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GC-MS profile of homemade fruit brandies

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ABSTRACT

This study aimed to analyze volatile congeners in different types of homemade fruit brandies by applying gas chromatography coupled with mass spectrometry (GC-MS). Volatile compounds were analyzed in seven samples, and the number of identified compounds in the studied samples varied between 12 and 35. An enriched volatile profile was determined for the plum samples, whereas the number of identified compounds was significantly reduced in the case of pear and raspberry samples. From a qualitative point of view, brandies obtained from different fruits showed significant differences because only two compounds (furfural and ethyl decanoate) among 60 identified were found to be common to all examined samples. Regarding the class of identified compounds, esters were the most dominant class identified in all samples, with ethyl lactate being the most prevalent compound except the raspberry brandy sample, which was dominated by alcohols, with pentanol being the major compound. The results obtained in this study have shown that brandies from different fruits are very different in both qualitative and quantitative composition of volatile compounds.

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

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Introduction

Fruit brandies are produced by the alcoholic fermentation and distillation of different fruits with or without stones. Unlike other types of spirits, fruit distillates are rich in volatiles due to high amounts of alcohols and esters. Four different groups of aroma compounds can be detected in the fruit brandies: primary aromatic compounds, which originate from the fruit during ripening; secondary aromatic components, formed during alcoholic fermentation; tertiary aromatic compounds, formed during the distillation process; and quaternary aromatic compounds, formed during the maturation process (Tešević et al., 2005). The quality of the brandy depends on the raw material used (Biernacka & Wardencki, 2012; Coldea et al., 2011; Hernandez-Gomez et al., 2005), fruit preparation (Radeka et al., 2008), fermentation (Matijašević et al., 2019; Soufleros et al., 2005), distillation (Arrieta-Garay et al., 2013; Lukić et al., 2011a; Madrera and Alonso, 2012; Matias-Guiu et al., 2016; Spaho, 2017.), and storage (Madrera et al., 2003; Tsakiris et al., 2014).

Rakija is the national drink of Serbia which can be made of almost any fruit, and each fruit has its specific *rakija* name (the name comes from the name of the fruits they are made from). It is interesting that although rakija is used for pleasure in the first place, it is also used as a cure in some cases. The most produced brandy in Serbia is *šljivovica* or plum brandy, a registered trademark today and the national drink of Serbia. The *rakija* is transparent and colorless when it is produced. Afterward, it can be stored in wooden barrels or with a piece of wood inside for extra aroma and a golden color.

This study aimed to determine the volatile composition of different homemade fruit brandies by applying gas chromatography coupled with mass spectrometry (GC-MS).

Experimental

Seven samples were analyzed. All the analyzed samples were homemade fruit brandies produced by the traditional method. In short, after the fermentation of the fruit, the brandy was obtained by double distillation. First, a soft distillate of 25 % without separation of fractions, then the second distillation with separation of 10% of the first one and separation of the middle fraction with 40% of alcohol. Four distillates were obtained from stone fruits - plums (R1 and R2), apricots

(R3), and peaches (R4); two distillates were obtained from pome fruits - apples (R5) and pears (R6); and finally, the distillate obtained from berry fruits - raspberries (R7).

Preparation of *rakija* for GC-MS analysis

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 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 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. The 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 60 compounds were identified and presented in Table 1. The ethyl esters were the most dominant class of the esters identified in all samples, with ethyl lactate being the most prevalent compound except in the raspberry brandy sample, where it was not even detected. Ethyl esters are produced during fermentation, and their content increases during aging (Silva and Malcata, 1999). This class of compounds contributes to the flavor with a pleasant fruity and flowery smell (Karagiannis and Lanaridis, 2002), so the presence of ethyl esters is beneficial for the spirit (Soufleros et al., 2001; Tešević et al., 2005). On the other hand, higher alcohols occur naturally in alcoholic beverages as by-products of alcoholic fermentation, and they are quantitatively the largest group of the volatile aroma compounds identified in the raspberry brandy sample (70.8%). The most dominant compound in this sample was pentanol with a contribution of 57.6%, while in the samples R2, R3 and R4 pentanol was present in concentrations less than 1% and not even detected in the samples R1, R5, and R6. According to the literature, the characteristic scent of raspberry brandy comes from terpenes of the ionone type (Nikićević et al., 2004; Robertson et al., 1995; Tapani, 1976). If we look at Table 1, it can be noticed that only two compounds (furfural and ethyl decanoate) among 60 identified were found to be common to all examined samples. Regarding the number of identified compounds, with 35 identified components, both plum distillates seem to possess the richest volatile composition, whereas only 12 compounds were found in pear and raspberry distillates. A comparison of the two plum sample compositions showed some qualitative and quantitative differences regarding the identified compounds. The content of esters in ”čačanska rodna” distillate was lower than that of the “ranka” sample, while the contents of alcohols and terpenoids were higher. Four compounds were exclusive to ”čačanska rodna” distillate: limonene, 2-methoxy-*p*-cresol, 2-phenyl ethyl acetate, and syringaldehyde. On the other hand, “ranka” distillate could be distinguished from the others by the presence of *(E)*-ethyl cinnamate, dodecanoic acid, and ethyl 9-hexadecenoate, which were detected only in this sample. Regarding the major compound, both samples were dominated by ethyl lactate with the contribution of 24.3% in the sample plum “ranka” and 20.1% in distillate obtained from plum “čačanska rodna”. Apricot distillate consisted of 30 components, six detected only in this sample (hexyl acetate, diethyl malonate, isopentyl isovalerate, terpinene-4-ol, geranyl acetate, and γ-undecalactone). In peach distillate, 18

