Volatile Compounds of Homemade Grape Brandy Determined by GC-MS Analysis

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ABSTRACT

The aim of this paper was to determine whether the addition of some ingredients to the same grape brandy after distillation affects the chemical composition of the volatile components by applying the gas chromatography coupled with mass spectrometry (GC-MS). Five samples were subjected to this study and a total of 57 compounds were identified. For all examined samples, esters were the most dominant class of compounds, but in different proportions. Ethyl decanoate was the most abundant compound in the sample L1 (grape brandy kept in an oak barrel) with the contribution of 29.1%, followed by ethyl octanoate (17.2%) and ethyl dodecanoate (14.8%). Sample L2 (grape brandy with summer truffles) was dominated by *n*-hexanol and ethyl lactate with similar contribution (18.1% and 17.8%, respectively). On the other hand, in the sample L3 (grape brandy with winter truffles) ethyl lactate was present with the contribution 44.8%. The dominant compounds in sample L4 (grape brandy with grains of coffee and dried grapes) were ethyl decanoate with contribution of 14.8% and phenyl ethyl alcohol (12.5%), while the two main volatiles of the sample L5 (grape brandy with young green walnuts) were diethyl succinate (22.9%) followed by ethyl lactate (21.9%). The results obtained in this study on volatile aromatic compounds in the analyzed grape brandies suggest that addition of some ingredients to the same grape brandy after distillation affects the chemical composition in both the number of aromatic compounds and their relative content.

Keywords: grape brandy, chemical composition, volatiles, GC-MS

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Introduction

Fruit spirits are popular alcohol beverages due to their unique flavour and very often they represent the national drink of the country. *Rakija* is the collective term for fruit brandy popular in the Balkans and it can be made from all fruit species containing sugar from which alcohol is produced during alcoholic fermentation. The best fruits to produce *rakija* are plums, cherries, apples, pears, apricots and quinces. In some countries, as well as in Serbia, *rakija* can also be made from grapes; there are two different types of grape spirits: "*loza*" – obtained through fermentation and distillation of the whole non-strained mash of grapes and "*komova rakija*" – the spirits where the grape pomace (grape residues) that is left over from winemaking is used as base.

Normally, *rakija* is colourless, unless herbs or other ingredients are added. Some types of *rakija* are kept in wooden barrels (oak or mulberry) for extra aroma and a golden colour, while sometimes plum and grape *rakija* are mixed with other ingredients, such as herbs, honey, sour cherries and walnuts, during the fermentation process and during the distillation or after that.

The main ingredients of these beverages are water and ethanol, and they account around 99% of the total content of the spirits but there are hundreds of different compounds, so-called congeners, present in very low concentrations that are responsible for the differences between spirits obtained from different fruits. It is well known that the chemical composition depends on the cultivar used for the production (Biernacka and Wardencki, 2012; Coldea et al., 2011; Hernandez-Gomez et al., 2005), grape processing method (Radeka et al., 2008), fermentation procedure (Matijašević et al., 2019; Soufleros et al., 2005), distillation technique (Arrieta-Garay et al., 2013; Lukić et al., 2011a; Madrera and Alonso, 2012; Matias-Guiu et al., 2016; Spaho, 2017), use of post distillation processes and maturation of the spirits (Madrera et al., 2003; Tsakiris et al., 2014). The aim of this paper was to determine whether the addition of some ingredients to the same grape brandy after distillation affects the chemical composition of the volatile components by applying the gas chromatography coupled with mass spectrometry (GC-MS).

Experimental

Five samples were analyzed. All the analyzed samples were homemade grape brandies produced by traditional method. First sample (L1) was grape brandy kept in an oak barrel, the second sample (L2) being grape brandy kept in an oak barrel to which summer truffles (100 - 200 g truffles per liter of fresh brandy) were added and which stood in brandy for about 3 months, the third sample (L3) was grape brandy to which winter truffles (100 - 200 g truffles per liter of brandy) were added and which stood in brandy for about a month, the fourth sample (L4) was grape brandy kept in an oak barrel to which was then added 40 grains of coffee and 10 grains of dried grapes, per liter of brandy, and which stood in brandy for about 6 months and the fifth sample (L5) was grape brandy to which was then added 40 young green walnuts per liter of brandy and left in the dark for a month and then filtered.

