	11.39	3.90	27.50	19.79	13.89	4.71	20.27	29.98	3.16	20.62	17.53	
24.9333	1.4	1202	640	2-Methyl-2-propen-1-ol		0.01											
25.0667	1.74	1215	802	2-Hexanol ^{a,e}													
26	2.77	1248	892	Styrene ^{d,e}	0.04		0.06	0.02		0.22	0.38	0.06	0.01	0.68	0.07		
26.2667	4.56	1258	1059	3-Methylbutyl butanoate ^{a,e}													
26.9333	1.62	1243	766	1-Pentanol ^{a,e}	0.34	0.32	0.49	0.36	0.29	0.25	0.08	0.14	0.10	0.08	0.10	0.43	
26.9333	1.53	1241	727	3-Methyl-3-buten-1-ol ^a	0.04	0.06	0.10	0.02	0.06	0.04	0.02	0.03	0.03	0.02	0.04		
30.9333	1.68	1305	840	4-Methyl-1-pentanol ^{a,e}			0.02	0.01	0.02	0.01	0.04			0.02			
31.3333	1.91	1313	903	2-Heptanol ^{a,e}	0.02	0.08	0.11	0.11	0.04			0.06		0.67	0.02	0.11	
31.3333	4.2	1324	1102	Ethyl heptanoate ^{a,e}	0.07	0.08	0.04	0.02	0.04	0.04	0.02	0.03		0.02	0.02		
32.4	4.35	1339	1111	cis-Rose oxide ^{a,e}													
32.9333	1.67	1335	813	Ethyl 2-hydroxypropanoate ^{a,e}	0.88		0.65	2.72		0.39	0.60				0.37		
33.4667	1.8	1343	870	1-Hexanol ^{b,e}	1.48	1.68	1.76	1.64	1.16	1.70	0.38	0.93	0.46	1.42	0.97	1.49	
34.1333	3.79	1366	1115	Heptyl acetate ^{a,e}													
34.1333	1.69	1355	852	trans-3-Hexen-1-ol ^a													
35.2	3.5	1381	1094	2-Nonanone ^{a,e}			0.07		0.01					0.01			
35.2	3.85	1378	1126	Methyl octanoate ^{a,e}	0.15		0.30	0.07	0.25	0.28	0.97	0.09	0.09	0.53	0.19	0.02	

