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SUPPLEMENTARY MATERIAL TO

Chemical characterization and differentiation of Montenegrin plum spirits obtained by two techniques of traditional batch distillation

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EXPERIMENTAL DETAILS

Sample preparation

Sample preparation for determination of main volatiles (acetaldehyde, ethyl-acetate, methanol, 1-propanol, i-butanol, 1-butanol, isoamyl alcohol, and 1-hexanol) in the plum brandies by GC-FID was carried out by adding 3 μL of 4-methyl-1-pentanol as an internal standard to 5 mL of brandy. A mixture of authentic standards is made by adding 3 μL of each compound to 5 mL of 40% ethanol.[1]

The extraction of minor aroma compounds for GC-FID–MS analysis was started by diluting an aliquot of 100 mL of plum beverage with 100 mL distilled water, followed by adding of 15 mL of dichloromethane, 1 mL of internal standard (methyl ester of 10-undecenoic acid, 1.8 mg/mL in dichloromethane), and continuously extracted on vortex for 3 min. The dichloromethane extract was dried over anhydrous magnesium sulfate, and concentrated under nitrogen flow to final volume of 1.5 mL.[1]

GC-FID analysis of major volatile compounds

GC-FID analysis of major volatile components (acetaldehyde, ethyl acetate, methanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, 2/3-methyl-1-butanol, and 1-hexanol) was carried out by the method described by Ivanović et al.[1] Briefly, a gas chromatograph Agilent 7890A (Agilent Technologies, Santa Clara, CA, USA) equipped with polar HP-INNOWax capillary column (30 m × 0.32 mm, 0.25 µm film thickness, Agilent Technology) was used. Temperature program: 10 min at 40 °C; 5 °C/min to 90 °C; 50 °C/min to 240 °C; 10 min at 240 °C. The injector temperature was 220 °C, and the detector temperature was 300 °C. Carrier gas was helium (108.5 kPa). For quantitative evaluation, 4-methyl-1-pentanol was used as an internal standard (IS). Thus, an ethanol solution containing 5 g/L 4-methyl-1-pentanol was added to 10mL of each sample. The analyses were performed in split mode 15:1. The injection volume was 1 µL. Identification of major volatile compounds was performed based on standard compounds.

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GC-FID-MS analysis of minor volatile compounds

GC-FID-MS analysis of minor volatile compounds was carried out by the method described by Ivanović et al.[1] Briefly, Agilent 7890A GC system (Agilent Technologies, Santa Clara, CA, USA) equipped with a 5975C mass selective detector (MSD) and a FID connected by capillary flow technology through a two-way splitter was used. A non-polar HP-5MSI capillary column (30 m × 0.25 mm, 0.25 µm film thicknesses Agilent Technology) was used. Temperature program: linearly increasing temperature at a rate of 3 °C/min in the range of 60 °C to 270 °C; 20 °C /min to 310 °C; 8 min at 310 °C. Helium was used as a carrier, auxiliary, and make up gas; inlet pressure was constant at 135.8 kPa (flow 1.0 mL/min at 210 °C), auxiliary pressure was 26.2 kPa, and FID make up flow was 25 mL/min. FID temperature was 300 °C. Split ratio was 5:1, and the injection volume was 1 µL for all analyses. Mass spectra were obtained by electron ionization with 70 eV at 200 °C. The quadrupole temperature was set to 150 °C, and MS range was 40–550 amu. The transfer line temperature was 315 °C. Minor volatile compounds identification was based on the linear RI relative to n-alkanes C8–C32 and their comparison with different reference spectra (Wiley 7, NIST 17 and RT locked Adams 4 databases) followed by Automated Mass spectral Deconvolution and Identification System (Amdis 32, ver 2.73) and NIST search, ver. 2.3.

The results of analysis of major and minor volatile compounds are presented in tables, separately for plum spirits obtained by single distillation, and separately for plum spirits obtained by double distillation. For each group of samples, the results are given in the form of minimum (Min) and maximum (Max) values of the concentration of a given compound in plum spirits of each group, as well as its concentration mean values ± standard deviation (Mean±SD) for each group of the samples. In the tables (from Table S-I to Table S-XII) shown in Supplementary, values given by bold numbers designated names and concentrations of compounds that were found in all plum spirit samples (produced by both distillation techniques). The representative GC-FID and GC-MS chromatograms are given in the Figure S-1 and Figure S-2.