Isolation of esters from *rakija*

Eighty milliliters of spirits were mixed with 80 mL of distilled water and 40 mL of CH_2Cl_2 in a 300 mL conical flask. Eight grams of NaCl was added and the mixture was stirred on a magnetic stirrer for 30 min. The layers were separated into a separating funnel and the organic layer was dried above of anhydrous $MgSO_4$. The extract was concentrated to 1 mL on a vacuum evaporator and directly analyzed by gas chromatography- mass spectrometry (GC-MS) (Tešević et al., 2005).

GC-MS analysis

GC-MS analyses were performed on an Agilent 7890 gas chromatograph with 7000B GC-MS-MS triple quadrupole system, operating in MS1 scan mode, and equipped with a fused-silica capillary column Agilent HP-5 MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The chromatographic analyses were carried out in the following conditions: He as a carrier gas at a flow rate of 1.0 mL/min, GC oven temperature was kept at 50 °C for 2.25 min and programmed to 290 °C at a rate of 4 °C/min. One μL of the concentrated extract was injected at split ratio 40:1. The injector and interface operated at 250 and 300°C, respectively. Post run: back flash for 1.89 min, at 280 °C, with helium pressure of 50 psi. Ionization mode was electronic impact at 70 eV. Mass range was set from 40 to 440 Da.

The percentage amounts of the separated compounds were calculated from the total ion chromatogram.

Identification of volatile compounds

Components were identified by comparison of their mass spectra with those of Wiley 6, Adams (2007), NIST 11 and Essential oils libraries, applied on Agilent Mass Hunter Workstation (B.06.00) and AMDIS (2.1, DTRA/NIST, 2011) software and confirmed by comparing of calculated retention indexes (relative to C_8-C_{32} *n*-alkanes) with the literary values of the retention indices.

Results and Discussion

The individual and mean values for each volatile found in all four samples are presented in Table 1. In the samples that were subjected to this study a total of 57 compounds were identified that belong to different groups, eight of them were found to be common to all. For all examined samples, esters were the most dominant class of compounds, but in different proportions. Esters are formed during the alcoholic fermentation and they represent the most common class of compounds that contribute to the aroma in the brandy (Ferrari et al., 2004; Silva and Malcata, 1999; Soufleros et al., 2001). The ethyl esters were the most dominant class of the esters identified in our samples and according to the literature they are produced during raw material fermentation and their content may increase or decrease during ageing (Genovese et al., 2013; Mamede et al., 2005; Tešević et al., 2005). Grape brandy that was kept in an oak barrel (L1) could be distinguished from the other samples by the highest relative amount of esters (89.1%). Among these, ethyl decanoate was the most abundant with the contribution of 29.1%, followed by ethyl octanoate (17.2%) and ethyl dodecanoate (14.8%). These compounds are produced during the raw material fermentation (Silva and Malcata, 1998) and they are contributing to the fruity and flowery smells at their relatively high levels (Madrera et al., 2013). Sample L2 was dominated by *n*-hexanol and ethyl lactate with similar contribution (18.1% and 17.8%, respectively). According to the literature, *n*-hexanol is originating only from raw material (Soufleros et al., 2004) and it is denominated as a rough indicator of the pressing degree (Lukić et al., 2011b) which presence can be associated with flower and herbaceous aromas. On the other hand, in the sample L3 ethyl lactate was present with the contribution 44.8% and it is considered to give the distillates a buttery flavour and smell of rancid butter and its presence can be linked to a malolactic fermentation (Léauté, 1990). The dominant compounds in sample L4 were ethyl decanoate with contribution of 14.8% and phenyl ethyl alcohol (12.5%) which is an aromatic alcohol and has a rose-like odour. Out of 28 compounds that were identified in the sample L4, 7 were exclusive to this sample. The most significant was caffeine which represented 7.1% of the sample. Caffeine is a purine alkaloid that occurs naturally in coffee beans. Alcoholic beverages (in our case-grape brandy) normally do not contain caffeine, so the presence of the caffeine in this sample is because it was extracted from the grains of coffee during the process of maceration. The two main volatiles of the sample L5 were diethyl succinate (22.9%) which gives a camphor-like character (Ferreira et al., 1999) and according to the literature derives mainly from bacterial spoilage (Karagiannis and Lanaridis, 2002), followed by ethyl lactate (21.9%). Among 27 components identified in this sample, five of them were detected only in this sample. Syringic acid (10.5%) is a phenol present in some distilled alcohol beverages and the presence of this compound only in sample L5 according to the previously published results (Colaric et al., 2005; Cosmulescu et al., 2010) lead us to the conclusion that it comes from young nuts that have been added. Another compound worth mentioning was juglone, which is a well-known component of walnut (Cosmulescu et al., 2010; Prasad, 2003; Stampar et al., 2006).

