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Volatile Components from Old Plum Brandies

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Summary

Gas chromatography and GC/MS methods were used to detect volatile components of three home-made natural old plum brandy samples and one sample of industrially-produced plum brandy. Gas chromatography and gas chromatography-mass spectrometric analysis of this extracts led to the identification of 99 components, including 46 esters, 7 hydrocarbons (alkanes and alkenes), 3 aldehydes, 9 alcohols, 1 lactone, 1 ketone, 8 acetals, 14 terpenes, 8 acids and 2 phenols. Ethyl esters of C_8–C_{18} acids were the most abundant in all samples. In addition, the content of methanol, ethanol and higher alcohols (C_3–C_5) was determined.

Key words: plum brandy, aroma, GC/MS, ethyl esters

Introduction

Plum brandy, as a distillate of *Prunus* crop plum fermented must, apart from the main elements, ethanol and water, contains numerous ingredients, the concentration of which varies within an average of 0.5–1.0 % depending on the raw material content, the way in which alcohol fermentation is carried out and the manner in which distillation is conducted. Apart from numerous valued components it contains, plum brandy can also contain some undesirable ingredients. This refers, first of all, to HCN, ethyl-carbamate and methanol. However, certain amounts of methanol must be present in fermented plum must distillates, in respect to the fact that its presence in them is considered to be a proof and indicator of authentic, natural, fruit origin.

Aromatic compounds are very important for the quality and aroma of alcoholic beverages. These compounds can be classified into four groups: primary aromatic compounds (whose entire aroma appears exactly as in 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). In a rich mixture of alcoholic beverages aromatic compounds are present in a small percentage.

Chemical compounds that give a beverage its characteristic flavour and aroma can be determined and used to classify the beverage as to the type and country of origin. Such analysis has important applications in product control and prevention of brand fraud. No sin-

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gle chemical in an alcoholic beverage is sufficient to distinguish one brand from another or to determine its quality. Various components found in beverages such as whisky, rum and plum brandy originate from the fermentation, distillation or ageing stages. Brandy, whisky and rum contain similar volatile fermentation alcohols. The concentrations of these components depend on their substrate of origin and on the yeasts used for fermentation (*1*). During the ageing process, volatile and nonvolatile phenolic compounds may be extracted from oak ageing barrels. The extent of the extraction depends on the age, type and size of the barrel (*2*). Some of the compounds found in alcoholic beverages may react with one another, dissociate, evaporate, or be absorbed, whereby their concentrations change during the ageing process (*3*).

Higher aliphatic aldehydes (nonanal and some others), 2-undecanone, benzaldehyde, damascenone, benzyl acetate, ethyl phenyl acetate, phenyl ethyl acetate, ethyl-3-phenylpropionate, methyl cinnamate, ethyl cinnamates, and several other compounds were the most significant contributors to the typical plum brandy-like flavour (*4*).

During the alcoholic fermentation of plum juice many esters can be formed, but the most significant ones are acetate esters of higher alcohols (ethyl acetate, isoamyl acetate, isobutyl acetate and 2-phenyl ethyl acetate) and ethyl esters of fatty acids (ethyl butyrate, ethyl lactate, ethyl caprinate, ethyl caprylate and ethyl capronate) (*5*).

Various extraction methods have been widely used for the analysis of volatile components of fruit brandies, such as distillation techniques, solvent extraction, solid phase extraction (SPE), solid phase microextraction (SPME), and stir bar sorptive extraction (SBSE) (*6–8*). Gas chromatography (GC) is a powerful tool in the analysis of alcoholic beverage products. Minimal sample preparation, in general, is required, since the samples are in the liquid state in an alcohol or alcohol/water matrix. The flavour compounds tend to be volatile in nature, which fulfills one of the main requirements of GC. General detectors, such as the flame ionization detector (FID), or more information-rich detectors, such as the mass selective detector (MSD), can be used.

The aim of this study was to compare the contents of volatile compounds in different plum brandies.

