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Volatile Components from Old Plum Brandies

Vele Tešević^{1*}, Ninoslav Nikićević², Anka Jovanović³, Dejan Djoković¹, Ljubodrag Vujisić⁴, Ivan Vučković⁴ and Mirjana Bonić⁵

¹Faculty of Chemistry, University of Belgrade, Studentski trg 16, SCG-11000 Belgrade, Serbia and Montenegro

²Faculty of Agriculture, University of Belgrade, Nemanjina 6, SCG-11080 Zemun, Serbia and Montenegro

³Institute of Public Health, 29 Novembra 54a, SCG-11000 Belgrade, Serbia and Montenegro

⁴Institute for Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, SCG-11000 Belgrade, Serbia and Montenegro

⁵Institute of Public Health, Zmaj Jovina 30, SCG-2400 Subotica, Serbia and Montenegro

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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-

^{*}Corresponding author; Phone: ++381 11 630 474; Fax: ++381 11 636 061; E-mail: vtesevic@chem.bg.ac.yu

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-H₂O 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 μ m 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 μ L 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 μ m 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

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

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.

Compound	Ι	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
<i>p</i> -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		
<i>c</i> -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
<i>t</i> -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	

Campoint 1<	Compound	T	п	III	IV	PI ^a
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Lay canada and a second and a second a	Ethyl cinnamate	1.07	0.72	0.46	0.01	1462
140084001 0.08 0.09 0.02 0.03 14/3 Propyl decanoate 0.14 0.15 0.24 1496 Ethyl undecanoate 0.09 0.01 0.05 1500 amuurolene 0.09 0.01 0.05 1500 Methyl dockanoate 0.14 0.25 0.31 1525 Isoburyl decanoate 0.14 0.25 0.31 1568 Heyl berazoate 0.02 0.03 0.04 1564 Naisyl-isoburyrate 0.25 0.05 0.03 0.04 1564 Samethyl buryl decanoate 0.26 0.27 0.35 1564 Samethyl buryl decanoate 0.06 0.26 0.27 0.35 1635 Cyclotertardecane 0.11 0.10 0.02 0.05 1635 Cyclotertardecane 0.11 0.10 0.11 1647 Sabolol oxide 0.09 0.33 0.11 0.09 1272 Tetradecanoate 0.26 0.14 <t< td=""><td>1 dedesarel</td><td>0.09</td><td>0.72</td><td>0.40</td><td>0.07</td><td>1402</td></t<>	1 dedesarel	0.09	0.72	0.40	0.07	1402