Table 1. Chemical composition of grape brandy volatiles.

				Content %				
No	RI	RN	Compound	L1	L2	L3	L4	L5

1	765	762	Pentanol	0.6	-	-	-	-
2	775	778	Ethyl butanoate	0.7	0.4	0.6	0.3	-
3	794	798	Ethyl lactate	4.3	17.8	44.8	-	21.9
4	805	827	3-Methylhexan-3-ol	-	3.5	-	-	-
5	810	815	Furfural	0.4	0.3	-	0.7	-
6	828	839	Ethyl 2-methylbutyrate	-	2.8	1.4	-	-
7	840	846	2-Methylbutanoic acid	-	2.8	2.1	-	-
8	852	858	*n*-Hexanol	0.8	18.1	8.5	1.7	-
9	861	867	Isopentyl acetate	0.4	2.1	0.9	0.3	2.2
10	948	955	1,1-Diethoxy-3-methyl-butane	-	0.6	-	-	0.3
11	954	959	Benzaldehyde	-	-	1.2	8.6	-
12	960	968	Ethyl 2-hydroxyisovalerate	-	-	0.5	-	-
13	968	977	1-(1-ethoxyethoxy)-Pentane	-	0.4	-	0.3	0.7
14	995	997	Ethyl hexanoate	2.3	0.4	0.9	0.8	1.0
15	1024	1024	Limonene	-	-	-	4.4	-
16	1030	1034	Benzyl alcohol	-	-	-	0.6	0.6
17	1054	1062	Ethyl 2-hydroxyhexanoate	-	0.4	1.1	-	0.5
18	1069	1067	*cis*-Linalool oxide	0.4	0.5	-	-	0.5
19	1085	1084	*trans*-Linalool oxide	-	-	-	0.4	0.3
20	1096	1095	Linalool	0.8	-	-	-	0.3
21	1100	1100	*n*-Nonanal	0.4	-	-	0.4	-
22	1110	1115	Phenyl ethyl alcohol	3.0	7.3	6.2	12.5	9.3
23	1164	1163	4-Ethyl-phenol	-	-	-	-	2.2
24	1167	1169	Ethyl benzoate	-	1.2	2.2	3.8	-
25	1175	1170	Octanoic acid	-	4.6	1.2	-	-
26	1177	1181	Diethyl succinate	3.0	-	2.7	-	22.9
27	1188	1186	α-Terpineol	0.5	-	-	0.2	-