Materials and Methods

Four Serbian old plum brandy samples were analyzed: (*i*) plum brandy Manastirka 45 % (sample **I**), industrially produced from Belgrade region, (*ii*) plum brandy Sokolova rakija 45 % (sample **II**), home-made from Užice region, (*iii*) plum brandy Valjevka 45 % (sample **III**), home-made from Valjevo region, and (*iv*) plum brandy Karanka 45 % (sample **IV**), home-made from Užice region.

Manastirka was distilled in 1990 in modified Charente type apparatus for simple distillation with the volume of 300 L. Above the apparatus body and cover was a short rectification column with 4 floors. The purpose of the column was to concentrate and purify alcohol-H_2O vapours in order to get a distillate with optimum amounts of ingredients. Sokolova, Valjevka and Karanka were distilled in 1992, 1997 and 1993, respectively, in Charente type apparatus for simple distillation with the volume of 100–150 L. The apparatus for Sokolova and Karanka did not have a column, only covers. Valjevka apparatus was suplied with air dephlegmator above the cover.

All distillates were maturated in oak barrels: Manastirka, 495 L, casks type *Quercus petreae* L. (*Quercus sessiliflora*); Sokolova, 700 L, casks type *Quercus pedunculata* (*Quercus robur*); Valjevka, 505 L, casks type *Quercus petreae* L. (*Quercus sessiliflora*); and Karanka, 1000 L, casks type *Quercus pedunculata* (*Quercus robur*).

GC and GC/MS analysis of volatile compounds

For a typical experiment, a 100-mL aliquot of each beverage was mixed with 50 mL of dichloromethane and continuously extracted (2 h). The extract was dried (2 h) over anhydrous sodium sulfate, and concentrated to 1.0 mL under nitrogen.

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 using a HP-5 (5 % diphenyl and 95 % dimethylpolysiloxane) fused silica capillary column, 30 m x 0.25 mm i.d., 0.25 μm film thickness. 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; flow rate was 1.6 mL/min at 45 °C. Injector temperature was 250 °C, detector temperature 280 °C, and injection mode splitless. An injection volume of 1.0 μL was used for the beverage extract.

Gas chromatographic-mass spectrometric (GC/MS) analysis was performed using an Agilent 6890 gas chromatograph coupled with an Agilent 5973 Network mass selective detector (MSD), in positive ion electron impact (EI) mode. The separation was achieved using an Agilent 19091S-433 HP-5MS fused silica capillary column, 30 m x 0.25 mm i.d., 0.25 μm film thickness. GC oven temperature was programmed from 60 to 285 °C at a rate of 4.3 °C/min. Helium was used as carrier gas, inlet pressure was 25 kPa, linear velocity was 1 mL/min at 210 °C. Injector temperature was 250 °C, and injection mode splitless. MS scan conditions: source temperature, 200 °C; interface temperature, 250 °C; E energy, 70 eV; mass scan range, 40–350 amu (atomic mass units). Identification of the components was done on the basis of retention index and the comparison with reference spectra (Wiley and NIST databases). Percentage (relative) of the identified compounds was computed from GC peak area.

GC analysis of alcohols

Determination of methanol, ethanol and higher alcohols (C_3–C_5) in the old plum brandies was carried out by adding 2.5 mL of *n*-butanol (1 %) as an internal standard to 2.5 mL of brandy. Prior to evaluation of ethanol content each brandy was diluted tenfold with water.

A CE INSTRUMENTS Model 8000^{Top} gas chromatograph equipped with a headspace autosampler and flame ionisation detector (FID) was used. The separation was achieved using a J&W Scientific DB – WAX fused silica capillary column, 30 m x 0.32 mm i.d., 0.25 μm film thickness. GC oven temperature was programmed from 30 °C (6 min) to 220 °C at the rate of 4.3 °C/min. Nitrogen was used as carrier gas; flow rate was 1 mL/min at 210 °C. Injector temperature was 220 °C, while detector temperature was 250 °C. The samples were injected with a 1:64.3 splitting.