Table 2 continued

DBFFAPxBPX-50		RI	HP-5xBPX-50	Compounds	Area (%) ^f											
RRT			RI		SL14	SL15	SL16	SL17	SL18	SL19	SL20	SL21	SL22	SL23	SL24	SL25
IID (min)		2D (s)														
35.3333	1.68	1375	859	<i>cis</i> -3-Hexen-1-ol ^{a,e}	0.03	0.04	0.10	0.03		0.16	0.08	0.02	0.01	0.05	0.04	0.08
36	2.16	1385	997	3-Octanol ^{a,e}	0.01	0.04	0.01	0.02	0.01	0.01		0.01		0.01		0.01
36.9333	1.63	1398	871	<i>trans</i> -2-Hexen-1-ol ^d												0.01
37.4667	1.63	1407	867	<i>cis</i> -2-Hexen-1-ol ^d		0.02	0.01									0.01
37.7333	2.08	1413	1003	2-Octanol ^a	0.02		0.01					0.02				
38.1333	4.42	1426	1198	Ethyl octanoate ^{a,e}	4.54	2.86	4.33	1.83	2.32	8.79	10.58	4.83	4.21	4.84	11.25	0.79
38.2667	3.39	1426	1090	α , <i>p</i> -Dimethylstyrene ^d												
38.8	2.69	1428	1072	Linalool oxide ^{a,e}	0.03	0.01	0.08	0.02	0.01		> 0.01	0.02		0.03		0.12
39.6	1.9	1443	981	1-Octen-3-ol ^{a,e}	0.02	0.05	0.05	0.07	0.02	0.04		0.02		0.02	0.02	0.01
40	1.88	1449	974	1-Heptanol ^{a,e}	0.10	0.11	0.15	0.07	0.09	0.08	0.04	0.05	0.03	0.05	0.04	0.09
40.2667	1.14	1443	685	Acetic acid ^{a,e}	2.10	0.94	1.06	1.32	0.74	0.46	1.15	0.58	0.81	0.83	1.09	0.49
40.5333	1.96	1455	989	6-Methyl-5-hepten-2-ol ^d			> 0.01									
40.9333	1.68	1461	832	Furfural ^{a,e}	0.93	1.14	0.44	0.31	0.57	0.32	1.13	0.40	0.52	0.30	0.39	0.34
42.2667	3.76	1487	1206	Decanal ^{a,e}	0.04					0.01	0.03		0.04	0.03		
43.3333	1.87	1497	914	2-Acetyl furan ^a	0.01	0.01					> 0.01					
43.8667	2.26	1510	1104	2-Nonanol ^{a,e}	0.02	0.10	0.23	0.03	0.05		0.04	0.09		0.23	0.03	0.08
44	2.26	1513	959	Benzaldehyde ^{a,e}	4.35	6.07	4.92	10.74	2.28	0.11	1.28	2.64	2.88	2.27	1.16	3.54
44.5333	4.46	1527	1296	Ethyl nonylate ^{a,e}	3.16	0.59	0.22	0.08	0.25	0.55	0.41	0.96	0.09	0.40	0.29	0.07
44.5333	3.07	1524	1161	<i>trans</i> -2-Nonenal ^{d,e}						> 0.01						
45.6	1.16	1527	694	Propanoic acid ^a	0.01	0.01	0.01							> 0.01		
45.6	2.22	1539	1100	Linalool ^{a,e}	0.06	0.11	0.01	0.07	0.04	0.02	0.03	0.09	0.03	0.03	0.01	0.10
45.8667	3.6	1546	1258	Linalool acetate ^a												
46.1333	2.02	1548	1072	1-Octanol ^{a,e}	0.13	0.09	0.18	0.08	0.09	0.08	0.10	0.10	0.05	0.08	0.07	0.09
46.6667	4.49	1562	1293	Bornyl acetate ^d												
47.2	6.46	1575	1426	Caryophyllene ^{d,e}		0.06										
47.6	1.94	1568	963.6	5-Methyl furfural ^a												
48.1333	4.11	1581	1326	Methyl decanoate ^{a,e}	0.25	0.13	0.21	0.04	0.30	0.37	1.80	0.17	0.13	0.26	0.23	0.04
48.4	2.87	1588	1179	4-Terpinenol ^{a,e}	0.02	0.06	0.01	0.01			> 0.01	0.05				
48.9333	2.07	1593	985	Benzonitrile ^a		0.01										
50.2667	2.38	1618	1147	β -Terpineol ^a												
50.5333	1.88	1620	916	Butyrolactone ^a	> 0.01	0.01								> 0.01		
50.5333	1.2	1620	812	Butanoic acid ^a	0.02		0.02									
50.6667	4.74	1625	1397	Ethyl decanoate ^{a,e}	6.99	6.30	7.86	1.38	12.25	2.66	2.76	10.80	2.14	0.71	2.20	1.15