ADDITIONAL RESULTS AND DISCUSSION

Minor volatile components

TABLE S-I. Alcohols in Montenegrin plum spirits (mg L^{-1})

No.[a]	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
11	3-hexenol	855	4.169	nd	0.128	0.046±0.054	nd	0.039	0.008±0.016
13	1-hexanol	866	4.378	0.857	24.267	6.202±9.007	1.083	11.723	4.043±3.876
27	1-heptanol	967	6.818	nd	1.983	0.534±0.746	nd	1.249	0.397±0.434
29	1-octen-3-ol	977	7.128	nd	0.108	0.025±0.044	nd	0.212	0.046±0.085
37	3-ethyl-4-methylpentan-1-ol	1021	8.518	nd	0.228	0.067±0.088	nd	0.299	0.072±0.115
40	benzyl alcohol	1034	9.005	2.311	9.804	6.377±2.974	1.186	6.526	3.700±2.018
46	1-octanol	1071	10.324	0.015	1.921	0.548±0.731	0.160	1.279	0.429±0.426
56	2-phenylethanol	1114	12.086	1.388	5.459	2.954±1.467	0.374	16.453	5.795±5.593
61	(*z*)-3-nonen-1-ol	1154	13.776	nd	0.987	0.185±0.396	nd	0.776	0.204±0.294
88	1-decanol	1274	19.008	nd	0.184	0.036±0.074	nd	0.318	0.053±0.130

[a]values given in bold were found in all plum spirit samples (produced by both distillation techniques);

TABLE S-II. Aldehydes in Montenegrin plum spirits (mg L-1)

No.[a]	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
5	furfural	833	3.790	0.115	0.750	0.390±0.240	0.005	1.986	0.877±0.745
18	heptanal	904	5.065	nd	0.470	0.096±0.188	nd	0.478	0.125±0.190
24	(*e*)-2-heptenal	956	6.509	nd	nd	nd	nd	0.078	0.024±0.038
25	benzaldehyde	962	6.689	0.447	17.376	7.132±6.670	0.573	23.789	12.863±9.319
34	octanal	1004	7.904	nd	0.164	0.035±0.066	nd	0.073	0.044±0.034
41	2-phenylacetaldehyde	1044	9.381	nd	nd	nd	nd	0.065	0.017±0.028
55	nonanal	1105	11.698	0.117	3.036	0.737±1.132	0.018	2.956	1.300±1.101
85	(*e*)-2-decenal	1263	18.534	nd	nd	nd	nd	0.143	0.059±0.058
98	(*e*,*e*)-2,4-decadienal	1319	21.010	nd	nd	nd	nd	0.010	0.002±0.004

[a]values given in bold were found in all plum spirit samples (produced by both distillation techniques);

TABLE S-III. Ketones in Montenegrin plum spirits (mg L^{-1})

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
58	3-Nonen-2-one	1140	13.185	nd	0.224	0.038±0.092	nd	0.085	0.015±0.034
99	5-Undecen-4-one	1321	21.128	nd	0.231	0.038±0.094	nd	0.035	0.006±0.014

TABLE S-IV. Lactones in Montenegrin plum spirits (mg L^{-1})

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
105	*γ*-Nonalactone	1365	23.027	nd	0.182	0.044±0.073	nd	0.067	0.021±0.031
122	*γ*-Decalactone	1469	27.492	nd	0.420	0.111±0.174	0.083	0.405	0.191±0.116
136	*γ*-Dodecalactone	1680	35.963	nd	0.410	0.085±0.162	0.012	0.377	0.192±0.126

TABLE S-V. Acetals in Montenegrin plum spirits (mg L^{-1})

No.[a]	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
12	1,1-diethoxy-2-methylpropane	857	4.206	nd	nd	nd	nd	0.047	0.014±0.020
19	2,2-diethoxy-ethanol	910	5.278	nd	0.083	0.026±0.038	nd	0.052	0.024±0.021
23	1,1-diethoxy-3-methylbutane	951	6.381	0.005	0.222	0.062±0.081	0.009	0.191	0.084±0.082
28	1-(1-ethoxyethoxy)-pentane	971	6.942	nd	0.112	0.033±0.052	nd	0.417	0.120±0.156
32	1,1-diethoxy-pentane	999	7.708	nd	0.083	0.015±0.033	nd	0.106	0.030±0.042
49	1,1,3-triethoxy-propane	1078	10.654	0.020	0.229	0.068±0.084	0.013	0.163	0.065±0.056
51	1,1-diethoxy-hexane	1094	11.251	0.013	0.594	0.131±0.228	0.006	0.496	0.144±0.181
69	1,1-diethoxy-heptane	1191	15.368	nd	nd	nd	nd	0.153	0.025±0.062
102	(2,2-diethoxyethyl)-benzene	1328	21.367	nd	0.004	0.001±0.002	nd	0.064	0.011±0.026
109	1,1-diethoxy-nonane	1386	24.018	nd	0.591	0.146±0.222	0.002	0.600	0.226±0.236

[a]values given in bold were found in all plum spirit samples (produced by both distillation techniques);

TABLE S-VI. Acids in Montenegrin plum spirits (mg L^{-1})

