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Characterization of volatile compounds of "Drenja", an alcoholic beverage obtained from the fruits of cornelian cherry

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Abstract: In this study, volatile compounds were analyzed in five samples of home-made spirit beverage made by the distillation of fermented fruits of cornelian cherry (*Cornus mas* L.). The major volatile compounds, besides ethanol, identified and quantified were: methanol, acetaldehyde, 1-propanol, ethyl acetate, 2-methyl-1-propanol, 1-butanol, amyl alcohols, 1-hexanol and 2-phenylethanol. The minor volatiles were submitted to liquid–liquid extraction with dichloromethane and analyzed by gas chromatography and gas chromatography/ /mass spectrometry (GC/MS). A total of 84 compounds were identified. The most abundant compounds were straight-chain free fatty acids, ethyl esters of C_6–C_{18} acids, limonene, 2-phenylethanol and 4-ethylphenol. Most of the compounds found in the "Drenja" spirits investigated in this study are similar to those present in other alcoholic beverages.

Keywords: *Cornus mas*; alcoholic beverage; fruit spirits; Cornelian cherry spirit; volatiles; GC/MS.

INTRODUCTION

Volatile compounds play an important role in the organoleptic characteristics of alcoholic beverages. In the complex mixture of alcoholic beverages, flavor compounds are present in small amounts. Several hundred compounds from different families, such as alcohols, esters, aldehydes, ketones, volatile acids, terpenes, *etc*., contribute to the flavor of a spirit. This great variety of volatile com-

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pounds with different polarities, volatilities and wide range of concentration ensures that the flavor of a spirit is very complex. The combination of all these compounds constitutes the character of spirit and differentiates one spirit from another.

Cornus is a very large genus comprising forty species in the form of shrubs and trees native to central and southern Europe and parts of western Asia.[1] Only a few species are grown for their fruits, with the cornelian cherry (*Cornus mas* L.) being the main representative. The sour and sweet juice of Cornelian cherry fruits contains a high amount of vitamin C. Furthermore, the fruits are rich in sugar, organic acids and tannin.[2] There are several reports about their use in traditional medicine and as a food preservative. For example, *C. officinalis*, a widely grown *Cornus* sp., is used in Chinese herbal medicine and is known for its tonic, analgesic and diuretic activities.[3] The fruits from several *Cornus* spp. are used to improve liver and kidney functions. It is also reported to have antibacterial, antihistamine, anti-allergic, antimicrobial and antimalarial activities.[4] In Europe, cornelian cherry fruits are used for food and cosmetic applications.[5]

The fruits of the cornelian cherry can be dark red, cherry red, pink or yellow. They can be oval, pear shaped or bottle shaped. The average fruit weight ranges from 5.0 to 8.0 g. The fruits are eaten fresh, dried, and pickled like olives, or they are used to produce jam, jelly, marmalade, syrup or wine.[6] "Drenja" distillate is the spirit beverage that comes from the distillation of fermented fruits of the cornelian cherry tree. This spirit is a traditional alcoholic beverage from various regions of Balkan Peninsula. Although plum, Williams pear, apricot and quince fruit spirits are by far more known, "Drenja" fruit spirit is worthy of attention by experts and consumers. "Drenja" fruit spirit has a very impressive and attractive aroma being luxurious with a little enigmatic velvety sense to the taste. This type of fruit spirit is quite different in comparison with other fruit brandies. The beverage is colorless or colored if maturated in oak vessels.

The objective of this work was to characterize, using the GC and GC/MS techniques, the major and minor volatile compounds of the not yet studied "Drenja" alcoholic beverage, obtained from cornelian cherry fruits.

EXPERIMENTAL

Samples

In order to perform this study, five samples (I–V) of "Drenja" spirit from homemade sources were analyzed. They were collected directly from the producers and all samples were produced by the same procedure.

Five samples of "Drenja" distillates were collected in Šipovljane close to the town Drvar (Bosnia and Herzegovina) in September, 2006. According to the local producers, the fermentation period lasted from 5 to 6 weeks. The household-produced brandies were the result of the spontaneous fermentation of cornelian cherry fruits with epiphytic microbiota participation. The distillation was realized using a traditional copper alembic of 80 L, which is a simplified type of the Charentais alembic. The fermented raw material was transferred to the vessel up to 3/4 of its capacity in order to be distilled. Before the beginning of heating, the alembic was hermetically closed with dough in order to prevent any vapor leakage. First distillation of the fermented mashes was performed without separation of the head. Redistillation was performed using the same device, but with the separation of 1 % of head, the heart (the heart average strength of alcohol was 60 % v/v) and a tail. The heart containing 60 % v/v of ethanol was diluted with distilled water down to 45 % v/v. All samples were placed in glass bottles and stored in the dark at 4 °C until they were analyzed. All tested samples were colorless and distinguished by a characteristic aroma and flavor.