compounds were detected and comprised 96.9% of the total. Peach brandy could be distinguished from the other samples because over 90% of the volatiles were ethyl esters (90.9%). A total of 27 components were detected in apple distillate, with 4-ethyl-phenol and 4-ethyl-2-methoxy-phenol that were detected only in this sample. These two compounds were previously detected in wine and beer due to a spoilage yeast *Brettanomyces* (Caboni et al., 2007). Compared to other fruit distillates analyzed in this study, pear distillate was dominated by ethyl lactate (51.9%) and phenyl ethyl alcohol (27.9%) which introduces a pleasant rose aroma.

Let's compare our results with previously published results related to the chemical and sensory characterization of brandy obtained from the "čačanska rodna" plum variety (Popović et al., 2019). It can be noticed that there are some significant differences in the volatile profile of our sample and the sample analyzed in the cited paper. In comparison to the results of Popović et al., where higher alcohols were the dominant class, with 3-methyl-1-butanol being the major compound followed by ethyl acetate, our sample was dominated by ethyl lactate while 3-methyl-1-butanol and ethyl acetate were not even detected. These differences can be explained by Popović et al. analyzing volatile compounds using the headspace method.

Table 1. Chemical composition of fruit brandy volatiles

				Content %						
No	RI	RN	Compound	R1	R2	R3	R4	R5	R6	R7
1	762	760	Isopentyl alcohol	-	-	-	-	-	-	15.4
2	765	762	Pentanol	-	0.9	0.7	0.5	-	-	67.3
3	775	778	Ethyl butanoate	0.3	0.7	2.8	-	0.4	-	-
4	794	798	Ethyl lactate	24.3	20.1	14.1	39.8	29.5	51.9	-
5	810	815	Furfural	0.7	0.8	0.5	0.6	2.6	0.7	4.5
6	828	839	Ethyl 2-methylbutyrate	-	-	-	-	0.5	-	-
7	840	846	2-Methylbutanoic acid	0.5	-	-	0.8	0.5	2.5	-
8	852	858	*n*-Hexanol	1.8	0.7	1.7	-	6.5	3.4	-
9	861	867	Isopentyl acetate	0.4	0.7	1.1	-	1.4	2.5	-