Prop/Read (a)0.090.090.090.09Ethly-L2-decadienoate0.090.010.051500e-muurolene0.090.010.051500Methyl dodecanoate0.140.250.311525Sobutyl decanoate0.140.250.311525Dodecanoic acid3.320.831.793.731568Hexyl benzoate0.020.030.041564Ehly I dodecanoate5.631.2061.3.4217.031576Sobutyl decanoate0.060.260.270.35564Sobutyl decanoate0.060.260.270.35569Popentadecadien-1-010.110.090.0315351546Sobutyl decanoate0.060.260.270.351546Sobutyl decanoate0.060.260.270.351546Sobutyl decanoate0.090.130.110.091535Sobutyl decanoate0.090.130.110.091547Sobutyl decanoate0.110.090.311547Sobutyl decanoate0.130.110.091537Sobutyl decanoate0.130.110.091727Yedodecalactone0.130.110.091727Yedodecanoate0.140.330.441700Sobutyl decanoate0.100.131727Sobutyl decanoate0.100.131727Hethyl thradecanoate <td>Propul decencete</td> <td>0.06</td> <td>0.08</td> <td>0.02</td> <td>0.03</td> <td>1475</td>	Propul decencete	0.06	0.08	0.02	0.03	1475
huly indecationate 0.14 0.13 0.24 1499 Gamma Calinate 0.09 0.06 0.08 1499 Pentalecance 0.09 0.06 0.08 1500 Methyl dodecanoate 0.014 0.25 0.31 1525 isobuty i decanoate 0.014 0.25 0.31 1525 isobuty i decanoate 0.014 0.009 0.09 0.09 Dodecanoic acid 3.32 0.83 1.79 3.73 1568 Hexyl bonzoate 0.02 0.03 0.04 Narisyl-isobutyrate 0.25 0.05 0.03 0.04 Nerolidol 0.06 0.26 0.27 0.35 Nethyl boly decanoate 0.06 0.26 0.37 0.03 Smethyl butyl decanoate 0.06 0.26 0.27 0.35 Smethyl butyl decanoate 0.06 0.26 0.27 0.35 Smethyl butyl decanoate 0.06 0.26 0.14 0.10 0.11 1647 Shabolo 0.04 0.09 0.03 Shabolo 0.04 0.09 0.03 Shabolo 0.04 0.09 0.13 0.11 0.09 0.13 Cyclotetradecanone 0.09 0.13 0.11 0.09 0.13 Cyclotetradecanone 0.09 0.13 0.11 0.09 0.11 1647 Ethyl tridecanoate 0.09 0.13 0.11 0.09 0.11 Shabolo 0.02 0.05 120 Cyclotetradecanone 0.09 0.13 0.14 0.20 1727 Heptadecanone 0.09 0.13 0.14 0.20 1727 Tetradecanote 0.14 0.13 0.14 0.20 1727 Tetradecanote 0.14 0.13 0.14 0.20 1727 Tetradecanote 0.01 0.05 0.03 Smethyl butyl dodecanoate 0.14 0.13 0.14 0.20 1727 Heptadecanote 0.04 0.05 Shabolo 0.03 0.14 0.02 1727 Heptadecanote 0.04 0.05 Shabolo 0.13 0.14 0.20 1727 Heptadecanote 0.01 0.13 0.14 0.20 1727 Tetradecanote 0.01 0.03 0.14 0.20 1727 Heptadecanote 0.01 0.05 0.3 0.24 Shabolo 0.03 0.14 0.12 0.10 Shabolo 0.03 0.04 Hethyl hexadecenoate 0.11 0.23 0.33 0.24 Hexadecanote 0.11 0.23 0.33 0.24 Hexadecanote 0.14 0.72 0.41 0.23 172 Shabolo 0.05 0.03 Shabolo 0.03 0.04 Shabolo 0.03 0.04 Shabolo 0.03 0.01 0.01 0.02 Shabolo 0.03 0.02 Shabolo 0.03 0.02 Shabolo 0.03 0.03 Shabolo 0.03	Ethyl undegengete	0.06	0.03	0.03	0.06	1406
Liny P-2 declaterable 0.09 0.01 0.05 1499 Pentadecane 0.09 0.01 0.05 1500 Methyl dodecanoate 0.14 0.25 0.31 1525 Isobutyl decanoate 0.09 0.09 0.09 1566 Dodecanoic acid 3.32 0.83 1.79 3.73 1568 Heyl benzoate 0.05 0.03 0.04 1564 Smethyl butyl decanoate 0.06 0.26 0.27 0.35 1.14 Smethyl butyl decanoate 0.06 0.26 0.27 0.35 1.564 Cyclotetradecane 0.09 0.13 0.11 0.09 1.50 1.50 Cyclotetradecane 0.09 0.13 0.11 0.11	Ethyl 2.2 decadionaata		0.14	0.15	0.24	1490