Alcoholic strength

The ethanol content in the distillates was determined using the pycnometric method according to the European Union.[7]

Analysis of volatile compounds in "Drenja"

Analysis of major volatile compounds in "Drenja" appears to correspond to the EU reference method for volatile compounds.[7] For determination of the major volatile compounds samples were injected directly into the gas chromatograph. The main components (methanol, acetaldehyde, 1-propanol, ethyl acetate, 2-methyl-1-propanol, 1-butanol, amyl alcohols, 1-hexanol and 2-phenylethanol), were identified by comparing their retention times with those of authentic compounds. Their concentrations were calculated from peak areas in GC chromatograms using 4-methyl-1-pentanol as internal standard.

An internal standard solution (1 mL) containing 5 g/L of 4-methyl-1-pentanol in ethanol was added to 10 mL sample of "Drenja". A two microliter aliquot was injected into a Hewlett Packard 5890 gas chromatograph. The compounds were separated on a Chrompack CP-Wax 52 CB fused silica column (polyethylene glycol stationary phase; 50 m×0.32 mm i.d. with 1.2 µm film thickness). The injection mode was split (1:1), and the injector temperature was 233 °C. The GC oven temperature was programmed from 40 to 222 °C at a rate of 4.3 °C/min with a final isotherm of 20 min. The carrier gas was hydrogen at a flow rate 1.02 mL/min. Detector (FID) temperature: 300 °C. H_2 flow rate: 40 mL/min. Air flow rate: 400 mL/min. Auxiliary gas (N_2) flow rate: 30 mL/min.

Extraction and concentration of minor volatile constituents

Two hundred milliliters of "Drenja" distillate was mixed with 200 mL of ultrapure water and then extracted with 40 mL of dichloromethane. NaCl (20 g) was added, and the mixture was stirred magnetically for 30 min. The layers were separated in a separation funnel, and the organic layer was dried (2 h) over anhydrous sodium sulfate. The extract was concentrated to 1.0 mL under nitrogen and directly analyzed by GC FID and GC/MS.

Gas chromatographic analysis was performed using a gas chromatograph HP 5890 equipped with a flame ionization detector (FID) and a split/splitless injector. The separation was achieved on a HP-5 fused silica capillary column, 30 m×0.25 mm i.d., 0.25 µm film thickness. The GC oven temperature was programmed from 50 °C (6 min) to 285 °C at a rate of 4.3 °C/min. Hydrogen was used as carrier gas at a flow rate of 1.6 mL/min at 45 °C. The injector temperature was 250 °C and the detector temperature 280 °C. The injection volume of the beverage extracts was 1.0 µL using the splitless mode. GC/MS analysis was performed using an Agilent 6890 gas chromatograph coupled with Agilent 5973 Network mass selective detector (MSD), operating in the positive ion electron impact (EI) mode. The separation was achieved on an Agilent 19091S-433 HP-5MS fused silica capillary column, 30 m×0.25 mm i.d., 0.25 µm film thickness. The GC oven temperature was programmed from 60 to 285 °C at a rate of 4.3 °C/min. Helium was used as the carrier gas, with an inlet pressure of 25 kPa and flow rate of 1 mL/min at 210 °C. The injector temperature was 250°C, employing the splitless injection mode. The MS scan conditions were: source temperature: 200 °C; interface temperature: 250 °C; energy of electron beam: 70 eV; mass scan range: 40–350 amu (atomic mass units). Identification of the components was based on retention indices and comparison with reference spectra (Wiley and NIST databases). Percentages (relative) of the identified compounds were computed from the corresponding GC peak areas.

Chemicals and reagents

All standards used in this study were supplied by Sigma-Aldrich (St. Louis, MO). 4-Methyl-1-pentanol was employed as an internal standard. Ethanol, NaCl, anhydrous sodium sulfate and dichloromethane were purchased from Merck (Darmstadt, Germany).