No.[a]	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
4	2-methyl-propanoic acid	832	3.744	nd	0.080	0.045±0.027	0.044	0.337	0.108±0.116
6	3-methyl-butanoic acid	837	3.856	0.001	0.277	0.133±0.091	0.096	0.577	0.278±0.168
10	2-methyl-butanoic acid	852	4.134	nd	0.282	0.070±0.111	nd	0.096	0.032±0.042
30	hexanoic acid	979	7.355	0.151	2.279	0.668±0.818	0.188	1.751	0.883±0.568
43	2-hydroxy-4-methyl-pentanoic acid	1057	9.869	0.014	0.436	0.211±0.168	0.085	0.485	0.267±0.169
68	octanoic acid	1158	15.170	0.146	3.031	1.044±1.143	0.167	3.109	1.425±1.307
89	nonanoic acid	1278	19.221	nd	1.427	0.277±0.567	nd	0.774	0.378±0.316
107	decanoic acid	1379	23.702	0.598	5.343	2.066±2.134	0.873	7.407	3.168±2.358
128	dodecanoic acid	1567	31.598	nd	1.342	0.480±0.628	nd	2.659	0.491±1.064
155	hexadecanoic acid	1961	46.059	nd	0.327	0.098±0.138	nd	0.987	0.293±0.387
160	linoleic acid	2136	51.572	nd	0.164	0.044±0.071	nd	0.271	0.078±0.109
161	oleic acid	2142	51.746	nd	0.133	0.032±0.055	nd	0.087	0.031±0.039

[a]values given in bold were found in all plum spirit samples (produced by both distillation techniques);

TABLE S-VII. Esters in Montenegrin plum spirits (mg L^{-1})

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
1	Ethyl butanoate	801	3.345	0.148	4.002	1.226±1.604	0.114	0.741	0.487±0.249
2	Ethyl lactate	820	3.506	6.449	24.246	15.195±7.075	7.874	42.199	20.480±13.018
7	Ethyl (Z)-2-butenoate	841	3.940	0.001	0.174	0.054±0.077	0.005	0.393	0.144±0.156
8	Ethyl 2-methylbutanoate	847	4.039	0.017	0.197	0.094±0.075	0.005	0.232	0.090±0.084
9	Ethyl 3-methylbutanoate	850	4.090	nd	0.398	0.132±0.154	nd	0.110	0.026±0.043
14	3-Methylbutyl acetate	875	4.520	0.151	0.800	0.436±0.301	0.133	1.371	0.753±0.510
15	2-Methylbutyl acetate	877	4.554	nd	0.289	0.110±0.113	0.076	0.323	0.197±0.099
17	Ethyl pentanoate	903	5.048	0.010	0.088	0.051±0.032	nd	0.062	0.022±0.024
26	Ethyl 2-hydroxy-3-methylbutanoate	964	6.776	nd	0.340	0.123±0.134	nd	0.089	0.020±0.036
33	Ethyl hexanoate	1001	7.762	0.237	3.213	1.030±1.195	0.136	1.294	0.710±0.432
36	Hexyl acetate	1014	8.247	nd	0.094	0.016±0.038	nd	0.048	0.009±0.019
42	Ethyl 2-furoate	1054	9.729	nd	0.050	0.010±0.020	nd	0.024	0.006±0.010
45	Isoamyl lactate	1069	10.234	nd	0.079	0.015±0.032	nd	0.333	0.112±0.136
48	2,3-Butandiol diacetate	1074	10.464	nd	0.257	0.043±0.105	nd	0.097	0.018±0.039
52	Methyl benzoate	1098	11.349	nd	0.174	0.051±0.066	nd	0.073	0.025±0.034
53	Ethyl heptanoate	1101	11.463	0.003	0.113	0.031±0.044	nd	0.020	0.008±0.008
57	Methyl octanoate	1126	15.556	nd	0.106	0.025±0.042	nd	0.040	0.016±0.016