10	948	955	1,1-Diethoxy-3-methyl-butane	0.3	0.3	-	-	-	-	-
11	954	959	Benzaldehyde	7.8	7.2	9.9	0.9	1.6	-	-
12	960	968	Ethyl 2-hydroxyisovalerate	0.5	-	-	0.5	0.5	-	-
13	995	997	Ethyl hexanoate	0.7	0.6	2.3	-	1.3	0.6	-
14	1009	1007	Hexyl acetate	-	-	2.3	-	-	-	-
15	1024	1024	Limonene	-	1.3	-	-	-	-	-
16	1030	1034	Benzyl alcohol	4.3	14.7	1.2	-	0.8	-	-
17	1054	1062	Ethyl 2-hydroxyhexanoate	0.3	0.5	0.4	0.9	0.7	1.4	-
18	1067	1067	Diethyl malonate	-	-	3.5	-	-	-	-
19	1069	1067	*cis*-Linalool oxide	0.7	0.3	-	-	-	-	-
20	1085	1084	*trans*-Linalool oxide	0.7	0.8	1.2	-	-	-	-
21	1096	1095	Linalool	-	0.2	5.5	-	-	-	1.5
22	1100	1100	*n*-Nonanal	0.3	-	-	-	-	-	0.9
23	1101	1103	Isopentyl isovalerate	-	-	2.2	-	-	-	-
24	1110	1115	Phenyl ethyl alcohol	1.3	2.6	0.4	-	6.7	27.9	-
25	1164	1163	4-Ethyl-phenol	-	-	-	-	1.1	-	-
26	1167	1169	Ethyl benzoate	6.2	5.6	5.4	3.9	2.1	-	-
27	1173	1170	Octanoic acid	-	-	-	-	-	0.5	-
28	1175	1174	Terpinen-4-ol	-	-	0.4	-	-	-	-
29	1177	1181	Diethyl succinate	3.2	4.1	0.6	2.5	10.0	1.1	-
30	1188	1186	α-Terpineol	0.4	-	2.2	-	-	-	0.9
31	1189	1188	2-Methoxy-*p*-cresol	-	2.1	-	-	-	-	-
32	1193	1194	Ethyl octanoate	3.5	2.7	4.0	2.2	5.9	2.8	-
33	1225	1246	Benzaldehyde diethylacetal	0.8	1.8	0.3	-	-	-	-
34	1241	1243	Ethyl 2-phenylacetate	-	-	-	-	0.4	-	-
35	1254	1254	2-Phenyl ethyl acetate	-	0.2	-	-	-	-	-
36	1268	1266	Ethyl salicylate	0.4	0.4	-	-	-	-	-

37	1276	1280	4-Ethyl-2-methoxy-phenol	-	-	-	-	1.3	-	-
38	1292	1295	Ethyl nonanoate	0.4	0.4	0.2	-	-	-	-
39	1355	1356	Eugenol	1.6	5.1	1.3	2.3	1.4	-	-
40	1370	1364	Decanoic acid	2.1	1.3	-	-	1.6	-	-
41	1377	1376	(*E*)-α-Ionol	-	-	-	-	-	-	1.9
42	1380	1379	Geranyl acetate	-	-	1.4	-	-	-	-
43	1381	1381	*n*-Nonanal diethyl acetal	0.8	0.3	-	-	-	-	-
44	1392	1392	Ethyl decanoate	8.0	3.8	6.8	3.8	9.2	1.8	1.2
45	1396	1393	Vanillin	-	0.3	2.2	-	-	-	-
46	1425	1422	(*E*)-α-Ionone	-	-	-	-	-	-	1.1
47	1463	1465	(*E*)-Ethyl cinnamate	0.3	-	-	-	-	-	-
48	1464	1465	γ -Decalactone	-	-	12.7	0.9	-	-	-
49	1561	1565	Dodecanoic acid	0.4	-	-	-	-	-	-
50	1570	1569	γ-Undecalactone	-	-	4.7	-	-	-	-
51	1590	1593	Ethyl dodecanoate	4.5	1.9	1.8	1.6	4.3	-	0.8
52	1657	1655	Syringaldehyde	-	0.6	-	-	-	-	-
53	1789	1795	Ethyl tetradecanoate	1.6	0.5	-	0.5	0.5	-	-
55	1967	1977	Ethyl 9-hexadecenoate	0.8	-	-	-	-	-	-
56	1988	1193	Ethyl hexadecanoate	3.7	4.6	-	16.3	2.5	-	-
57	2156	2163	Ethyl linoleate	1.4	2.5	-	8.8	1.2	-	-
58	2162	2173	Ethyl linolenate	1.4	1.8	-	10.1	0.7	-	0.9
60	2820	2833	Squalene	-	-	-	-	-	-	0.9
Number of constituents				35	35	30	18	27	12	12
Total identified				86.4	92.4	93.8	96.9	95.2	97.1	97.3
Alcohols				7.4	18.9	4.0	0.5	14.0	31.3	82.7
Esters				61.9	51.1	48.9	90.9	71.1	62.1	2.9
Others				17.1	22.4	40.9	5.5	10.1	3.7	11.7

Compounds are 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: R1-plum "ranka" brandy; R2-plum "čačanska rodna" brandy; R3-apricot brandy; R4-peach brandy; R5-apple brandy; R6-pear brandy; R7-raspberry brandy.

Conclusion

The qualitative and quantitative composition of the tested brandies obtained from plums, apples, pears, peaches, apricots, and raspberries is very different, even in samples obtained from different cultivars of the same species. This composition difference determines the odor and taste of each fruit brand.

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Conflict-of-Interest Statement

All authors declare that they have no conflict of interest.

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