Table 2 continued

DBFFAPxBPX-50		RI	HP-5xBPX-50	Compounds	Area (%) ^f									
RT			RI											
ID (min)	2D (s)													
50.9333	3.19	1631	1264	<i>trans</i> -2-Decenal ^{d,e}	0.01	> 0.01	> 0.01	> 0.01	> 0.01					
51.2	2.22	1633	1044	Benzeneacetaldehyde ^{a,e}				0.02						
51.6	2.34	1640	1067	Acetophenone ^{a,e}	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
52	3.81	1652	1355	Citronellyl acetate ^{a,e}										
52.1333	2.17	1653	1175	1-Nonanol ^{a,e}	0.94	0.30	0.53	0.14	0.32	0.35	0.30	0.51	0.06	0.15
52.5333	1.36	1656	857	2-Furanmethanol ^a	0.01	0.02	> 0.01	> 0.01	> 0.01	> 0.01	0.01	> 0.01	0.01	0.01
53.0667	4.17	1661	1413	Decyl acetate ^{a,e}						0.01	0.03		0.01	
53.0667	2.63	1671	1152	p-Vinylanisole ^{a,e}	0.05	0.01	0.65	0.07	1.13	1.13	0.13	0.01	0.01	0.06
53.2	2.55	1670	1181	Diethyl butanedioate ^{a,e}	0.08	2.60	0.02	0.15	0.05	0.03	0.04	0.15	0.06	0.08
54	2.46	1669	1192	α -Terpineol ^{a,e}	0.03	0.04	0.14	0.02	0.01	0.01		0.05	0.01	0.01
54.4	2.62	1692	1216	<i>trans</i> , <i>trans</i> -2,4-Nonadienal ^a										0.03
54.5333	2.17	1691	1054	γ -Hexalactone ^a										
55.8667	2.51	1719	1165	Phenylmethyl acetate ^{a,e}	0.02	0.43	0.03	0.03	0.02	0.01	> 0.01	0.01	0.02	0.09
57.3333	3.53	1748	1384	Geraniol acetate ^e										
57.6	2.51	1751	1180	Methyl benzeneacetate ^a	0.01	0.02	0.01		> 0.01	> 0.01	0.01		0.01	0.02
57.7333	1.62	1749	915	2(5H)-Furanone ^a										
57.7333	2.06	1725	1177	Epoxylinole ^e			> 0.01							
57.7333	2.28	1754	1273	1-Decanol ^{a,e}	0.02	0.03	0.03	0.01	0.01	0.01	0.03	0.02	0.01	0.01
58	2.13	1758	1229	β -Citronellol ^{a,e}	0.01	0.01	0.01	0.01				0.01		0.01
58.2667	2.5	1766	1197	Methyl salicylate ^{a,e}	0.05	> 0.01	0.08	0.01	0.03	0.03	0.02	0.01	0.01	0.04
58.8	3.83	1776	1396	α -Damascone ^a			> 0.01							
59.4667	2.2	1787	1262	<i>cis</i> -4-Decen-1-ol ^{a,e}	0.01									
59.6	4.52	1790	1530	Citronellyl butyrate ^a										
59.7333	2.1	1790	1229	Nerol ^{a,e}			0.01							
59.7333	4.34	1787	1526	Methyl dodecanoate ^{a,e}	0.11	0.08	0.15	0.01	0.18	0.21	0.60	0.07	0.08	0.32
60	2.77	1798	1273	Ethyl salicylate ^{a,e}	0.12	0.10	0.18	0.03	0.06	0.04	0.03	0.04	0.05	0.04
60.4	3.57	1805	1388	β -Damascone ^{a,e}	0.03	0.04	0.03		0.03		0.01	0.02	0.03	0.03
60.5333	1.72	1808	1075	1-Phenylethanol ^{a,e}										
61.8667	4.86	1829	1595	Ethyl dodecanoate ^{a,e}	5.59	3.22	1.13	0.61	1.47	2.79	7.20	1.75	2.01	2.45
62.2667	2.07	1838	1256	Geraniol ^{a,e}	0.01	0.02	0.02	0.01	0.01		> 0.01	0.01	> 0.01	0.01
62.6667	4.27	1883	1539	Geraniol butyrate ^a										
63.7333	1.59	1869	1034	Benzyl alcohol ^{a,e}	0.07	0.74	0.16	0.13	0.07	0.02	0.02	0.05	0.01	0.01
65.4667	1.76	1901	1124	2-Phenylethanol ^{a,e}	0.16	0.13	0.12	0.03	0.07	0.03	0.17	0.04	0.09	0.05

Table 2 continued

DBFFAPxBPX-50		RI	HP-5xBPX-50	Compounds	Area (%) ^f									
RT			RI											
ID (min)	2D (s)													
65.6	2.41	1905	1260	γ -Octalactone ^{a,e}										
67.3333	1.4	1941	1159	2-Ethylhexoic acid ^a	0.01									
69.8667	2.88	1991	1567	Nerolidol ^{a,e}	0.01		> 0.01							> 0.01
70.1333	4.56	1994	1727	Methyl tetradecanoate ^{a,e}	0.02	0.03	0.03	0.01	0.04	0.02	0.02	0.02	0.01	0.01
71.0667	2.51	2017	1368	γ -Nonanolactone ^{a,e}	> 0.01									
71.3333	1.95	2024	1287	4-Ethylguaiacol ^{a,e}				> 0.01						
72.1333	4.97	2035	1796	Ethyl tetradecanoate ^{a,e}	0.64	0.79	0.78	0.09	0.51	0.48	0.87	0.58	0.46	0.57
72.6667	1.4	2051	1174	Octanoic acid ^{a,e}	0.07	0.07	0.03	0.02	0.02	0.01	0.05	0.02	0.02	0.01
73.4667	2.51	2068	1390	Methyl cinnamate ^a										
73.4667	2.61	2069	1287	δ -Nonalactone ^a										
75.0667	4.65	2097	1829	Methyl pentadecanoate ^{a,e}										
75.8667	2.71	2120	1468	Ethyl cinnamate ^{a,e}	0.01	0.01	0.01	0.01	0.01	0.06	0.08	0.02	0.01	0.04
76.4	2.61	2133	1474	γ -Decalactone ^{a,e}		> 0.01								
77.6	1.98	2159	1362	Eugenol ^{a,e}	0.02	0.01	0.02	0.01	0.02	> 0.01	> 0.01	> 0.01	> 0.01	> 0.01
79.7333	4.77	2202	1929	Methyl hexanoate ^{a,e}	0.05	0.11	0.05	0.01	0.02	0.02	0.02	0.08	0.03	0.01
81.3333	5.21	2241	1997	Ethyl hexanoate ^{a,e}	0.69	1.35	0.64	0.41	0.41	0.41	0.29	1.32	0.49	0.16
81.4667	2.72	2248	1578	γ -Undecanolactone ^a										
82.2667	1.51	2267	1392	Decanoic acid ^{a,e}	0.03	0.04	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01
85.6	2.63	2338	1724	Farnesol ^a	0.01									
86.2667	2.82	2364	1682	γ -Dodecalactone ^{a,e}		0.01								
89.8667	5.33	2447	2195	Ethyl octadecanoate ^{a,e}				0.01						
94.1333	1.67	2557	1401	Vanillin ^{a,e}										