28	1189	1188	2-Methoxy-*p*-cresol	-	0.3	-	-	-
29	1193	1194	Ethyl octanoate	17.2	1.9	4.2	5.7	4.1
30	1225	1246	Benzaldehyde diethylacetal	-	-	-	3.2	-
31	1241	1243	Benzene acetic acid, ethyl ester	-	0.8	0.5	-	-
32	1254	1254	2-Phenyl ethyl acetate	-	-	-	-	0.4
33	1276	1280	4-Ethyl-2-methoxy-phenol	-	-	-	-	1.0
34	1292	1295	Nonanoic acid, ethyl ester	0.4	-	-	0.3	-
35	1346	1347	Triacetin	-	-	1.0	-	-
36	1355	1356	Eugenol	-	-	-	0.5	-
37	1370	1364	Decanoic acid	2.1	4.0	0.9	-	2.4
38	1381	1381	*n*-Nonanal diethyl acetal	-	-	-	0.5	-
39	1392	1392	Ethyl decanoate	29.1	4.2	7.1	14.8	4.1
41	1396	1393	Vanillin	-	-	-	0.3	-
42	1465	1467	Ethyl-(2*E*,4*Z*)-decadienoate	-	2.3	1.4	-	-
43	1498		Juglone	-	-	-	-	1.8
44	1561	1565	Dodecanoic acid	0.3	0.2	-	-	0.4
45	1570	1569	γ-Undecalactone	-	-	-	-	-
46	1590	1593	Ethyl dodecanoate	14.8	1.1	2.1	7.6	1.0
47	1640	1641	Isoamyl decanoate	0.7	-	-	-	-
48	1657	1655	Syringaldehyde	-	-	-	1.1	-
50	1789	1795	Ethyl tetradecanoate	2.3	-	-	-	-
51	1817	1823	Syringic acid	-	-	-	-	10.5
52	1841	1842	Caffeine	-	-	-	7.1	-
53	1967	1977	Ethyl 9-hexadecenoate	0.9	-	-	0.2	-
54	1988	1193	Ethyl hexadecanoate	7.2	1.6	2.0	4.7	0.5
55	2156	2163	Ethyl linoleate	2.7	4.9	1.7	2.0	0.3
56	2162	2169	Ethyl oleate	-	1.7	1.2	-	-

57	2162	2173	Linolenic acid, ethyl ester	3.1	-	-	1.5	-
Number of constituents				25	27	24	28	24
Total identified				98.4	86.2	96.4	84.5	89.2
Alcohols				4.4	28.9	14.7	14.8	9.9
Esters				89.1	43.6	75.3	42.0	58.9
Others				4.9	13.7	6.4	27.7	20.4

Compounds listed in order of elution on a HP-5 MS column. RI: experimentally determined retention indices on the mentioned column by co-injection of a homologous series of *n*-alkanes C_8-C_{32}; RN: NIST Chemistry WebBook Retention indices; -: not detected. Samples: L1-grape brandy kept in an oak barrel; L2-grape brandy kept in an oak barrel with summer truffles; L3- grape brandy with winter truffles; L4-grape brandy kept in an oak barrel with coffee grains of dried grapes; L5-grape brandy with young green walnuts.

Conclusion

The results obtained in this study on volatile aromatic compounds in the analyzed grape brandies suggest that addition of some ingredients to the same grape brandy after distillation affects the chemical composition in both the number of aromatic compounds and their relative content. Ethyl esters from middle-chain fatty acids (octanoic, decanoic and dodecanoic) which make up over 60% of the samples L1 are contributing to the fruity and flowery smells of the sample. The volatile composition of the samples L2 and L3 was qualitatively rather similar, so their quite distinct organoleptic characteristics can be attributed to the differences between their volatile concentrations. The herbaceous odour of sample L2 can be explained by the domination of the *n*-hexanol. On the other hand, ethyl lactate which was the most abundant compound in the sample L3 is considered to give the distillates a buttery flavour and smell of rancid butter. Ethyl decanoate and phenyl ethyl alcohol are responsible for a fruity and rose-like odour of the sample L4, while the dominant presence of diethyl succinate gives a camphor-like character of the sample L5. Also, for samples L1, L2 and L4 it has been observed the presence of furfural which can be explained by the fact that these samples were kept in the oak barrel (while the samples L3 and L5 were not), since there are some studies that reports that volatile compounds extracted from the barrel wood are mainly furanic and phenolic compounds.

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Conflict-of-Interest Statement

All authors declare that they have no conflict of interest.

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