Statistical analysis

Each component was present in samples I–V and the mean ±*SE* for each value was calculated. The statistical analysis was performed using Origin software package version 7.0. The error bars in the figures indicate the standard error of the mean. The statistical significance of difference between the data pairs was evaluated by analysis of variance (one-way Anova) followed by the Tukey test. A statistical difference was considered significant at $p < 0.01$. The concentrations of the volatile components were recalculated on the basis of 100 % v/v ethanol (AA) and are expressed as g/hL AA.

RESULTS AND DISCUSSION

The main components of the distillate were ethanol and water, with a series of volatile substances that distil together and comprise a smaller portion of the spirit. These volatile substances, together with the components that are present in higher proportions, give distinctive flavor characteristics to the “Drenja”. The nature and composition of these components depend on the characteristics of the raw material, and on the fermentation and distillation processes.

A typical chromatogram for the “Drenja” samples is shown in Fig. 1. The chromatograms of the other samples showed the same pattern as those in Fig. 1,

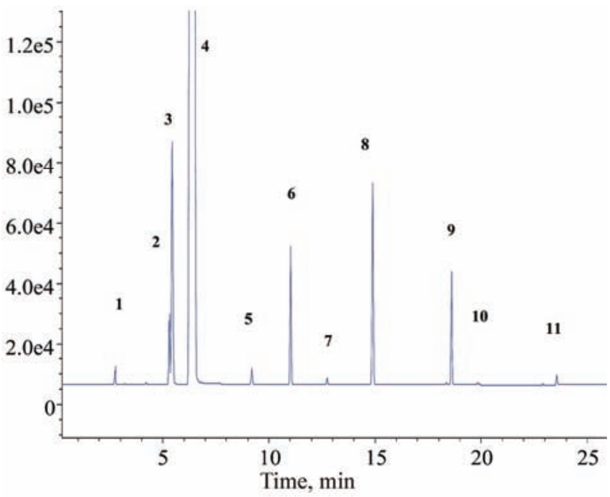

Fig. 1. Gas chromatogram obtained after direct injection of “Drenja” distilate: **1**: acetaldehyde; **2**: ethyl acetate; **3**: methanol; **4**: ethanol; **5**: 1-propanol; **6**: 2-methyl-1-propanol; **7**: 1-butanol; **8**: 2/3-methyl-1-butanol **9**: 4-methyl-1-pentanol (internal standard); **10**: 1-hexanol; **11**: 2-phenylethanol.

although the peak heights were different in each case. The retention times for the major compounds and their concentrations are summarized in Table I. The alcohols found were ethanol, methanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, 1-hexanol, 2-phenylethanol and a mixture of 2-methyl-1-butanol and 3-methyl--1-butanol. As these isomers can be resolved only under specific chromatogramphic conditions, they are usually reported together as 2/3-methyl-1-butanol.

TABLE I. Concentrations of the major volatile compounds in "Drenja" samples (g/hL AA, unless otherwise indicated)

Compound	Sample					Average
	I	II	III	IV	V	*SE*(*yEr*±)[a]
Ethanol (% vol)	45.0	42.6	45.0	46.2	45.0	44.76±0.59
Acetaldehyde	1.71	31.32	28	28.46	5.31	18.96±6.36
Ethyl acetate	306.6	159.0	205.3	211.2	107.1	197.84±33.01
Methanol	242	752	743	556	772	613±100.6
1-Propanol	30.0	16.9	25.3	13.2	25.3	22.14±3.07
2-Methyl-1-propanol	45.8	112.4	90.2	80.7	144.9	94.8±16.49
1-Butanol	3.2	4.9	4.8	2.8	7.1	4.56±0.76
2/3 Methyl-1-butanol	148.9	238.5	204.2	179.6	263.5	206.94±20.39
1-Hexanol	35.6	12.5	13.4	48.5	3.1	22.62±8.39
High alcohols (total)	224.7	372.7	324.5	276.3	440.8	327.80±37.47
2-Phenylethanol	28.6	32.6	36.2	39.1	12.2	29.74±4.72

[a]Standard error of the predicted y-value for each x in a regression

Comparisons of the differences in pairs of the major components present in "Drenja" are given in Table II, from which it can be seen that there are usually significant statistical differences ($p < 0.01$; $p < 0.05$). No significant differences were found between acetaldehyde and 1-propanol, 1-butanol, 1-hexanol and 2-phenylethanol; between 2-methyl-1-propanol and 1-hexanol and 2-phenylethanol; between ethyl acetate and 2/3 methyl-1-butanol; between 2/3 methyl-1-butanol and 1-hexanol; and between 1-hexanol and 2-phenyl ethanol.