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
63	Benzyl acetate	1165	14.251	nd	0.320	0.099±0.121	nd	0.437	0.200±0.184
64	Ethyl benzoate	1171	14.552	1.017	15.634	5.949±5.620	1.311	9.923	5.056±3.436
67	Diethyl succinate	1182	14.998	0.392	5.289	1.593±1.892	0.122	1.970	0.894±0.649
72	Methyl salicylate	1196	15.570	nd	0.636	0.170±0.234	nd	1.288	0.271±0.503
73	Ethyl octanoate	1199	15.696	0.898	4.318	2.132±1.562	0.287	4.763	2.314±1.582
80	Hexyl 2-methylbutanoate	1238	17.448	nd	0.085	0.015±0.034	nd	0.052	0.017±0.027
81	Hexyl 3-methylbutanoate	1238	17.446	nd	nd	nd	nd	0.030	0.005±0.012
82	Ethyl phenylacetate	1246	17.812	nd	0.079	0.026±0.033	0.003	0.140	0.049±0.049
84	2-Phenylethyl acetate	1258	18.332	0.007	0.271	0.067±0.101	0.012	0.423	0.239±0.139
86	Diethyl malate	1270	18.819	nd	0.280	0.047±0.114	nd	nd	nd
87	Ethyl salicylate	1272	18.935	0.054	2.335	0.557±0.881	nd	1.062	0.293±0.406
95	Ethyl nonanoate	1299	20.114	0.052	0.694	0.229±0.241	0.009	0.433	0.268±0.162
96	Nonanyl acetate	1313	20.774	nd	nd	nd	nd	0.048	0.017±0.021
101	Methyl decanoate	1326	21.369	0.003	0.017	0.009±0.005	nd	0.180	0.058±0.068
103	Ethyl phenyllactate	1352	22.437	0.010	0.421	0.134±0.157	nd	0.183	0.059±0.070
108	Ethyl (*Z*)-cinnamate	1381	23.741	nd	0.016	0.003±0.006	nd	0.568	0.219±0.238
110	Ethyl (*E*)-4-decenoate	1389	24.147	nd	0.095	0.030±0.034	nd	0.142	0.038±0.058
111	Ethyl decanoate	1397	24.485	0.803	2.870	1.734±0.910	0.288	8.304	3.033±2.980
117	2-Methylbutyl benzoate	1438	26.234	nd	0.038	0.014±0.013	nd	0.058	0.021±0.024
119	3-Metylbutyl octanoate	1448	26.610	nd	0.010	0.002±0.004	nd	0.172	0.039±0.068
121	Ethyl (*E*)-cinnamate	1467	27.396	0.028	1.132	0.440±0.532	0.012	0.779	0.364±0.306
125	Methyl dodecanoate	1526	29.864	nd	nd	nd	nd	0.055	0.009±0.022
126	Ethyl 3-hydroxy-tridecanoate	1536	30.278	nd	0.030	0.006±0.012	nd	nd	nd
130	Ethyl dodecanoate	1595	32.691	0.186	0.596	0.328±0.190	0.085	3.735	1.041±1.404
131	Phenylethyl hexanoate	1644	34.570	nd	nd	nd	nd	0.072	0.016±0.029
132	2-Methylbutyl decanoate	1646	34.653	nd	nd	nd	nd	0.187	0.031±0.076
133	3-Methylbutyl decanoate	1649	34.783	nd	nd	nd	nd	0.050	0.008±0.021
137	Diethyl azelate	1689	36.344	nd	0.060	0.020±0.028	nd	0.061	0.032±0.025
146	Ethyl tetradecadienoate	1758	38.887	nd	nd	nd	nd	0.090	0.015±0.037
147	Methyl pentadecanoate	1759	38.999	nd	0.008	0.001±0.003	nd	0.078	0.025±0.036
148	Ethyl *p*-methoxycinnamate	1762	39.004	nd	0.117	0.019±0.048	nd	nd	nd
149	Ethyl 9-tetradecenoate	1763	39.093	nd	0.002	0.000±0.001	nd	0.245	0.088±0.096
150	Ethyl 9-tetradecenoate (isomer)	1771	39.441	nd	0.027	0.005±0.011	nd	0.093	0.034±0.037

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
151	Ethyl tetradecanoate	1794	40.270	nd	0.075	0.029±0.032	0.009	0.502	0.189±0.190
153	Phenylethyl octanoate	1850	42.155	nd	0.021	0.004±0.009	nd	0.107	0.028±0.046
156	Ethyl 9-hexadecenoate	1974	46.492	nd	0.056	0.016±0.023	nd	0.192	0.084±0.076
158	Ethyl hexadecanoate	1994	47.203	0.043	0.452	0.191±0.200	0.018	1.995	0.760±0.807
159	Methyl linoleate	2097	50.443	nd	nd	nd	nd	0.091	0.025±0.040
163	Ethyl linoleate	2169	52.532	0.043	0.450	0.183±0.170	nd	2.965	0.986±1.196
164	Ethyl oleate	2175	52.719	nd	0.232	0.070±0.109	nd	0.766	0.223±0.300
165	Ethyl linolenate	2172	52.742	nd	0.053	0.026±0.021	nd	0.950	0.165±0.385
167	Ethyl octadecanoate	2201	53.518	nd	nd	nd	nd	0.108	0.046±0.053

[a]values given in bold were found in all plum spirit samples (produced by both distillation techniques);

TABLE S-VIII. Benzenoids in Montenegrin plum spirits (mg L^{-1})

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
16	styrene	896	4.897	nd	0.089	0.035±0.042	nd	0.136	0.058±0.051
60	4-vinylanisole	1153	13.721	nd	0.067	0.018±0.029	0.006	0.467	0.253±0.175

TABLE S-IX. Terpenoids in Montenegrin plum spirits (mg L^{-1})

