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Gas-chromatographic analysis of volatile compounds in different types of commercial alcoholic beverages

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ABSTRACT

In this study, volatile compounds were analysed in seven samples of different types of commercial alcoholic beverages available in stores in the Republic of Serbia. A total of 75 volatile compounds were detected by the gas chromatographic-mass spectrometric (GC/MS) method. Regarding the class of identified compounds, esters were the most dominant class identified in samples *Prirodna prepečenica*, *Metaxa* and *Whiskey*; *Tequila* and *Quince brandy* were dominated by higher alcohols, while in the samples *Pelinkovac* and *Travarica*, other classes of compounds were identified as the main. The major volatile compounds identified in tested samples were different. *Prirodna prepečenica* and *Travarica* were dominated by ethyl lactate; *Metaxa* was dominated by diethyl malate; *Quince brandy* had the highest amount of *n*-hexanol; most dominant compound in *Tequila* was benzyl alcohol; *Whiskey* was dominated by phenyl ethyl alcohol, while in *Pelinkovac trans*-thujone was identified as major compound. The results obtained in this study have shown that tested alcoholic beverages have different qualitative and quantitative compositions regarding the volatile compounds.

Keywords: alcoholic beverages, chemical composition, volatiles, GC-MS

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Introduction

Based on raw materials and production methods, alcoholic beverages can be divided into different classes: beer, wine, cider and distilled spirits. Spirits are made from many raw materials that contain sugar or starch, which is converted into sugar by malting. Various brandies are made from fruit mash (plums, cherries, apples, pears, apricots, and quinces); vodkas are produced from potatoes, tequila is distilled from a mash made from cactus, while the base of all types of whisky is malted grains. Quality and composition of spirits depends on the raw material that is used (Biernacka and Wardencki, 2012; Coldea et al., 2011; Hernandez-Gomez et al., 2005) and the production process (Arrieta-Garay et al., 2013; Lukić et al., 2011; Madrera et al., 2003; Madrera and Alonso, 2011; Matias-Guiu et al., 2016; Matijašević et al., 2019; Radeka et al., 2008; Soufleros et al., 2005; Spaho, 2017; Stamenković and Stojanović, 2020; Tsakiris et al., 2014). An important role in the organoleptic characteristics and quality of alcoholic beverages has various volatile compounds (such as alcohols, esters, volatile acids, terpenes, *etc*.) present in different concentrations. Besides volatile compounds, there are several different groups of non-volatile compounds that also contribute to the flavour of the spirits. Terpenes, which can be present in alcoholic beverages, are mainly derived from the raw material that is used for distillation, or they can be subsequently added to the beverage after the distillation to improve the flavour. Aside from ethanol (the most abundant compound besides water) and methanol (alcohol with toxic effect), higher alcohols that are formed during fermentation can also be detected in alcoholic beverages. The presence of higher alcohols can have both positive and negative impacts on the aroma, and flavour depending on concentration. Esters are aromatic compounds with a pleasant aroma, and therefore, the presence of these compounds has a positive effect on the aroma of spirits. Different groups of aroma compounds that can be detected in the brandies can originate from the fruit (primary aromatic compounds) or can be formed during alcoholic fermentation (secondary aromatic components), during the distillation process (tertiary aromatic compounds) and the maturation process (quaternary aromatic compounds) (Tešević et al., 2005).

As a part of our ongoing investigation on the composition of the volatile components of alcoholic beverages (Stamenković and Stojanović, 2020), this study aimed to determine the volatiles composition of seven different commercial brandies by applying the gas chromatography coupled with mass spectrometry (GC-MS).

Experimental

Seven samples were analyzed: *Prirodna prepečenica* (Takovo, Gornji Milanovac); *Tequila* Camina real gold (Tequila Cascahulin, Mexico); *Metaxa* (S.&E.&A. Metaxa, A.B.E., produce of Greece); *Quince brandy* (Simex Original); *Pelinkovac* (Gorki list); *Viski* (Longmorn) and *Travarica* (Podrumi manastira Tvrdoš).