Ethanol

The fermentation of fruit mashes relies on the conversion of fruit sugars to ethanol by yeast. The Embden–Meyerhof–Parnas Pathway (EMP) is a well-known process for the conversion of sugars to ethanol by yeast. This pathway proceeds by degrading the sugar to acetaldehyde, which is then reduced to ethanol. The yield of ethanol is dependent upon the initial concentration of the total sugar present in the fruit, which is measured as the total dissolved sugar present in the liquid mash. All samples exhibited ethanol contents ranging from 42.6 to 46.2 % v/v. The EC regulation 1576/89 established general manufacturing procedures of marc distillates and fixed common analytical composition limits, *i.e.*, 86 % v/v of ethanol as the highest proof for the crude distillate and 37.5 % v/v as the minimal proof at bottling.[8]

TABLE II. Statistical significance of the difference between data pairs; the statistical significance of the difference between the data pairs was evaluated by analysis of the variance (one-way Anova) followed by the Tukey test. Analysis of the variance followed by the least significance at $p < 0.01$

Compound	Acetaldehyde	Ethyl acetate	Methanol	1-Propanol	2-Methyl-1-propanol	1-Butanol	2/3 Methyl-1-butanol	1-Hexanol	High alcohols	2-Phenylethanol
Ethanol	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.05$
Acetaldehyde		$p < 0.01$	$p < 0.01$	N.s.[a]	$p < 0.01$	N.s.	$p < 0.01$	N.s.	$p < 0.01$	N.s.
Ethyl acetate			$p < 0.01$	$p < 0.01$	$p < 0.05$	$p < 0.01$	N.s.	$p < 0.01$	$p < 0.05$	$p < 0.01$
Methanol				$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.05$	$p < 0.01$
1-Propanol					$p < 0.01$	$p < 0.01$	$p < 0.01$	N.s.	$p < 0.01$	N.s.
2-Methyl-1-propanol						$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$
1-Butanol							$p < 0.01$	N.s.	$p < 0.01$	$p < 0.01$
2/3 Methyl-1-butanol								$p < 0.01$	$p < 0.05$	$p < 0.01$
1-Hexanol									$p < 0.01$	N.s.
High alcohols (total)										$p < 0.01$

[a]No statistical difference ($p > 0.05$)

Methanol

Methanol is a very important compound in the production of fruit brandies and it is similar to ethanol in taste and smell; however, it is toxic and potentially dangerous if present in high concentrations.[9] Methanol production is associated with the enzymatic degradation of the methoxy groups of pectin, as well as the acidic degradation of pectin. The methanol content in the analyzed samples ranged between 242 and 772 g/hL AA (maximum legal limit 1000 g/hL of 100 % vol. ethanol).[8] In comparisons with other fruit pomace distillates (apple, cherry, pear and plum),[10] "Drenja" has a similar level of methanol. Filajdić and Djuković found 1.41–8.85 g/hL AA methanol in Yugoslavian plum brandies, with higher levels occurring in home-made brandies.[11] Relatively low methanol concentrations have been determined in grape distillates (0.13–0.67 g/hL AA) owing to the small amounts of pectins in the raw materials.[12]

Acetaldehyde

The most common aldehyde present in distilled fruit spirits is acetaldehyde. It is a compound arising from the fermented raw materials, and its level increases during distillation and aging.[13] It is also considered to be mainly the result of spontaneous or microbial-mediated oxidation. In cornelian cherry spirits, as with other distilled fruit spirits, acetaldehyde is usually seen as an undesirable aroma and discarded with the head fraction. European-style spirits are defined by law; however, the regulation provides no limits for acetaldehyde for any of the distilled spirits, which are manufactured by fermentation with retention of the organoleptic properties of their raw materials (*e.g.*, rum, whisky, brandy and fruit spirit). The concentration of acetaldehyde was found to range from 1.71 to 31.32 g/hL AA (Table I). Other spirit beverages usually contain very different acetaldehyde levels, ranging from 153–1073 mg/ hL AA in some grape brandies, *e.g.*, Greek Tsipouro and Portuguese Bagaceiras (1330 mg/ hL AA).[12,14]