RT retention time, RI retention index

^aSigma-Aldrich (St. Louis, USA)^bMicrochem (Pezinok, Slovakia)^cMerk KGaA (Darmstadt, Germany)^dSAFC Biosciences (Lenexa, USA)^ecompounds separated on the column setup HP-5 xBPX-50^fArea (%)—the ratio of the compounds area to total peaks areas of identified compounds

dimension. The injector port temperature was set at 220 °C, while the helium carrier gas flow rate was kept constant at 1 ml/min. Oven temperature was 40 °C was kept for 10 min then programmed to 240 °C with a rate of 2 °C/min and kept for 5 min. The modulator trapping was operated at 30 °C higher temperature compared to actual oven temperature with a modulation period of 8 s. The second column was operated at 10 °C higher temperature offset than the primary column, and the transfer line was heated at 240 °C. The temperature of ion source of TOFMS was hold at 230 °C, and detector voltage was set at 1700 V during the analysis. Energy of 70 eV was used for electron impact ionization source. The signal acquisition rate of 100 spectra/s within a mass range of m/z 29–450 was applied. The measured chromatograms were evaluated using LECO ChromaTOF 4.21 software and US National Institutes of Standards and Technology (NIST08) mass library. Identification of compounds were additionally confirmed by comparison of retention factors and mass fragmentation patterns of authentic standards.

Results and discussions

Sensory analysis

Sensory evaluation results indicated significant differences in the flavour profile of analyzed plum brandies (the supplementary 1). It should be noted that despite a marked plum aroma, samples were also described with additional fruity aroma notes (e.g. apple, sour and sweet cherries, apricot, banana, pear, citrus etc.) and the other aroma notes such as beet, caramel, conifer, and nutmeg (Fig. 1). The plum brandies of varieties “Chrudimer”, “Presenta” and “Blue Free” were highly estimated by panellists which seemed quite promising for further beverage production. These samples showed similar sensory profile defined as strong “plum” aroma, odour of “marzipan”, additional fruit or flower notes with some “stones”, “spicy flavours” and “sweetness” attributes. Whereas sensory characteristics like “dimness”, “fusel alcohols” and “acidity” resulted in poor aroma quality of the plum brandies made from varieties “Cacak Fruitful” and “Top Taste”.

Sample preparation

Liquid–liquid extraction into pentane and solid-phase microextraction with different coating material were used as sample preparation techniques for extraction of volatile organic compounds from a plum brandy samples. Overall, 60 compounds were common to both methods, while 34 additional compounds were extracted