Sensory analysis

Sensory assessment of plum brandy samples was performed using modified Buxbaum model of positive ranking. This model is based on 5 sensorial experiences rated by maximum 20 points. The samples of plum brandies were subjected to sensory evaluation by a panel comprising 5 qualified testers, all of them highly experienced in sensory testing.

Results and Discussion

The volatile compounds identified in the four spirits are presented in Table 1. A total of 71, 71, 81 and 76 free aroma compounds were identified in the plum brandy samples I, II, III and IV, respectively, including alcohols, esters, monoterpene, carbonyl compounds, lactones, acids, volatile phenols and acetal compounds.

Table 1. Aroma composition of the plum brandies I–IV (%)

Compound	I	II	III	IV	RI[a]
Isoamyl acetate	0.72	0.21	0.11	0.13	876
2-methyl butyl acetate	0.32		0.05	0.07	880
Ethyl pentanoate	0.21		0.07	0.09	898
1,1-diethoxybutane			0.05	0.04	
1,1-diethoxy-2-methyl propane	0.12				
Methyl hexanoate			0.02		927
α-pinene	0.14				939
1,1-diethoxy-3-methyl butane	0.19	0.15	0.15	0.11	
Benzaldehyde	1.33	0.97	0.60	0.65	961
Heptanol	0.20	0.07		0.02	969
β-myrcene	0.15				991
Ethyl hexanoate	3.08	1.62	1.36	1.33	996
p-cymene	0.21	0.03	0.04		1026
Limonene		0.02	0.01		1031
Benzyl alcohol	0.36	0.06	0.05	0.07	1060
γ-terpinene	0.26		0.03		1062
Pentyl cyclopropane	0.17		0.02		
c-linalool oxide	0.11	0.05	0.02	0.08	1074
1,1,3-triethoxypropane	0.20		0.04	0.05	
t-linalool oxide			0.04	0.08	1088
1,1-diethoxyhexane	0.08	0.34	0.32	0.42	
Ethyl heptanoate	0.03		0.04	0.02	1095
Linalool	0.12		0.03	0.05	1098
Nonanal	0.30	0.93	0.53	0.51	1098
β-phenyl ethyl alcohol	0.37	0.09	0.05	0.10	1110
Methyl octanoate	0.13	0.11	0.11	0.09	1125
Benzyl acetate	0.03			0.01	1163
Ethyl benzoate	13.46	4.35	2.32	4.10	1170
1,1-diethoxyheptane	0.08	0.14	0.08	0.06	
α-terpineol	0.20	0.06		0.05	1189
Ethyl octanoate	9.99	6.36	6.34	6.23	1195
Decanal		0.03	0.03	0.03	1204
Methyl nonanoate			0.03	0.03	1225
Citronellol	0.03		0.03		1228
t-geraniol	0.04	0.04	0.01	0.01	1255
Ethyl salicylate	2.37	1.19	0.74	1.20	1267
1,1-diethoxyoctane			0.05	0.14	
Ethyl nonanoate	1.61	1.66	1.62	2.23	
Methyl decanoate	0.18	0.26	0.35	0.35	1326
2-methyl propyl benzoate	0.09		0.03		
Isobutyl octanoate			0.01	0.01	
Ethyl-3-phenylpropionate	0.60	0.29	0.13	0.65	