Ethyl acetate

Ethyl acetate is one of the most important esters due to its unpleasant flavor at higher concentrations. High ethyl acetate concentrations are indicative of prolonged storage of the raw material and probable acetic bacterial spoilage. It was generally found at higher levels than the usual values for Tsipouro,[12] melon,[15] and Mezcal,[16] but lower than Bagaceiras[14] and Orujo.[17] Filajdić and Djuković found a very high ethyl acetate content (4648 mg/ hL AA) in home-made plum brandies.[11]

Higher alcohols

Higher alcohols (also known as fusel alcohols) are secondary yeast metabolites, which can have both positive and negative impacts on the aroma and flavor of a spirit. Excessive concentrations of higher alcohols can result in a strong, pungent smell and taste, whereas optimal levels impart fruity characters (Table I).

Higher alcohols are present in alcoholic beverages and are formed in small amounts by yeast, from sugars and from amino acids metabolism (Ehrlich mechanism) during the alcoholic fermentation process. The most common fusel alcohols in distilled spirits include: 2-butanol, isobutanol, 1-butanol, 1-propanol and amyl alcohols. Branched-chain higher alcohols, amyl alcohol, active amyl alcohol and isobutanol were the main fusel alcohols in "Drenja". The amyl alcohols (2/3 methyl-1-butanol) content of the analyzed samples was in the range of 148.9–263.5 g/hL AA. 2-Methyl-1-propanol concentrations were in the range of 45.8–144.9 g/hL AA. The content of higher alcohols in the studied samples was similar to that of various distillates, such as Bagaceiras,[14] Tsipouro[12] and Mouro.[18] The minimum of total higher alcohols are fixed by the Regulating Commission at 200 g/ hL AA of pure alcohol and all samples were within these limits.

1-Propanol

1-Propanol has a pleasant, sweetish odor, but excessive concentrations will introduce solvent notes that mask all the positive notes in distillates.[19] The concentration of 1-propanol was found to range from 13.2 to 30.0 g/hL AA (Table I).

1-Hexanol

1-Hexanol is not an alcoholic fermentation product. When the fruits are not ripe enough, high 1-hexanol concentrations in spirits are observed.[20] The 1-hexanol concentrations in the studied samples ranged between 3.1 and 48.5 g/hL AA. Previous studies revealed much lower 1-hexanol contents (20–83 mg/hL AA) in Yugoslavian plum brandies.[11] However, high hexanol concentrations (64–316 mg/hL AA) were determined in Portuguese Bagaceiras, as well as in apple, pear and grape pomace spirits (102–154 mg/hL AA).[14]

2-Phenylethanol

2-Phenylethanol introduces a pleasant aroma, resembling that of roses, to distillates and derives from L-phenylalanine through the metabolic reaction of *Saccharomyces cerevisiae* during carbonic anaerobiosis.[21] The high concentrations of 2-phenylethanol (12.2–39.1 g/hL AA) imparts a positive influence on the "Drenja" aroma. High levels of 2-phenylethanol have been found in, *e.g.*, Greek Tsipouro 12 (28–234 mg/hL AA) and spirits produced from blueberries, probably resulting from a high concentration of phenylalanine in the raw material.[18]

Minor compounds in "Drenja"

The minor volatile compounds identified in these spirits are presented in Table III. A total of 84 free aroma compounds were identified, including alcohols, esters, monoterpenes, carbonyl compounds, lactones, free acids, volatile phenols and acetals.

TABLE III. Relative percentages of the minor volatile compounds in "Drenja" samples (I–V)