Preparation of *rakija* for GC-MS analysis

Eighty millilitres of spirits were mixed with 80 mL of distilled water and 40 mL of CH_2Cl_2. Eight grams of NaCl was added, and the mixture was stirred on a magnetic stirrer for 30 minutes. The layers were separated into a separating funnel, and the organic layer was dried above 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 a 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 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 a split ratio of 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 an 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_{40} *n*-alkanes) with the literary values of the retention indices.

Results and Discussion

In the samples subjected to this study, a total of 75 compounds were identified and presented in Table 1. In the individual samples of *Prirodna prepečenica* (L1), *Tequila* (L2), *Metaxa* (L3), *Quince brandy* (L4), *Pelinkovac* (L5), *Whiskey* (L6) and *Travarica* (L7), a total of 30, 17, 16, 20, 18, 20 and 33 volatile compounds were identified, respectively. Esters were the most dominant class of the compounds identified in samples L1, L3 and L6; alcohols were dominant in L2 and L4, while in the samples L5 and L7, components that do not belong to alcohols or esters were the most abundant compounds. It can be noticed (Table 1), that furfural was the only compound that was present in all samples with the different contributions. A high concentration of furfural may have a toxic effect on the human organisms, while in low concentration, the presence of this compound contributes to the aroma and flavour of fruit distillates. The most dominant compound in sample L1 was ethyl lactate (22.8%), followed by benzyl alcohol (22.4%). Ethyl lactate was also identified as a major compound in sample L7 with the contribution of 15.2%. With 33 identified components, *Travarica* (L7) seems to possess the wealthiest volatile composition, with 10 compounds that were exclusive to this sample. The sample L5 differs from others because in this sample, higher alcohols were not detected at all. Tributyl acetylcitrate was the only ester that was identified in this sample, with the contribution of 15.3%. The most dominant in this sample were compounds that do not belong either to alcohols or esters (65.1%), with *trans*-thujone (19.8%) as a major component. The main difference between *Pelinkovac* and all the other samples is that in this sample, terpenes were qualitatively and quantitatively the largest group of compounds. Higher alcohols were quantitatively the largest group of the volatile aroma compounds identified in the sample L4 (42%). The most dominant compound in this sample was *n*-hexanol with the contribution of 40.5%, while in the samples L1 and L7, hexanol was present in the concentration of 2.8% and 0.5%, respectively and not even detected in the samples L2, L3, L5 and L6. Sample L6 (*Whiskey*) was dominated by phenyl ethyl alcohol with the contribution of 27.9%. This component is responsible for the rose-like aroma in spirits (Ferrari et al., 2004). Sample L3 (*Metaxa*) could be distinguished from the other samples by the highest relative amount of esters (75.9%) with diethyl malate as the main component (44.9%). This ester was detected only in the *Metaxa* sample, and its presence contributes to the sweet, caramellike odour of the spirit. Regarding the *Tequila* sample (L2), the most dominant compounds were alcohols with benzyl alcohol as the main component (14.7%). This compound contributes to the pleasant sweet, floral aroma. By comparing the chemical composition of *Prirodna prepečenica* with our previously published results of homemade plum brandy (Stamenković and Stojanović, 2020), it can be noticed that regarding the major compound, all tree samples were dominated by ethyl lactate and with similar contribution (24.3% in the sample plum “ranka”, 20.1% in distillate obtained from plum “čačanska rodna” and 22.8% in *Prirodna prepečenica*). On the other hand, Agalarov et al. (2017) were investigating quince brandy as one of the traditional fruit brandies produced in Azerbaijan, and the obtained results were quite different compared to ours. In the sample from Azerbaijan, the most dominant volatile compounds were ethyl acetate and acetaldehyde, two compounds that were not even detected in our sample.