by LLE, and 15–20 compounds were only obtained by SPME. A wider variety of alcohols like 2-pentanol, 3-pentanol, 2-hexanol, terpenoid alcohols (borneol, *cis*- and *trans*-carveols) and perillyl alcohol was detected in pentane extracts. Additionally, a SPME profile was enriched with 2-butanol, 2,3-butanediol, caryophyllene, butyrolactone, menthol, citronellol and carvone. Five types of SPME fibres such as PDMS, PA, CAR/PDMS, DVB/PDMS and DVB/CAR/PDMS were used in the experimental study. The efficiency of SPME extraction is generally controlled by several factors including polarity, volatility and shape of an analyte, structure of fibre coating, and complexity of sample (Pawliszyn 2012). In the case of PA and PDMS polymeric coatings, absorption is a dominant mechanism associated with thickness of fibre coating as well as polarity of compounds. Consequently, non-polar terpenes (e.g. γ -terpinene and myrcene) were more effectively extracted by PDMS fibre, and polar PA layer provided additional sorption of 2,3-butanediol and butyrolactone. For DVB/PDMS, CAR/PDMS and DVB/CAR/PDMS fibres, adsorption of analytes is controlled by coating porosity, where DVB is a mesoporous polymer and CAR is mainly microporous molecular sieve. In our case, CAR/PDMS fibre was not so effective for extraction of esters, especially for fatty acids with long carbon chain (e.g. ethyl 2-methylbutyrate, ethyl pentanoate, methyl undecanoate, ethyl pentadecanoate, methyl hexadecanoate). DVB/PDMS layer showed poor affinity for alcohols and carbonyl compounds with lower molecular weight (e.g. 2,3-butanedione, 2-alcohols C_5 – C_8 , *cis*-3-hexen-1-ol, *trans*-2-hexenal). Since a triple phase of DVB/CAR/PDMS coating combines the characteristics of both adsorbents, which could be particularly seen in the case of 2-butanol and carvone, its capacity was worse compared to the fibres with a single adsorbent. Simultaneously, this fibre covered a wider variety of analytes and was used for the further studies.

Analysis of plum brandies produced from different plum varieties

The plum brandies were analyzed on two sets of column combinations, HP-5-BPX-50 (conventional “nonpolar $\times$ medium-polar” setup) and DBFFAP-BPX-50 (reversed “polar $\times$ medium-polar” setup). It was found that 2D separation space of the “reversed” combination of columns was more exploited with better peak distribution (Fig. 2). Furthermore, the received ordered chromatographic profile for the most common classes of compounds considerably simplified the interpretation of chromatograms. These column setups were discussed in detail in our previous study (Vyvierska et al. 2015). In general,

Fig. 1 Aroma profiles of the selected plum brandies

Fig. 2 GCxGC–TOFMS chromatograms of the plum brandy distilled from “Chrudimer” plum variety with the column combinations of DBFFAP and BPX-50 (a), and HP-5 and BPX-50 (b)

from 91 to 195 compounds were tentatively identified in plum brandies, and among them 124 compounds were confirmed with authentic standards (Table 2). The concentration of compounds confirmed was calculated as relative content of compounds in area % (ratio of the compound TIC area to total TIC peaks areas of identified compounds). The richest VOC profile was observed for the sample produced from “Chrudimer”, “Cacak Fruitful”, “Cacak Early”, “Hanita” plum varieties, while distillates from “Gabrovská”, “Presenta”, “Amers”, “Elena” and “President” varieties showed poorest VOC profile. The VOC profiles of some plum brandies are shown on Fig. 3 and in supplementary 2.

Alcohols

Similarly to the results obtained by Satora and Tuszyński (2008), alcohols were one of the most common classes of compounds detected in the plum brandies (Fig. 4). Unsaturated and saturated straight-chain C_3 – C_9 alcohols and *cis*-3-hexanol were also found to be abundant compounds in juices obtained from *P. domestica* plums (Ismail et al. 1981). The whole homological series of *n*-alcohols (C_3 – C_{10}) excluding 1-butanol, as well as branched alcohols e.g. 2-methyl-1-propanol and 3-methyl-1-butanol, aromatic alcohols (benzyl alcohol, 2-phenylethanol) and furfuryl alcohol were present in all studied samples. In alcoholic beverages, a content and type of amino acids mainly

Fig. 3 GCxGC-TOFMS chromatograms of the plum brandies produced from varieties

Fig. 4 The average distribution of main classes of compounds detected in the plum brandies

determines the composition of higher (fusel) alcohols which are produced by transamination and oxidative deamination processes. Moreover, certain amounts of higher alcohols could be present in plums and plum juice. Aldehydes and ketones are considered as immediate precursors of metabolisms, which are reduced by alcohol dehydrogenases to the corresponding alcohols (Velíšik 2014). The influence of fusel alcohols on aroma of alcoholic beverages depends on their concentration, e.g. fruity notes at optimal levels or a strong, pungent smell at excessive content (Swiegers et al. 2005). 1-Propanol was one of the most abundant *n*-alcohol identified in the plum brandies, while a content of the other homologous did not exceed 1% of contribution to the VOC profile except for 1-hexanol. The relatively low amount of alcohols with carbon number higher than 5 is considered to be connected with the specificity of alcohol dehydrogenases to the