Compound	*RI*[a]	I	II	III	IV	V
Ethyl lactate	810.5	tr[b]	tr		tr	
Butyl acetate	812	tr			tr	
Furfural	830	1.14	1.89	1.85	1.22	5.49
1.1-Diethoxybutane				0.54	tr	
Hex-3-(*Z*)-en-1-ol	847		tr		tr	
Isopentyl acetate	876	2.03	3.70	0.62	1.06	1.73
Acetic acid, pentyl ester	847		0.82			
Hexan-1-ol	859	5.14	3.34	3.05	6.78	2.75
1.1-Diethoxy-3-methyl propane		0.28		0.77		
2-Methyl-butyric acid					1.56	
Phenylethyl acetate		0.33			0.22	tr
Ethyl pentanoate	900		1.28			
Methyl hexanoate	925		0.70			0.43
1.1-Diethoxy-3-methylbutane	955	0.65			1.61	
1.1-Diethoxypentane		0.54	0.83	1.68	1.32	1.24
Butyl propionate					0.90	0.65
Oct-1-en-3-ol	978	1.73	tr	2.67	4.62	1.28
Benzaldehyde	961	1.51			0.77	
Ethyl hexanoate	996	1.28	1.96	1.47	1.68	1.90
p-Cymene	1026	0.87	tr	0.53	2.20	
Limonene	1031	2.33	1.00	2.74	6.85	3.24
1.1-Diethoxyhexane		0.43	0.17			
Benzyl alcohol	1032	0.90	tr	1.20		1.37
Nonanal	1075	0.11		0.87	0.16	
2-Phenylacetaldehyde	1042	0.21	tr	0.23		0.13
Octanol	1070	0.32	0.82	0.12	0.78	0.88
cis-Linalool oxide	1074	1.12	0.12	0.32	0.13	1.10
trans-Linalool oxide	1088	1.10	0.59	1.23	0.76	0.64
Linalool	1096	1.11	0.26	1.32	1.52	0.76
Nonanal	1098		0.13			
Methyl benzoate	1098	0.32		0.43		0.34
2-Phenylethanol	1110	10.64	8.86	9.16	8.82	16.00
Methyl octanoate	1125	0.21	0.30			
Nerol oxide	1153	0.52	0.26	0.56	0.31	0.76
Benzyl acetate	1163	tr		0.76		0.34
1-Nonanol	1171	0.18	tr	0.34	0.21	0.64
4-Ethylphenol		0.60	3.44	3.21	3.65	1.78
Diethyl succinate		2.47		0.54	0.34	0.65
Ethyl benzoate	1170	4.81		0.85	1.05	0.99
Octanoic Acid	1175	3.48	10.17	3.58	2.13	4.21
Ethyl octanoate	1195	3.24	5.82	5.68	7.58	10.53
α-Terpineol	1189	0.93	0.67	0.77	0.54	0.98
Decanal	1204	0.21	0.14	0.21	0.11	0.11
Ethyl phenylacetate	1244	0.68	0.43	0.33	0.31	0.76
Phenylethyl acetate	1256	2.39	0.12	0.43	0.13	0.88
Methyl salicylate	1190	0.85	0.21	0.12	0.34	0.12

TABLE III. Continued

Compound	*RI*[a]	I	II	III	IV	V
Ethyl salicylate	1267	0.48	0.23	0.12	0.32	0.15
Decan-1-ol	1272	0.21	tr		0.11	
Nonanoic acid	1275	1.02	2.59			
Methyl decanoate	1326	0.76	tr	0.87		1.09
Eugenol	1356	0.23		0.76	0.11	0.66
Ethyl (4*E*)-decenoate	1382		tr			
Decanoic acid		3.47		4.25	5.91	4.28
Ethyl decanoate	1394	2.20	18.40	5.13	6.37	10.72
Caryophyllene	1418	0.64	0.44	0.65	0.56	0.34
Vanillin	1391	0.22	tr		0.17	0.12
Isoamyl octanoate	1446		0.39			
Ethyl (Z)-cinnamate	1466	0.89	0.48	0.87	0.39	0.76
α-Humulene	1454		tr			
1-Dodecanol	1473	0.12	0.14		0.11	
α-Muurolene	1499		0.14			
Methyl dodecanoate	1527	0.13	0.16		0.23	
δ-Cadinene	1524	0.56	0.55	0.32	0.54	0.65
Nerolidol	1534	0.54		0.34	0.33	0.23
Dodecanoic acid	1568	2.28	1.35	1.89	1.56	1.21
Ethyl dodecanoate	1576	2.60	7.48	5.33	3.51	4.36
3-Methylbutyl pentadecanoate	1642	0.14	0.12	0.22	0.10	0.13
α-Cadinol	1653	0.23	0.33			
Tetradecan-1-ol	1676	0.21	tr			
Farnesol(2*Z*,6*E*)	1694	0.33	0.13			
Methyl tetradecanoate	1727	0.32	0.26	2.94	0.21	5.27
Tetradecanoic acid		0.44	0.49	0.11	0.32	0.21
Ethyl tetradecanoate	1793	0.58	0.94	2.00	0.66	0.88
Isopropyl miristate	1809	0.22	tr	0.57		
Phenethyl octanoate	1849	0.12	0.18			
Methyl hexadecanoate	1927	1.22	1.46	1.34	1.20	1.86
Hexadecanoic acid	1968	1.00	0.54	0.87	0.65	0.76
Ethyl hexadecanoate	1993	3.90	1.90	3.74	1.15	3.42
Methyl linoleate	2092	0.18	0.24	0.54	0.21	
Methyl oleate	2093	1.22	0.46	0.21	0.33	
9.12-Octadecadienoic acid	2094	0.51	0.40	0.11	0.32	
Ethyl linoleate	2177	6.50	3.22	6.06	2.40	4.34
Ethyl oleate	2180	2.80	2.41	4.60	3.10	2.77
Ethyl stearate	2194		0.35			
Total		89.70	93.41	92.02	90.31	90.89