Table 1. Chemical composition of commercial alcoholic beverages

				Content (%)						
No	RI	RN	Compound	L1	L2	L3	L4	L5	L6	L7
1	762	760	Isopentyl alcohol	-	-	-	0.9	-	-	-
2	765	762	Pentanol	0.6	-	-	-	-	-	-
3	766	766	Cyclopentanone	-	3.1	-	-	-	-	-
4	775	778	Ethyl butanoate	0.7	1.9	1.0	2.6	-	0.3	-
5	780	780	Dihydro-2-methyl-3-furanone	-	2.2	-	-	-	-	-
6	794	798	Ethyl lactate	22.8	12.7	9.9	4.0	-	-	15.2
7	810	815	Furfural	0.6	1.8	1.7	4.8	0.6	0.9	0.6
8	852	858	*n*-Hexanol	2.8	-	-	40.5	-	-	0.5
9	856	872	1-Butoxy-1-ethoxyethane	-	-	-	-	-	-	0.6
10	861	867	Isopentyl acetate	0.3	0.5	-	2.3	-	0.9	0.4
11	926	924	α-Pinene	-	-	-	-	-	-	4.8
12	940	946	Camphene	-	-	-	-	-	-	1.0
13	948	955	1,1-Diethoxy-3-methyl-butane	-	-	0.5	-	-	-	-
14	954	959	Benzaldehyde	1.7	-	0.5	0.7	-	-	-
15	958	957	2-Acetylfuran	-	2.6	-	-	-	-	-

16	968	977	1-(1-ethoxyethoxy)-pentane	-	-	-	-	-	-	1.3
17	995	997	Ethyl hexanoate	0.6	0.7	0.9	1.0	-	1.0	0.4
18	1009	1007	Hexyl acetate	-	-	-	2.3	-	-	-
19	1018	1020	*p*-Cymene	-	-	-	-	0.4	-	1.6
20	1024	1024	Limonene	-	-	-	-	-	-	1.1
21	1025	1026	Eucalyptol	-	-	-	-	1.0	-	7.7
22	1030	1034	Benzyl alcohol	4.3	14.7	1.2	-	0.8	-	-
23	1069	1067	*cis*-Linalool oxide	0.8	0.9	-	-	-	-	0.2
24	1085	1084	*trans*-Linalool oxide	1.2	0.6	-	-	-	-	-
25	1096	1095	Linalool	-	1.1	-	-	0.8	-	0.6
26	1100	1100	*cis*-Thujone	-	-	-	-	8.1	-	7.1
27	1110	1115	Phenyl ethyl alcohol	1.3	2.6	0.4	-	6.7	27.9	-
28	1010	1012	*trans*-Thujone	-	-	-	-	19.8	-	2.3
29	1038	1041	Camphor	-	-	-	-	-	-	2.7
30	1048	1048	Menthone	-	-	-	-	3.3	-	-
31	1058	1058	*iso*-Menthone	-	-	-	-	1.8	-	-
32	1062	1065	Borneol	-	-	-	-	-	-	1.7
33	1063	1061	*neo*-Menthol	-	-	-	-	0.7	-	-
34	1164	1163	4-Ethyl-phenol	0.4	-	-	-	-	-	-
35	1167	1169	Ethyl benzoate	4.8	-	-	-	-	-	-
36	1070	1067	Menthol	-	-	-	-	3.2	-	-
37	1075	1074	Terpinen-4-ol	-	-	-	-	5.3	-	0.8
38	1173	1170	Octanoic acid	-	-	-	-	-	2.0	-
39	1177	1181	Diethyl succinate	4.4	-	10.0	0.8	-	1.5	12.7
40	1188	1186	α-Terpineol	1.2	3.9	1.4	-	0.8	-	1.1
41	1193	1194	Ethyl octanoate	1.5	4.1	4.8	5.7	-	8.6	0.7
42	1204	1204	Verbenone	-	-	-	-	-	-	6.0