Compound	I	II	III	IV	RI[a]
Eugenol	0.58	0.78	0.49	0.72	1356
2-methoxy-4-propylphenol			0.03	0.09	
Decanoic acid	1.26		0.12	0.91	
1,1-diethoxynonane		3.13	0.49		
Ethyl-9-decanoate	0.13	0.11			
Ethyl decanoate	14.03	14.89	15.25	19.88	1394
Methyl eugenol	0.15				1401
3-methyl butyl benzoate	0.20	0.10	0.07	0.18	1430
Isoamyl octanoate	0.04	0.10	0.10	0.14	1446
Dihydro-β-ionol	0.11	0.02		0.08	
4-methoxy ethyl benzoate	0.05		0.01		
Undecanoic acid				0.01	
Ethyl cinnamate	1.27	0.72	0.46	0.87	1462
1-dodecanol	0.08	0.08	0.02	0.05	1473
Propyl decanoate	0.06	0.05	0.05	0.06	
Ethyl undecanoate		0.14	0.15	0.24	1496
Ethyl-2,2-decadienoate				0.08	
α-muurolene		0.06	0.08		1499
Pentadecane	0.09		0.01	0.05	1500
Methyl dodecanoate	0.14	0.25	0.31		1525
Isobutyl decanoate		0.10	0.09	0.09	
Dodecanoic acid	3.32	0.83	1.79	3.73	1568
Hexyl benzoate		0.02			1576
Ethyl dodecanoate	5.63	12.06	13.42	17.03	1576
Anisyl-isobutyrate	0.25	0.05	0.03	0.04	
Nerolidol		0.01			1564
3-methyl butyl decanoate	0.06	0.26	0.27	0.35	
6,9-pentadecadien-1-ol		0.14			
1,13-tetradecadiene		0.10	0.09	0.03	
Bisabolol oxide	0.09			0.05	1635
Cyclotetradecane	0.11	0.10	0.12	0.19	
γ-dodecalactone	0.26	0.14	0.10	0.11	1647
Ethyl tridecanoate	0.09	0.13	0.11	0.09	
2-pentadecanone		0.04	0.05		
Heptadecane		0.02		0.04	1700
Methyl tetradecanoate	0.14	0.13	0.14	0.20	1727
Tetradecanoic acid	0.21	1.64	1.90	1.82	
Cyclotetradecane		0.04	0.04		
9-hexadecenoic acid		0.15	0.19	0.13	
Ethyl tetradecanoate	1.29	3.90	4.35	3.99	1793
3-methyl butyl dodecanoate	0.10	0.53	0.42	0.27	
2-phenyl ethyl octanoate		0.01	0.01	0.02	
1-nonadecanol	0.07	0.14	0.12	0.10	
Ethyl pentadecanoate	0.11	0.23	0.33	0.24	
Methyl 9-hexadecenoate		0.05	0.05	0.03	
Methyl hexadecanoate	0.14	0.27	0.41	0.23	1927
Hexadecanoic acid	0.66	0.24	0.55	0.39	1968
Ethyl-9-hexadecenoate	0.75	2.22	2.18		
Eicosane	0.05			0.02	2000
Ethyl hexadecenoate	4.59	10.37	13.87	6.93	1993
2-phenyl ethyl octanoate		0.04	0.03	0.02	
9,12-octadecadienoic acid	0.09	0.25	0.32	0.13	2092
9,12,15-octadecatrienoic acid	0.03	0.10	0.13	0.19	
Hexadecane-1,2-diol		0.20	0.25	0.37	
Ethyl linoleate	4.48	6.30	9.72	5.16	2177
Ethyl oleate		4.56			2180
Ethyl stearate	0.39	0.55	1.35	0.29	2194

[a]Retention index on DB-5 and according to *n*-paraffins

General composition of plum brandies was in accordance with previous studies carried out on Yugoslavian plum brandy (*9*).

Ethyl esters of C_8–C_{18} fatty acids were the most abundant in all samples. Fatty acid esters contribute to the flavour of the destillates with a pleasant fruity and flowery smell (*10*), indicative of the quality of the spirit (*11*). Among these, ethyl decanoate is the most abundant of all esters. The ethyl esters, which are produced during the fermentation of raw materials, are transferred to the spirits and their content increases during aging (*12*). Isoamyl acetate, 2-methyl butyl acetate and benzyl acetate constitute the acetic acid ester group, which are mostly responsible for the flowery and fruity aroma of the distillates (*13*). Table 1 shows that isoamyl acetate is present in the highest concentration among these three acetates.