No.[a]	compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
22	*α*-pinene	934	5.917	nd	nd	nd	nd	0.038	0.006±0.016
31	(*e*)-dehydroxylinalool oxide	994	7.589	nd	nd	nd	nd	0.032	0.005±0.013
35	(*z*)-dehydroxylinalool oxide	1009	8.084	nd	0.115	0.019±0.047	nd	0.069	0.018±0.029
38	*o*-cymene	1023	8.575	nd	nd	nd	nd	0.143	0.038±0.062
39	limonene	1029	8.823	nd	0.024	0.004±0.010	nd	0.674	0.194±0.269
47	(*z*)-linalool oxide (furanoid)	1073	10.451	0.054	1.577	0.431±0.571	nd	0.679	0.181±0.249
50	(*e*)-linalool oxide (furanoid)	1089	11.067	0.059	2.070	0.584±0.754	0.030	0.853	0.367±0.307
54	linalool	1102	11.513	0.074	1.403	0.426±0.517	0.055	1.287	0.427±0.446
59	(*z*)-*β*-terpineol	1145	13.404	nd	nd	nd	nd	0.045	0.007±0.018
65	(*z*)-linalool oxide (pyranoid)	1173	14.671	nd	0.184	0.064±0.078	nd	0.296	0.067±0.120
66	terpinen-4-ol	1178	14.826	nd	0.339	0.066±0.136	nd	0.293	0.067±0.119
70	*α*-terpineol	1192	15.405	0.031	1.044	0.401±0.471	nd	0.923	0.428±0.383
74	*p*-menthen-1-ene-9-al	1217	16.505	nd	nd	nd	nd	0.092	0.016±0.037
75	(*e*)-carveol	1222	16.740	nd	nd	nd	nd	0.046	0.011±0.018
83	linalool acetate	1256	18.215	0.006	0.668	0.240±0.281	nd	0.618	0.197±0.229

[a]values given in bold were found in all plum spirit samples (produced by both distillation techniques);

TABLE S-X. Sesquiterpenoids in Montenegrin plum spirits (mg L^{-1})

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
114	longifolene	1408	24.883	nd	nd	nd	nd	0.100	0.017±0.041
124	(*e,e*)-*α*-farnesene	1511	29.209	nd	nd	nd	nd	0.178	0.030±0.073
127	(*e*)-nerolidol	1566	31.529	nd	0.118	0.034±0.054	nd	0.286	0.077±0.108
134	*α*-bisabolool oxide b	1656	35.091	nd	0.081	0.030±0.038	nd	0.052	0.011±0.021
138	(*z,e*)-2,6-farnesol	1723	37.614	nd	0.091	0.035±0.033	nd	0.251	0.067±0.096

TABLE S-XI. Isoprenoids in Montenegrin plum spirits (mg L^{-1})

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
90	vitispirane	1280	19.311	nd	0.045	0.009±0.018	nd	0.061	0.010±0.025
118	dihydro-*β*-ionol	1447	26.573	nd	0.079	0.022±0.032	nd	0.040	0.008±0.016
123	(*e*)-*β*-ionone	1487	28.286	nd	0.020	0.003±0.008	nd	nd	nd
181	squalene	2828	70.246	nd	0.096	0.017±0.038	nd	0.014	0.005±0.006

TABLE S-XII. Hydrocarbons in Montenegrin plum spirits (mg L^{-1})

No.	Compound	RI	RT (min)	Single distillation (n=6)			Double distillation (n=6)		
				Min	Max	Mean±SD	Min	Max	Mean±SD
168	tricosane	2301	56.534	nd	0.043	0.007±0.018	nd	0.024	0.004±0.010
169	tetracosane	2401	59.365	nd	0.030	0.005±0.012	nd	0.029	0.005±0.012
173	pentacosane	2507	62.004	nd	0.039	0.010±0.016	nd	0.057	0.016±0.025
174	hexacosane	2607	64.543	nd	0.031	0.015±0.013	nd	0.059	0.027±0.021
177	heptacosane	2706	67.071	nd	0.094	0.016±0.038	nd	0.074	0.027±0.030
179	octacosane	2801	69.442	nd	nd	nd	nd	0.033	0.005±0.013
182	nonacosane	2902	71.842	nd	0.501	0.084±0.204	nd	0.099	0.022±0.038

Just about half out of all minor compounds identified in traditional home made plum spirits from Romania and Serbia,[2,3] were also common to the analyzed Montenegrin plum spirits. In other words, there are significantly different GC-MS aromatic profiles of plum spirits from different regions of the Balkans.