substrate and a decreased rate of reduction processes of corresponding aldehydes (Knee 1993) and distillation cut temperature. Overall, the concentration of 1-alcohols was generally higher compared to their 2- and 3-isomers. For example, 2-hexanol, 2-octanol and 3-pentanol were present only in a few samples, especially in distillates from “Chrudimer”, “Top King” and “Švestka domácí” varieties. The presence of 3-pentanol contributed to herbal notes of aroma typical for alcoholic beverages. It should be also mentioned that 2-butanol originated from bacterial action and 1-hexanol, commonly have negative influence on flavour at elevated concentration (Spaho et al. 2013). 1-Hexanol is not a fermentation product, and usually is found in higher concentration in plum fruits (Chai et al. 2012). The structure of branched fusel alcohols is primarily determined by parent branched-chain amino acids. Similarly to other alcoholic beverages (Vyviurska et al. 2015; Câmara et al. 2007; García-Llobodanim et al. 2008), 2-methylpropanol (*iso*-butyl alcohol), 3-methyl-1-butanol (*iso*-amyl alcohol) and 2-methyl-1-butanol (active amyl alcohol) were detected at highest abundance among branched higher alcohols. However, active amyl alcohol typical for plum fruits (Pino and Quijano 2012) was not present in “Tolar”, “Topper”, “Tophit” and “Presenta” samples. 4-Methyl-1-pentanol (*iso*-hexyl alcohol) was observed only at the trace level, and not detected in the brandies made from the plum varieties “Stanley” and “President”.

Unsaturated alcohols arise from reduction of unsaturated aldehydes which are commonly formed by enzymatic cleavage of linoleic and linolenic acids (Serot et al. 2001). In general, unsaturated alcohols, especially C₆ compounds,

contribute to herbaceous and green notes of alcoholic beverages aroma. 3-Methyl-3-buten-1-ol, 1-penten-3-ol, *cis*-3-hexen-1-ol, 1-octen-3-ol were the most common unsaturated alcohols detected in the studied plum brandies. On the contrary to *cis*-3-hexen-1-ol, *cis*-2-hexen-1-ol was merely observed in the brandies from plum varieties “Cacak Early”, “Cacak Fruitful”, “Katinka”, “Top King” and “Durancie”. Whereas their geometrical isomer *trans*-2-hexen-1-ol and *trans*-3-hexen-1-ol were quite specific for “Chrudimer” or “Elena” varieties, respectively. The same observation was found for 2-methyl-2-propen-1-ol identified only in “Durancie” sample. The other detected unsaturated alcohols 6-methyl-5-hepten-2-ol (sulcatol) and *cis*-4-decen-1-ol were established in a few samples which was mainly fermented from cultivars Chrudimer”, “Cacak Early”, “Hanita”.

Aromatic alcohols such as benzyl alcohol and its higher homologue 2-phenylethanol, originated from phenylalanine through different metabolic processes, were found in all plum brandies. Overall, brandies produced from fermenting fruits with stones are characterized with larger quantities of benzyl alcohol. Despite 2-phenylethanol identified as a component of plum fruit and described with “cooked plum-like” aroma (Ismail et al. 1981), its isomer 1-phenylethanol was detected only in distillate from “Chrudimer” variety. In this case, heterocyclic alcohols were mainly represented by furfuryl alcohol which is a degradation product of sugars.

Esters

In general, esters are produced by yeast during fermentation in a reaction between alcohols and acyl-CoA molecules. They are crucial intermediates for production of free organic acids (Lea and Piggott 2003). During aging of alcoholic beverages formation of esters continues through acidolysis, alcoholysis and transesterification processes (Velišik 2014). Since acetyl-CoA and ethanol are main products of catabolism of glucose, acetates and ethyl esters were usually dominant esters in the plum brandies. At the same time, ethyl ester of nonanoic acid and methyl cinnamate were reported to be important components of plum fruits (Ismail et al. 1981). Overall, esters significantly contribute to sweet fruity notes of beverages. Among methyl esters, those derivatives of salicylic acid and even chain length saturated C₆–C₁₆ fatty acids were found in all samples, whereas methyl esters of pentadecanoic acid and benzenoacetic acid were specific only for “Chrudimer” sample. Similar to the previous results, the ethyl ester profile of the plum brandies generally includes ethyl esters of even chain length saturated C₄–C₁₆ carboxylic acids and ethyl esters of nonanoic, cinnamic and salicylic acids, diethyl butanedioate. Plum brandies fermented from