Table 2. Content of ethanol, methanol and high alcohols in plum brandies (I–IV)

Sample	φ(ethanol)	φ(methanol)	φ(higher alcohols (C_3–C_5))[b]
	%	%	%
I	38.64	0.22	0.14
II	38.50	0.13	0.09
III	44.95	0.54	0.16
IV	45.56	0.44	0.19

[b]Total content of *n*-propanol, isobutanol, isoamyl alcohol and *n*-pentanol

Table 3. Sensory analyses of the old plum brandies

Plum brandy samples	Assessment characteristics					
	Colour (max 1 pts)	Clearness (max 1 pts)	Distinction (max 2 pts)	Odour (max 6 pts)	Taste (max 10 pts)	Total (max 20 pts)
Manastirka	1	1	2	5.6	9.0	18.6
Sokolova rakija	1	1	2	5.3	8.8	18.1
Valjevka	1	1	2	5.4	8.9	18.3
Karanka	1	1	2	5.3	8.8	18.1

Long chain fatty acids, decanoic, dodecanoic, tetradecanoic, and hexadecanoic acid have less strong effect on the flavour of the distillates (*11,14*). Table 1 shows that hexanoic acid has the highest mean value of all these acids, followed by dodecanoic acid, decanoic acid and tetradecanoic acid.

The oldest plum brandy (sample **I**) contained higher concentration of some ingredients than other two (sample **II** and **III**), such as: benzaldehyde, ethyl benzoate, ethyl salicylate and ethyl cinamate. Also, benzyl alcohol and β-phenyl ethyl alcohol, which are known aromatic alcohols, were found at higher concentrations in the sample **I**. β-phenyl ethyl alcohol introduces a pleasant aroma to distillates, resembling to rose (*15*).

The aromatic terpene compounds, α-pinene and β-myrcene, were detected only in sample **I**. Eugenol, with an aroma of cloves, was detected in all samples and therefore is very important for the aroma of these spirits. Significant differences were not found for the mean concentration of eugenol in the spirits from these four plum brandies.

Ethanol content is very important for the mouthfeel and flavour of alcoholic beverages. Ethanol content of brandies ranges from 38–45 % (Table 2).

Sensory evaluation

The results of the sensory evaluations of the four plum brandy samples are given in Table 3. Total sensory quality of plum brandies is between 18.10 and 18.60, which is a very high score. According to the results of the performed sensory ranking, the best rated brandy is sample **I**, which was rated with very high score by 5 examiners (total sensory characteristics 18.60). These diferences between apparatus style and heterogeneous maturation conditions cause different sensorial evaluations of brandies.

Conclusions

The obtained results have shown that the production of plum brandies has significant influence on the aroma constituents and the quality of brandies. Changes in the distillation system and aging time induce considerable modifications to the volatile composition of plum brandies. Besides the esters, fatty acids, and fusel alcohols already identified in many types of spirits, other volatile compounds have been identified. Some terpene compounds, such as limonene, β-myrcene, α-pinene, α-terpineol, γ-terpinene, *cis/trans* linalool oxide, linalool, *t*-geraniol, citronellol, α-muurolene and nerolidol, were identified for the first time in this type of spirit. These compounds may originate from the plum.

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Hlapljivi sastojci šljivovice

Sažetak

Metode plinske kromatografije i kombinacija plinske kromatografije i masene spektrometrije upotrijebljene su za detekciju hlapljivih komponenti u tri uzorka domaće šljivovice i jednom industrijski proizvedenom uzorku. Plinskokromatografskom metodom i kombinacijom plinskokromatografske i masene spektrometrijske analize ekstrakata identificirano je 99 komponenata, od čega su 46 esteri, 7 ugljikovodici (alkani i alkeni), 3 aldehidi, 9 alkoholi, 1 lakton, 1 keton, 8 acetali, 14 terpeni, 8 kiseline i 2 fenoli. U svim uzorcima dominantni su bili etil esteri C_8-C_{18} kiselina. Osim toga određen je udjel metanola, etanola i viših alkohola (C_3-C_5).