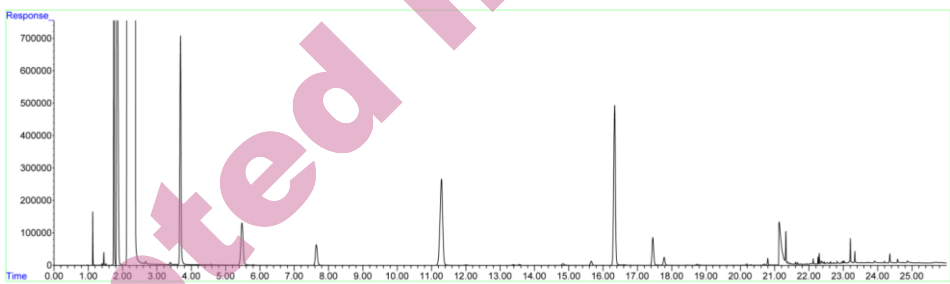

Figure S-1. GC-FID chromatogram of Montenegrin plum spirit sample

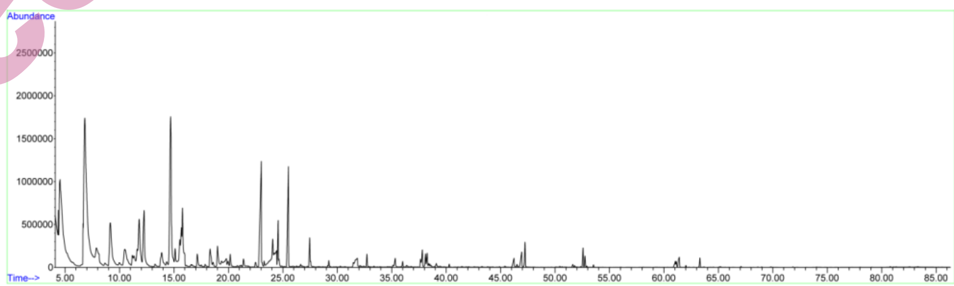

Figure S-2. GC-MS chromatogram of Montenegrin plum spirit sample

Pearson's correlation analysis (Correlations between common volatile compounds)

Although methanol and acetaldehyde were found in all samples, these compounds did not correlate significantly (results not shown) with other compounds typical of all plum spirits. In most cases (Table S-XIII), a significant positive Pearson's correlation was established between the content of 38 volatile components common for all the plum spirits analyzed. Significant negative values of correlation coefficient were observed only in a few cases: ethyl acetate and 3-methylbutanoic acid (r = - 0.61), 1-propanol and 2-phenylethanol (r = - 0.77), 1-propanol and 2-phenylethyl acetate (r = - 0.62). It is obvious that the compounds with negative correlation have different distillation dynamics (some of them are distilled mainly in the head fraction, and others in the tail fraction.).

Values of some correlation coefficients were as follow: ethyl hexanoate and ethyl octanoate (r = 0.79), ethyl octanoate and ethyl decanoate (r = 0.82), ethyl dodecanoate and ethyl octanoate (r = 0.68), 2/3-methyl-1-butanol and 3-methylbutyl acetate (r = 0.85), 2-phenylethanol and 2-phenylethyl acetate (r = 0.67). The obtained values of the mentioned correlation coefficients were similar but slightly higher than those, for the same components, found in various fruit brandies and other distilled beverages.[4,5]

It is interesting that octanoic acid, as one of the typical ingredients generated during alcoholic fermentation as a yeast metabolite, correlated significantly with other typical yeast metabolites, such as 2-methyl-1-propanol, 2/3-methyl-1-butanol, 2-phenylethanol, 3-methylbutanoic acid, hexanoic acid, decanoic acid, ethyl hexanoate, ethyl octanoate, ethyl decanoate, 3-methylbutyl acetate, 2-phenylethyl acetate. A similar pattern in terms of correlations was found for other components that are formed primarily during alcoholic fermentation of the plum mash. On the other hand, linalool originating from plum fruit correlated significantly mainly with plum spirit components also originating from fruits, providing the typical plum aroma, such as 1-hexanol, 1-octanol, nonanal, benzaldehyde, ethyl nonanoate, ethyl benzoate, ethyl (*E*)-cinnamate, and (*E*)-linalool oxide (furanoid).

Statistically significant correlation was not found between the concentrations of analysed components and the sensory evaluation scores of the plum spirits (results not shown). According Brandes et al.,[6] it is relatively easy to establish a correlation between the content of the components that adversely affect sensory characteristics of fruit spirits, such as free fatty acids (they give a tail-like character of the distillates), but it is difficult to determine the correlation between sensory evaluation score and components considered to contribute positively to the aroma of fruit spirits. As we have already noted under the Materials and methods, the analysed plum spirit samples were of good quality, without sensory defects, free from extraneous and unpleasant odour and taste.

TABLE S-XIII. Correlation matrix of 38 (6 major and 32 minor) volatile components quantified in all plum spirit samples