Drinkuloritie 0.00 1975 Methyl dodecanoate 0.01 0.05 1500 Methyl dodecanoate 0.14 0.25 0.31 1525 Isobutyl decanoate 0.02 1576 1576 Dodecanoic acid 3.32 0.83 1.79 3.73 1568 Hexyl benzoate 0.02 1776 1576 1576 Anisyl-isobutyrate 0.25 0.05 0.03 0.04 1664 Nerolidal 0.01 0.01 1564 1564 1564 1564 Smethyl butyl decanoate 0.06 0.26 0.27 0.35 1635 Cycloterindecanien-1-0 0.11 0.10 0.09 0.3 1635 Cycloterindecane 0.09 0.13 0.11 0.01 1647 Ethyl tridecanoate 0.09 0.13 0.11 1647 Ethyl tridecanoate 0.09 0.13 0.11 1727 Terradecanoa 0.14 0.13 0.14 1700 <td>a-muurolopo</td> <td></td> <td>0.06</td> <td>0.08</td> <td>0.08</td> <td>1/00</td>	a-muurolopo		0.06	0.08	0.08	1/00
Inductance 0.09 0.01 0.03 1.00 Methyl docanoate 0.10 0.09 0.09 Dodecanoic acid 3.32 0.83 1.79 3.73 1568 Heyl benzoate 0.02 0.34 1.703 1576 Ethyl dodecanoate 5.63 12.06 13.42 17.03 1576 Anisyl-isobutyrate 0.25 0.03 0.04 1 164 Samethyl butyl decanoate 0.06 0.26 0.27 0.3 1576 Gapentadcacdien-1-01 0.09 0.03 1 1.64 1.7 Ja-tetradecadiene 0.11 0.10 0.12 0.19 1.635 Cyclotetradecanote 0.10 0.11 0.11 1.647 Perhadecanote 0.11 0.10 0.11 1.647 Perhadecanote 0.11 0.13 0.14 0.20 1.727 Perhadecanote 0.14 0.13 0.14 0.21 1.64 Phyl tetradecanoate 0	Pontadagana	0.00	0.00	0.00	0.05	1500
Methyl roddecanolate 0.14 0.23 0.31 153 Dodecanolc acid 3.32 0.83 1.79 3.73 1568 Hexyl benzoate 0.02 1576 1576 1576 Ethyl dodecanolte 0.62 0.03 0.04 1576 Smethyl butyl decanoate 0.25 0.05 0.03 0.04 1564 S-methyl butyl decanoate 0.06 0.26 0.27 0.35 6.9 S-methyl butyl decanoate 0.00 0.09 0.03 1635 6.9-pentalecadien-1-01 0.14 0.10 0.12 0.19 1635 Siabolo loxide 0.09 0.13 0.11 0.10 0.11 1647 Ethyl ridecanote 0.26 0.14 0.10 0.11 1647 Pentadecanone 0.04 0.05 1635 1700 Methyl thradecanoate 0.14 0.13 0.14 0.20 1707 Vethyl Ethyl adecanoate 0.14 0.13 0.14 0.20 1727 <td>Mothyl dodocanoato</td> <td>0.09</td> <td>0.25</td> <td>0.01</td> <td>0.05</td> <td>1500</td>	Mothyl dodocanoato	0.09	0.25	0.01	0.05	1500
Isoling detailate 0.10 0.09 0.09 Dodecanoic acid 3.2 0.83 1.79 3.73 1568 Hexyl berzoate 0.02 1576 1576 Ansjvl-isobutyrate 0.25 0.05 0.03 0.04 Nerolidol 0.01 1564 3.42 17.03 1576 Somethyl butyl decanoate 0.06 0.26 0.27 0.35 1564 Somethyl butyl decanoate 0.06 0.26 0.27 0.35 1564 Sobolo vide 0.09 0.03 1563 1555 1555 1555 Cyclotetradecane 0.10 0.10 0.12 0.19 179 Y-dodecalactone 0.26 0.14 0.10 0.11 1647 Ethyl tridecanoate 0.09 0.13 0.11 0.09 1727 Tetradecanoic acid 0.14 0.13 0.14 0.20 1727 Tetradecanoic acid 0.10 0.53 0.42 0.72 1733 <	Isobutyl docenoate	0.14	0.23	0.00	0.00	1525
Dode and a data 3.32 0.33 1.79 3.73 1.305 Hexyl berzoate 0.2 13.42 17.03 1576 Ethyl dode anoate 0.25 0.05 0.03 0.04	Dedecanois acid	2 22	0.10	0.09	0.09	1569
Incy for bottome 0.02 1.3.42 17.03 15.76 Anisyl-isobutyrate 0.25 0.05 0.03 0.04	Hovel honzoato	5.52	0.03	1.79	5.75	1500