[a]Retention index on DB-5 according to *n*-paraffins; [b]trace (less than 0.1 %)

Ethyl esters and fatty acids are the main components of “Drenja” aroma and have an important sensorial influence in these distilled alcoholic beverages. Ethyl esters contribute to the flavor with a pleasant fruity and flowery smell,[21] indicative of the quality of the spirit.[22,23] Ethyl hexanoate supplies the aroma of fruit (banana, green apple, *etc.*) and its presence, along with other ethyl esters, is beneficial for the spirit. The ethyl esters, hexanoate, octanoate, decanoate and dodecanoate, which are produced during the fermentation, pass into the spirits and their content increases during aging.[24] The dominant esters are the ethyl esters of fatty acids and acetates of higher alcohols. Ethyl hexanoate and ethyl octanoate predominated in the analyzed "Drenja" distillates. Long-chain fatty acids, octanoic, nonanoic, dodecanoic, tetradecanoic and hexadecanoic acid, have a smaller influence on the flavor of distillates.[23,25] Table III shows that the most abundant among the present acids were octanoic, nonanoic, decanoic, dodecanoic and hexadecanoic acid.

The terpene profile was similar in all the distillates. Six monoterpenes were detected in the "Drenja" distillates: limonene, *cis*- and *trans*-linalool oxide, linalool, nerol oxide and α-terpineol. Of these, only limonene was previously reported as a constituent of the volatile fraction of cornelian cherry fruit.[22] The terpene profile of the "Drenja" distillates may be the result of heat-catalyzed, acid hydrolysis of glycosylated terpenol precursors during distillation.

CONCLUSIONS

In the "Drenja" distillates, volatile compounds that pose health hazards or organoleptic faults, such as methanol or acetaldehyde, were found at levels lower than those established by the EU. Quantitatively, the higher alcohols were the largest group of the volatile composition in the "Drenja" distillates. There were statistically significant differences ($p < 0.01$; $p < 0.05$) in the major components present in the studied "Drenja" compared with ethanol. The ethyl esters and fatty acids formed enzymatically during the fermentation process constitute important groups of aroma compounds that contribute to the "fruity" note to the sensory properties of "Drenja" distillates. Moreover, the compounds that contribute to the typical flavor characteristics of the "Drenja" distillate, such as 2-phenylethanol, limonene and 4-ethylphenol, are desirable for this specific distillate. It seems that the complex and luxurious aroma of "Drenja" spirits depends on the subtle balance of the various mentioned functionalized compounds.

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ИЗВОД

КАРАКТЕРИЗАЦИЈА ИСПАРЉИВИХ КОМПОНЕНТИ «ДРЕЊЕ», АЛКОХОЛНОГ ПИЋА ДОБИЈЕНОГ ИЗ ПЛОДОВА ДРЕЊИНЕ (*Cornus mas*)

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У раду су анализиране испарљиве компоненте у пет узорака алкохолних пића, домаће израде, добијених дестилацијом ферментисаних плодова дрењине (*Cornus mas* L.). Главна испарљива једињења, која су одређена и квантификована, су: метанол, 1-пропанол, етил-ацетат, 2-метил-1-пропанол, 1-бутанол, изоамил-алкохоли, 1-хексанол и 2-фенилетанол. Мање заступљена испарљива једињења су екстрахована дихлорметаном и анализирана комбинацијом гасне хроматографије и масене спектрометрије (GC/MS). Идентификована су укупно 84 једињења. Најзаступљенија једињења била су етил естри масних киселина са C_6–C_{18}, слободне масне киселине, лимонен, 2-фенилетанол и 4-етилфенол. Већина једињења нађена у "дрењи" су слична онима која су присутна и у другим алкохолним пићима.

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