C/C	EA	1P	2M1P	1B	2/3M1B	1H	A13	A40	A46	A56	Ad55	Ad5	Ad25	Ac6	Ac30	Ac43	Ac68	Ac107
EA	1	/	/	/	/	/	/	/	/	/	/	/	/	-0.61	/	/	/	/
1P	/	1	/	/	/	/	/	/	/	-0.77	/	/	/	/	/	/	/	/
2M1P	/	/	1	/	0.74	/	/	/	/	/	/	/	/	0.66	/	/	0.65	/
1B	/	/	/	1	/	0.99	0.90	/	0.82	/	0.58	/	/	/	/	/	/	/
2/3M1B	/	/	0.74	/	1	/	/	/	/	0.78	/	/	/	0.68	/	/	0.79	0.70
1H	/	/	/	0.99	/	1	0.89	/	0.82	/	0.59	/	/	/	/	/	/	/
A13	/	/	/	0.90	/	0.89	1	0.59	0.96	/	0.78	/	/	/	0.69	/	/	/
A40	/	/	/	/	/	/	0.59	1	0.58	/	/	/	/	/	/	0.70	/	/
A46	/	/	/	0.82	/	0.82	0.96	0.58	1	/	0.79	/	/	/	0.65	/	/	/
A56	/	-0.77	/	/	0.78	/	/	/	/	1	/	/	/	/	/	/	0.62	/
Ad55	/	/	/	0.58	/	0.59	0.78	/	0.79	/	1	0.59	0.62	/	0.75	/	0.68	0.62
Ad5	/	/	/	/	/	/	/	/	/	/	0.59	1	0.79	/	/	/	/	/
Ad25	/	/	/	/	/	/	/	/	/	/	0.62	0.79	1	/	/	0.78	/	/
Ac6	-0.61	/	0.66	/	0.68	/	/	/	/	0.82	/	/	/	1	/	/	0.68	/
Ac30	/	/	/	/	/	/	0.69	/	0.65	/	0.66	/	/	/	1	/	0.89	0.89
Ac43	/	/	/	/	/	/	/	0.70	/	/	/	/	0.78	/	/	1	/	/
Ac68	/	/	0.65	/	0.79	/	/	/	/	0.62	0.68	/	/	0.68	0.89	/	1	0.91
Ac107	/	/	/	/	0.70	/	/	/	/	/	0.62	/	/	/	0.89	/	0.91	1
At23	/	/	/	0.62	/	0.65	0.80	/	0.76	/	0.80	0.70	0.82	/	0.63	0.64	/	/
At49	/	/	/	0.77	/	0.78	0.94	/	0.94	/	0.87	/	0.64	/	0.72	/	/	0.59
At51	/	/	/	0.79	/	0.80	0.93	/	0.93	/	0.92	/	0.59	/	0.66	/	/	/
E1	/	/	/	/	/	/	/	0.71	0.59	/	/	/	/	/	/	/	/	/
E33	/	/	/	0.76	/	0.75	0.89	0.59	0.88	/	0.70	/	/	/	0.86	/	0.74	0.74
E73	/	/	/	/	0.60	/	/	/	/	/	/	/	/	/	0.89	/	0.86	0.94
E95	/	/	/	0.67	/	0.69	0.86	/	0.84	/	0.87	/	0.66	/	0.89	0.59	0.70	0.77
E111	/	/	/	/	0.65	/	/	/	/	/	/	/	/	/	0.70	/	0.68	0.84
E130	/	/	/	/	/	/	/	/	/	/	/	/	/	/	0.58	/	/	0.75
E158	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	0.71
E8	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	0.58
E14	/	/	/	/	0.85	/	/	/	/	0.80	/	/	/	0.69	0.71	/	0.86	0.82
E84	/	-0.62	/	/	/	/	/	/	/	0.67	0.79	/	0.64	0.65	0.61	/	0.61	/
E2	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	0.68	/	/
E64	/	/	/	0.67	/	0.70	0.89	0.79	0.89	/	0.66	/	0.76	/	0.59	0.77	/	/
E121	/	/	/	/	/	/	0.77	0.71	0.82	/	0.60	/	0.68	/	0.62	0.70	/	0.63
E7	/	/	/	/	0.88	/	/	/	/	0.87	/	/	/	0.80	0.67	/	0.85	0.75
E67	/	/	/	0.79	/	0.76	0.86	0.71	0.75	/	/	/	/	/	0.73	0.65	/	/
T50	/	/	/	0.91	/	0.89	0.96	0.68	0.92	/	0.60	/	/	/	/	/	/	/
T54	/	/	/	0.73	/	0.76	0.92	/	0.96	/	0.83	/	0.64	/	0.62	/	/	/