Lady toolectation 5.00 12.00 12.00 13.00 13.00 Ansyl-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 1 1 1.13-tetradecadiene 0.10 0.09 0.03 1 Y-dodecalactone 0.26 0.14 0.10 0.11 1647 Ethyl tridecanoate 0.09 0.13 0.11 0.09 2 2 1647 1700 Methyl tetradecanoate 0.04 0.05 1700 1700 1700 1700 Methyl tetradecanoate 0.14 0.13 0.14 0.20 1727 Tetradecanoic acid 0.21 1.64 1.90 1.82 2 Oydectandate 0.10 0.53 0.42 0.27 2 Phenadecenoic acid 0.10 0.53 0.42 0.27 2	Ethyl dodocanoato	5.62	12.06	12 / 2	17.02	1576
Antsy bodity face 0.03 0.04 154 3-methyl butyl decanoate 0.06 0.26 0.27 0.35 5 6.9-pentadecadien-1-ol 0.14 0.09 0.03 5 1.13-tetradecadeine 0.01 0.09 0.03 5 Sabolol oxide 0.09 0.11 0.10 0.11 1647 Syndotetradecane 0.11 0.10 0.12 0.19 1647 Syndotetradecane 0.26 0.13 0.11 0.09 1647 Ethyl tridecanoate 0.09 0.13 0.11 0.09 1700 Atteradecanone 0.14 0.13 0.14 0.20 1727 Tetradecanoic acid 0.21 1.64 1.90 1.82 1793 Synethyl butyl dodecanoate 0.10 0.53 0.42 0.27 1793 Synethyl butyl dodecanoate 0.10 0.53 0.42 0.27 1793 Synethyl butyl dodecanoate 0.07 0.14 0.12 0.10	A nigyl isobutyrate	0.25	0.05	0.02	0.04	1570
Netrodial 0.01 1.04 3-methyl butyl decanoate 0.06 0.26 0.27 0.35 6.9-pentadecadien-1-ol 1.13 1.14 1.13 1.13 1.13-tetradecadiene 0.09 0.03 1635 Syclotetradecane 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 1.29 2-pentadecanone 0.02 0.04 0.05 1700 Methyl tetradecanoate 0.14 0.13 0.14 0.20 1727 Tetradecanoic acid 0.21 1.64 1.90 1.82 1793 Stenethyl butyl dodecanoate 0.04 0.04 0.02 1793 3-methyl butyl dodecanoate 0.10 0.53 0.42 0.27 9-hexadecenoic acid 0.07 0.14 0.12 0.10 1.13 2-phenyl ethyl octanoate 0.11 0.23 0.33	Nerolidal	0.25	0.03	0.03	0.04	1564
Sinterly Dury declation 0.00 0.20 0.27 0.33 6/9pentadecadien-1-0l 0.14 0.09 0.03 Bisabolol oxide 0.09 0.05 1635 Cyclotetradecadien-10 0.10 0.12 0.19 Yaddecalactone 0.26 0.14 0.10 0.11 1647 Ethyl tridecanoate 0.26 0.14 0.10 0.11 1647 Heptadecano 0.09 0.13 0.11 0.09 2 Vertadecanoate 0.02 0.04 0.700 1727 Heptadecanoate 0.14 0.13 0.14 0.20 1727 Tetradecanoic acid 0.21 1.64 1.90 1.82 2 Cyclotetradecano 0.21 1.64 1.90 1.82 2 Systematic acid 0.21 1.64 1.90 1.82 2 Cyclotetradecanoate 0.10 0.53 0.42 0.27 2 Phexadecenoia acid 0.10 0.53 0.4	2 methyl hutyl decanoate	0.06	0.01	0.27	0.25	1364
1.3-tertadecadiene 0.14 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 tridecanote 0.09 0.13 0.11 0.09 2 2-pentadecanone 0.02 0.04 0.05 1727 Tetradecanoic acid 0.11 1.64 1.90 1.82 Cyclotetradecanoate 0.21 1.64 1.90 1.82 Cyclotetradecanoate 0.21 1.64 1.90 1.82 Cyclotetradecanoate 0.10 0.53 0.42 0.27 Smethyl butyl dodecanoate 1.00 0.01 0.02 2.27 2-phenyl ethyl octanoate 0.01 0.01 0.02 2.27 2-phenyl ethyl octanoate 0.07 0.14 0.12 0.10 1-nonadecanol 0.07 0.14 0.12 0.10 Methyl b-hexadeceno	6.9-poptadocadion_1-ol	0.00	0.20	0.27	0.55	