cultivars “Chrudimer”, “Cacak Beauty”, “Tolar” and “Gabrovská” also contained ethyl ester of the longest fatty acid chain (C₁₈). Ethyl derivatives of odd number carboxylic acids or branched carboxylic acids such as ethyl pentanoate, ethyl heptanoate, ethyl 2-methylbutanoate and ethyl 3-methylbutanoate were more specific and appeared in some plum brandies. For the majority of samples, ethyl lactate formed during the fermentation from malic acid and ethanol (McKay et al. 2011) was an important part of the ester profile (0.39–2.71%). Similar to its parent alcohol, 3-methylbutyl acetate characterized with strong pear aroma was found at significant level compared to the other esters. At the same, a few specific esters like 3-methylbutyl butanoate and heptyl acetate were typical only for the brandy produced from variety “Chrudimer”.

Carbonyl compounds

The greatest diversity of carbonyl compounds was found for the samples obtained from plum varieties “Cacak Beauty”, “Chrudimer”, “Stanley” and “Cacak Early”. Aldehydes are important intermediates in higher-alcohol production, and conditions that favour higher-alcohol production also support the formation of small quantities of aldehydes (Lea and Piggott 2003). Among aldehydes, benzaldehyde previously found also in plum fruits (Ismail et al. 1981) was detected with high abundance (1–10%) in all the samples. Enzymatic degradation of amygdalin in the fruit stones is the main source of benzaldehyde responsible for bitter almond aroma of the alcoholic beverages. On the contrary, its higher derivatives such as benzeneacetaldehyde with a distinct green flavour and 4-methoxybenzaldehyde as well as aliphatic decanal and *trans*-2-decenal were significantly less common in studied plum brandies. The other unsaturated aldehydes were specific for the particular samples, e.g. *trans*-2-nonenal was present in the samples of “Cacak Beauty”, “Chrudimer” and “Vlaška”; *trans,trans*-2,4-nonadienal was established only in the sample “Cacak Beauty”. Heterocyclic aldehydes formed through dehydrating reactions of monosaccharides were represented by furfural and 5-methylfurfural. The first one furanoid was identified in all samples, whereas its higher homologue 5-methylfurfural was identified in samples “Cacak Fruitful”, “Haganta” and “Tophit”. Methylketones occur in alcoholic beverages as by-products of 2-alcohol synthesis, and in our case, acetophenone predominated among the others. Whereas 2-nonanone was found in one-third of the samples, and 2-heptanone was typical only for the plum brandies received from “Topper” and “Katinka” varieties. Moreover, in the half of the cases, the VOC profile was completed with 2,3-butanedione which had an unpleasant buttery flavour, and 2,3-pentanedione.

Acids

The biosynthesis of fatty acids is more complicated in comparison to other volatile compounds. Usually it occurs during alcoholic fermentation initiated in the yeast cell by formation of acetyl coenzyme A (Berger 2007). In general, 6 carboxylic acids were identified and confirmed with authentic standards, and among them acetic acid was dominant. This fact could be caused by additional production of acetic acid during and/or after fermentation through oxidation of ethanol under aerobic conditions (Berger 2007). The content of the other carboxylic acid was significantly lower (propanoic, butanoic, 2-ethylhexanoic acids) and these compounds were presented only in a few plum brandies. According to Ismail et al. (1981) the composition of carboxylic acids depends mainly on the applied yeast strain and to a lesser extent on the used raw material.

Terpenes and terpenoids

Since terpenes are linked to sugar molecules as non-volatile glycosides in plants, fruit ripen process and conditions of hydrolysis are responsible for the overall aroma perception of alcoholic spirit. As can be noticed, in the plum brandies terpenes were mainly represented by monoterpenes, monoterpene derivatives and sesquiterpenes with sweet floral odours. The presence of myrcene, 4-terpinelol, α -terpineol, linalool, linalool oxide, and nerol was previously mentioned in *Prunus domestica* plum fruit (Pino and Quijano 2012). Linalool contributing to “plum-like” aroma (Ismail et al. 1981) is the only one of terpenoids found in the all studied samples. Whereas its oxidation product epoxylinalool was less common and more specific for the plum brandies “Chrudimer”, “Cacak Early”, “Cacak Fruitful”, “Katinka”, “Top King”. The other common terpenoids include monoterpene alcohols (β -citronellol, geraniol, α -terpineol, 4-terpineol), sesquiterpene alcohols (nerolidol, farnesol) and linalool oxides obtained by cyclisation of epoxylinalool. It is interesting that sesquiterpene caryophyllene was found only in the plum brandies fermented from varieties “Chrudimer” and “Durancie”. Especially enriched terpenoid profile was established for the brandy fermented from plum cultivar “Chrudimer”, where the presence of myrcene with strong spicy notes and a wide variety of monoterpenes derivatives (linalool acetate, geraniol acetate, geraniol butyrate, *cis*-rose oxide, bornyl acetate, citronellyl acetate, citronellyl butyrate) may correlate with pleasant aroma notes of this sample.