43	1225	1246	Benzaldehyde diethylacetal	0.3	-	-	-	-	-	-
44	1226	1233	5-Hydroxymethylfurfural	-	-	14.0	-	6.0	-	-
45	1264	1271	Diethyl malate	-	-	44.7	-	-	-	-
46	1268	1266	Ethyl salicylate	0.8	-	-	-	-	-	-
47	1287	1289	*trans*-Sabinyl acetate	-	-	-	-	9.7	-	-
48	1287	1289	Thymol	-	-	-	-	-	-	5.9
49	1292	1295	Ethyl nonanoate	0.3	-	-	-	-	-	-
50	1355	1356	Eugenol	2.9	-	-	-	-	-	-
51	1370	1364	Decanoic acid	1.3	-	-	-	-	3.4	-
52	1382	1383	(*E*)-β-Damascenone	-	-	-	1.0	-	-	-
53	1392	1392	Ethyl decanoate	3.6	8.7	3.5	10.5	-	20.9	0.3
54	1396	1393	Vanillin	0.4	-	0.5	-	-	0.5	-
55	1425	1422	(*E*)-α-Ionone	-	-	1.2	-	-	-	-
56	1463	1465	(*E*)-Ethyl cinnamate	1.8	-	-	-	-	-	-
57	1484	1487	(*E*)-β-Ionone	-	-	-	1.4	-	-	-
58	1561	1565	Dodecanoic acid	-	-	-	-	-	0.7	-
59	1570	1569	γ-Undecalactone	-	-	-	2.2	-	-	-
60	1590	1593	Ethyl dodecanoate	2.8	3.4	1.1	4.8	-	17.0	-
61	1640	1641	Isoamyl decanoate	-	-	-	-	-	0.3	-
62	1657	1655	Syringaldehyde	-	-	-	-	-	1.1	-
63	1671	1671	*n*-Tetradecanol	-	-	-	-	-	1.8	-
64	1789	1795	Ethyl tetradecanoate	0.6	-	-	0.6	-	3.6	-
65	1873	1874	*n*-Hexadecanol	-	-	-	-	-	2.9	-
66	1967	1977	Ethyl 9-hexadecenoate	-	-	-	-	-	5.7	-
67	1988	1993	Ethyl hexadecanoate	3.2	1.0	-	1.3	-	8.0	0.3
68	2050	2056	Manool	-	-	-	-	-	-	1.6
69	2156	2163	Ethyl linoleate	0.7	-	-	0.5	-	-	-

70	2162	2169	Ethyl oleate	1.1	-	-	-	-	0.4	-
71	2162	2173	Ethyl linolenate	-	-	-	-	-	-	1.1
72	2255	2253	Tributyl acetylcitrate	-	-	-	-	15.3	-	-
73	2486	2500	Pentacosane	-	-	-	-	1.1	-	0.5
74	2586	2600	Hexacosane	-	-	-	-	1.4	-	0.6
75	2685	2700	Heptacosane	-	-	-	-	1.1	-	-
Number of constituents				30	17	16	20	18	20	31
Total identified				95.0	93.2	96.2	88.5	80.4	96.9	83.0
Alcohols				34.2	44.0	0.5	42.0	/	20.1	2.1
Esters				50.0	33.0	75.9	36.4	15.3	68.2	31.1
Others				10.8	16.2	19.8	10.1	65.1	8.6	49.8

Compounds listed in order of elution on an HP-5 MS column. RI: experimentally determined retention indices on the mentioned column of a homologous series of *n*-alkanes C_8-C_{40}; RN: NIST Chemistry WebBook Retention indices; -: not detected. Samples: L1-*Prirodna prepečenica*, Takovo; L2-*Tequila*, Camina real gold; L3-*Metaxa*; L4- *Quince brandy*, Simex Original; L5-*Pelinkovac*, Gorki list; L6-*Whiskey*, Longmorn; L7-*Travarica*, Podrumi manastira Tvrdoš.

Conclusion

Detailed GC-MS analyses of extracts of the seven tested brandies were performed, and the qualitative and quantitative composition of the tested brandies were compared. Tested brandies were dominated by a different class of compounds. The major volatile compounds identified in tested samples were different, which was expected bacause each of the samples had its unique and characteristic aroma.

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Conflict-of-Interest Statement

All authors declare that they have no conflict of interest.

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