Interfact advantance 0.09 0.05 1635 Bisabolo toxide 0.09 0.11 0.12 0.19 Cyclotetradecane 0.26 0.14 0.10 0.11 1647 Ethyl tridecanoate 0.09 0.13 0.11 0.09 2 2-pentadecanone 0.02 0.04 0.07 1700 Methyl tetradecanoate 0.14 0.13 0.14 0.20 1727 Tetradecanic acid 0.21 1.64 1.90 1.82 - Cyclotetradecane 0.21 1.64 1.90 1.82 - Oycloteradecane 0.15 0.19 0.13 - - 9-hexadecenoic acid 0.10 0.53 0.42 0.27 - 2-phenyl ethyl codecanoate 0.10 0.53 0.42 0.27 - 2-phenyl ethyl codacanoate 0.10 0.53 0.42 0.27 - 1-nonadecanoat 0.07 0.14 0.12 0.10 - 1-nonadecanoate 0.11 0.23 0.33 0.24 -	1 13 totradocadiono		0.14	0.09	0.03	
Distribution of the description of the descript	Bisabolol ovide	0.09	0.10	0.09	0.05	1635
Cycloteridectate 0.11 0.10 0.12 0.19 y-docealactone 0.26 0.14 0.10 0.11 1647 Ethyl tridecanoate 0.09 0.13 0.11 0.09 2-pentadecanoate 0.04 0.05 Heptadecano 0.02 0.04 0.05 1700 Methyl tetradecanoate 0.14 0.13 0.14 0.20 1727 Tetradecanoic acid 0.21 1.64 1.90 1.82 1700 Cyclotetradecane 0.21 1.64 1.90 1.82 1793 Symethyl butyl dodecanoate 0.10 0.53 0.42 0.27 1793 S-methyl butyl dodecanoate 0.07 0.14 0.12 0.10 100 1-nonadecanol 0.07 0.14 0.12 0.10 110 2-phenyl ethyl octanoate 0.11 0.23 0.33 0.24 114 Methyl Phexadeconoate 0.11 0.23 0.33 0.24 114 Heyladecanoate	Cyclototradocano	0.09	0.10	0.12	0.05	1055
Proceedation 0.09 0.14 0.19 0.11 0.09 2-pentadecanoate 0.09 0.01 0.01 0.09 1700 Methyl tetradecanoate 0.14 0.13 0.14 0.20 1727 Tetradecanoic acid 0.21 1.64 1.90 1.82 1727 Tetradecanoic acid 0.21 1.64 1.90 1.82 1727 Cyclotetradecane 0.04 0.04 0.04 0.04 0.04 1.82 1733 Phexadecenoic acid 0.21 1.64 1.90 1.32 1.33 1.42 1700 Phexadecenoic acid 0.21 1.64 1.90 1.82 1733 1.82 1733 Smethyl butyl dodecanoate 0.10 0.53 0.42 0.27 1793 1793 3-methyl butyl dodecanoate 0.10 0.53 0.42 0.27 11 10.02 1001 11 10.02 11 10.02 11 10.91 11 11 11 <t< td=""><td>v-dodecalactone</td><td>0.26</td><td>0.10</td><td>0.12</td><td>0.19</td><td>1647</td></t<>	v-dodecalactone	0.26	0.10	0.12	0.19	1647
Liny intercation 0.07 0.15 0.17 0.05 Heptadecanoe 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 1227 Cyclotetradecane 0.04 0.05	Ethyl tridecanoate	0.20	0.14	0.10	0.09	1047
Periadecane 0.01 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 1.82 Cyclotetradecane 0.04 0.04 0.04 0.04 0.04 0.04 0.04 0.04 0.04 0.04 0.01 0.05 <td>2-pentadecanone</td> <td>0.09</td> <td>0.13</td> <td>0.05</td> <td>0.07</td> <td></td>	2-pentadecanone	0.09	0.13	0.05	0.07	
Methyl tetradecanoate 0.14 0.13 0.14 0.20 1727 Tetradecanoate 0.21 1.64 1.90 1.82 Cyclotetradecane 0.04 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 0.14 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 - - Ethyl 9-hexadecenoate 4.59 10.37 13.87 6.93 1993 2-phenyl ethyl octanoate 0.09 0.25 0.32	Hentadecane		0.02	0.00	0.04	1700