Lactones and miscellaneous compounds

Lactones, as important components of fruity notes of fermented alcoholic beverages are formed from amino acids

through the processes of oxidative deamination and decarboxylation (Berger 2007). Three lactones, γ -hexalactone, γ -octalactone and γ -decalactone were previously reported to be responsible for plum-like aroma (Ismail et al. 1981). In this study, the brandies obtained from “Elena”, “Presenta” and “Gabrovská” cultivar did not contain lactone compounds at all. A marked dominance of γ -lactones was evident for the majority of samples, as well as a typical feature here was a presence of 2(5H)-furanone and butyrolactone. Sample “Chrudimer” was characterized by the reachest diversity of lactones involving γ -lactones in the C₈–C₁₂ range, butyrolactone, γ -crotonolactone and δ -octalactone. In addition, γ -nonanolactone, γ -decalactone and γ -dodecalactone were mainly detected in the VOC profile of the samples obtained from “Cacak” plum cultivars and a few more samples.

Among fragrances formed during degradation of phenolic acids, eugenol was established to be the most common compound. Vanillin and 4-ethylguaiacol were mainly identified in the plum brandies fermented from “Cacak” plum cultivars. A majority of the samples contained styrene with a characteristic terpenic odour, and 4-vinylanisole was present in one-third of the cases. A phenolic flavour *p*, α -dimethyl styrene and benzonitrile appeared to be quite specific for the plum brandies produced from “Hanita”, “Chrudimer” and “Durancie” plums, respectively. Metabolites of oxidative degradation of carotenoids were generally represented by β -damascenone, whereas α -damascone was detected only in the brandies fermented from “Chrudimer” and “Katinka” plum varieties.

Conclusion

Complete analysis of the plum brandies produced from 25 plum cultivars was carried out with comprehensive two-dimensional gas chromatography and sensory evaluation. Two sample preparation procedures were tested and compared, namely liquid–liquid extraction and solid phase microextraction. Regarding to quantity and diversity of compounds, extraction with pentane was more efficient, however 2-butanol, 2,3-butanediol, caryophyllene, butyrolactone, menthol, citronellol and carvone were sorbed only by SPME fibre. As the result, triple phase DVB/CAR/PDMS fibre coating with combined properties was applied for determination of the VOC profile of the plum brandy. The combination of DBFFAP–BPX-50 columns was more appropriate for analysis of plum brandies than HP-5–BPX-50 column setup, because of better separation characteristics. Overall, the analysed plum brandies were distinguished by the presence of a number of identified compounds, since 91–195 compounds were tentatively identified in the samples, and 124 of them were confirmed

by analysis of authentic standards. Alcohols e.g. 1-propanol, 2-propanol, 3-methyl-1-butanol, 1-hexanol, ethyl esters of even chain length saturated C₆–C₁₂ carboxylic acids, acetic acid and benzaldehyde were dominant components of the VOC profile of the plum brandies. Specific compounds found only in the particular samples mainly belongs to unsaturated fusel alcohols (e.g. 2-methyl-2-propen-1-ol, *trans*-3-hexen-1-ol and 1-octen-3-ol), unsaturated aldehydes (*trans*-2-nonenal, *trans,trans*-2,4-nonadienal), monoterpene derivatives (e.g. linalool acetate, geraniol acetate, geraniol butyrate). Furthermore, it should be noted that the brandy produced from “Chrudimer” plum variety was characterized by broad variety of γ -lactones and terpenoids, whereas the samples obtained from “Elena”, “Presenta” and “Gabrovská” cultivars did not include any lactone compounds. The variation of composition of the plum brandies were confirmed by the sensory evaluation, and the samples described by strong “plum” aroma, odour of “marzipan”, additional fruit or flower notes (e.g. the plum brandies fermented from the cultivars “Chrudimer”, “Presenta”, “Blue Free”) were highly estimated by panellists.

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