Article Control 0.11 0.12 1.164 1.90 1.82 Tetradecanoic acid 0.21 1.64 1.90 1.82 Symphonic acid 0.04 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 0.02 1 1-nonadecanol 0.07 0.14 0.12 0.10 1 </td <td>Methyl tetradecanoate</td> <td>0.14</td> <td>0.13</td> <td>0.14</td> <td>0.20</td> <td>1727</td>	Methyl tetradecanoate	0.14	0.13	0.14	0.20	1727
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 0.14 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 1927 Hexadecanoic acid 0.66 0.24 0.55 0.39 1968 Ethyl 9-hexadecenoate 0.75 2.22 2.18 1927 Eicosane 0.05 0.02 0.00 13 0.02 9,12-octadecadienoic acid 0.09 0.25 0.32 0.13 2092 9,12-octadecadienoic acid 0.09 0.25 0.37 <	Tetradecanoic acid	0.21	1.64	1 90	1.82	1727
9-hexadecenoic acid 0.15 0.19 0.13 9-hexadecenoic acid 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	Cyclotetradecane	0.21	0.04	0.04	1.02	
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 1927 Hexadecanoic acid 0.66 0.24 0.55 0.39 1968 Ethyl hexadecanoate 0.75 2.22 2.18 100 1933 Ethyl 9-hexadecenoate 0.75 2.22 2.18 1933 1993 2-phenyl ethyl octanoate 0.05 0.37 13.87 6.93 1993 2-phenyl ethyl octanoate 0.09 0.25 0.32 0.13 2092 9,12-octadecadienoic acid 0.09 0.25 0.37 13 2092 9,12,15-octadecatrienoic acid 0.03 0.10 0.13 0.19 14 Hexadecane-1,2-diol 0.03 0.10 0.13 0.19<	9-hexadecenoic acid		0.15	0.19	0.13	
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 0.07 0.14 0.12 0.10 Methyl 9-hexadecenoate 0.05 0.05 0.03 1927 Methyl hexadecanoate 0.14 0.27 0.41 0.23 1927 Hexadecanoic acid 0.66 0.24 0.55 0.39 1968 Ethyl Pentadecenoate 0.75 2.22 2.18 1927 Hexadecenoate 0.05 0.03 0.02 2000 Ethyl-9-hexadecenoate 0.75 2.22 2.18 2000 Ethyl hexadecenoate 0.05 0.32 0.13 2092 9,12-octadecatienoic acid 0.09 0.25 0.32 0.13 2092 9,12-octadecatrienoic acid 0.03 0.10 0.13 0.19 1933 9,12,15-octadecatrienoic acid 0.03 0.10 0.13 0.19 194 Hexadecane-1,2-diol	Ethyl tetradecanoate	1.29	3.90	4.35	3.99	1793
2-phenyl ethyl octanoate 0.01 0.01 0.02 2-phenyl ethyl octanoate 0.07 0.14 0.12 0.10 Ethyl pentadecanoate 0.11 0.23 0.33 0.24 Methyl 9-hexadecenoate 0.14 0.27 0.41 0.23 1927 Hexadecanoate 0.14 0.27 0.41 0.23 1927 Hexadecanoate 0.14 0.27 0.41 0.23 1927 Hexadecanoate 0.66 0.24 0.55 0.39 1968 Ethyl 9-hexadecenoate 0.75 2.22 2.18	3-methyl butyl dodecanoate	0.10	0.53	0.42	0.27	1,70
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 Hexadecanoit acid 0.66 0.24 0.55 0.39 1968 Ethyl-9-hexadecenoate 0.75 2.22 2.18 2000 Ethyl hexadecenoate 0.05 0.03 0.02 2000 Ethyl hexadecenoate 0.05 0.37 13.87 6.93 1993 2-phenyl ethyl octanoate 0.09 0.25 0.32 0.13 2092 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 14 Hexadecane-1,2-diol 0.20 0.25 0.37 14 14 Ethyl linoleate 4.48 6.30 9.72 5.16 2177 Ethyl oleate 4.56 1.35 0.29 2180 <td>2-phenyl ethyl octanoate</td> <td>0110</td> <td>0.01</td> <td>0.01</td> <td>0.02</td> <td></td>	2-phenyl ethyl octanoate	0110	0.01	0.01	0.02	
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	1-nonadecanol	0.07	0.14	0.12	0.10	
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	Ethyl pentadecanoate	0.11	0.23	0.33	0.24	
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	Methyl 9-hexadecenoate	0111	0.05	0.05	0.03	
Hexadecanoic acid 0.66 0.24 0.55 0.39 1968 Ethyl-9-hexadecenoate 0.75 2.22 2.18	Methyl hexadecanoate	0.14	0.27	0.41	0.23	1927
Ethyl-9-hexadecenoate 0.75 2.22 2.18 2000 Ethyl hexadecenoate 0.05 0.02 2000 Ethyl hexadecenoate 4.59 10.37 13.87 6.93 1993 2-phenyl ethyl octanoate 0.09 0.25 0.32 0.13 2092 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 14 Hexadecane-1,2-diol 0.20 0.25 0.37 2177 2180 Ethyl linoleate 4.56 2180 2180 2180 Ethyl stearate 0.39 0.55 1.35 0.29 2194	Hexadecanoic acid	0.66	0.24	0.55	0.39	1968
Endy 0.05 0.02 2000 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-octadecadienoic acid 0.03 0.10 0.13 0.19 14xadecane-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 2180 Ethyl stearate 0.39 0.55 1.35 0.29 2194	Ethyl-9-hexadecenoate	0.75	2.22	2.18		
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 stearate 0.39 0.55 1.35 0.29 2194	Eicosane	0.05			0.02	2000
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 stearate 0.39 0.55 1.35 0.29 2194	Ethyl hexadecenoate	4.59	10.37	13.87	6.93	1993
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 stearate 0.39 0.55 1.35 0.29 2194	2-phenyl ethyl octanoate		0.04	0.03	0.02	
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 stearate 0.39 0.55 1.35 0.29 2194	9.12-octadecadienoic acid	0.09	0.25	0.32	0.13	2092
Hexadecane-1,2-diol 0.20 0.25 0.37 Ethyl linoleate 4.48 6.30 9.72 5.16 2177 Ethyl stearate 0.39 0.55 1.35 0.29 2194	9.12.15-octadecatrienoic acid	0.03	0.10	0.13	0.19	
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	Hexadecane-1,2-diol	0.00	0.20	0.25	0.37	
Ethyl oleate 4.56 2180 Ethyl stearate 0.39 0.55 1.35 0.29 2194	Ethyl linoleate	4.48	6.30	9.72	5.16	2177
Ethyl stearate 0.39 0.55 1.35 0.29 2194	Ethyl oleate		4.56			2180
	Ethyl stearate	0.39	0.55	1.35	0.29	2194

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

Sample	$\varphi(\text{ethanol})$	φ (methanol)	φ (higher alcohols (C ₃ –C ₅)) ^b		
Sample	%	%	%		
Ι	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		

^bTotal content of *n*-propanol, isobutanol, isoamyl alcohol and *n*-pentanol

5 5	1							
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		

Table 3. Sensory analyses of the old plum brandies

zyl 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.

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 C₈-C₁₈ kiselina. Osim toga određen je udjel metanola, etanola i viših alkohola (C₃-C₅).