TABLE S-XIII. Continuing

C/C	At23	At49	At51	E1	E33	E73	E95	E111	E130	E158	E8	E14	E84	E2	E64	E121	E7	E67	T50	T54
EA	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
1P	/	/	/	/	/	/	/	/	/	/	/	/	-0.62	/	/	/	/	/	/	/
2M1P	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
1B	0.62	0.77	0.79	/	0.76	/	0.67	/	/	/	/	/	/	/	0.67	/	/	0.79	0.91	0.73
2/3M1B	/	/	/	/	/	0.60	/	0.65	/	/	/	0.85	/	/	/	/	0.88	/	/	/
1H	0.65	0.78	0.80	/	0.75	/	0.69	/	/	/	/	/	/	/	0.70	/	/	0.76	0.89	0.76
A13	0.80	0.94	0.93	/	0.89	/	0.86	/	/	/	/	/	/	/	0.89	0.77	/	0.86	0.96	0.92
A40	/	/	/	0.71	0.59	/	/	/	/	/	/	/	/	/	0.79	0.71	/	0.71	0.68	/
A46	0.76	0.94	0.93	0.59	0.88	/	0.84	/	/	/	/	/	/	/	0.89	0.82	/	0.85	0.92	0.96
A56	/	/	/	/	/	/	/	/	/	/	/	0.80	0.67	/	/	/	0.87	/	/	/
Ad55	0.80	0.87	0.92	/	0.70	/	0.87	/	/	/	/	/	0.79	/	0.66	0.60	/	/	0.60	0.83
Ad5	0.70	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/	/
Ad25	0.82	0.64	0.59	/	/	/	0.66	/	/	/	/	/	0.64	/	0.76	0.68	/	/	/	0.64
Ac6	/	/	/	/	/	/	/	/	/	/	/	0.69	0.65	/	/	/	0.80	/	/	/
Ac30	0.63	0.72	0.66	/	0.86	0.89	0.89	0.70	0.58	/	/	0.71	0.61	/	0.59	0.62	0.67	0.73	/	0.62
Ac43	0.64	/	/	/	/	/	0.59	/	/	/	/	/	/	0.68	0.77	0.70	/	0.65	/	/
Ac68	/	/	/	/	0.74	0.86	0.70	0.68	/	/	/	0.86	0.61	/	/	/	0.85	/	/	/
Ac107	/	0.59	/	/	0.74	0.94	0.77	0.84	0.75	0.71	0.58	0.82	/	/	/	0.63	0.75	/	/	/
At23	1	0.90	0.86	/	0.69	/	0.87	/	/	/	/	/	/	/	0.85	0.78	/	0.71	0.70	0.84
At49	0.90	1	0.96	0.58	0.88	0.60	0.92	/	/	/	/	/	/	/	0.89	0.86	/	0.78	0.84	0.95
At51	0.86	0.96	1	/	0.79	/	0.87	/	/	/	/	/	/	/	0.81	0.71	/	0.66	0.82	0.95
E1	/	0.58	/	1	0.74	0.66	/	/	/	/	/	/	/	/	0.64	0.83	/	0.61	/	/
E33	0.69	0.88	0.79	0.74	1	0.79	0.89	/	/	/	/	/	/	/	0.82	0.84	/	0.89	0.82	0.81
E73	/	0.60	/	0.66	0.79	1	0.78	0.82	0.68	0.65	0.64	0.76	/	/	/	0.71	0.74	0.61	/	/
E95	0.87	0.92	0.87	/	0.89	0.78	1	/	/	/	/	/	0.62	/	0.83	0.82	/	0.79	0.72	0.87
E111	/	/	/	/	/	0.82	/	1	0.96	0.89	0.74	0.67	/	/	/	/	0.77	/	/	/
E130	/	/	/	/	/	0.68	/	0.96	1	0.92	0.66	/	/	/	/	/	/	/	/	/
E158	/	/	/	/	/	0.65	/	0.89	0.92	1	0.65	/	/	/	/	/	/	/	/	/
E8	/	/	/	/	/	0.64	/	0.74	0.66	0.65	1	/	/	/	/	/	/	/	/	/
E14	/	/	/	/	/	0.76	/	0.67	/	/	/	1	0.70	/	/	/	0.88	/	/	/
E84	/	/	/	/	/	/	0.62	/	/	/	/	0.70	1	/	/	/	0.64	/	/	/
E2	/	/	/	/	/	/	/	/	/	/	/	/	/	1	/	/	/	/	/	/
E64	0.85	0.89	0.81	0.64	0.82	/	0.83	/	/	/	/	/	/	/	1	0.91	/	0.82	0.87	0.89
E121	0.78	0.86	0.71	0.83	0.84	0.71	0.82	/	/	/	/	/	/	/	0.91	1	/	0.75	0.71	0.85
E7	/	/	/	/	/	0.74	/	0.67	/	/	/	0.88	0.64	/	/	/	1	/	/	/
E67	0.71	0.78	0.66	0.61	0.89	0.61	0.79	/	/	/	/	/	/	/	0.82	0.75	/	1	0.86	0.68
T50	0.70	0.84	0.82	/	0.82	/	0.72	/	/	/	/	/	/	/	0.87	0.71	/	0.86	1	0.84
T54	0.84	0.95	0.95	/	0.81	/	0.87	/	/	/	/	/	/	/	0.89	0.85	/	0.68	0.84	1

/ - P>0.05[NS] (r values < 0.58 not shown); P<0.05* (r values 0.58-0.71); P<0.01** (r values 0.72-0.85); P<0.001*** (r values 0.86-0.99); Major volatile components: **EA**-ethyl acetate; **1P**-1-propanol; **2M1P**-2-methyl-1-propanol; **1B**-1-butanol; **2/3M1B**-2/3-methyl-1-butanol; **1H**-1-hexanol; Minor volatile components: **A-Alcohols** (**A13**-1-hexanol; **A40**-benzyl alcohol; **A46**-1-octanol; **A56**-2-phenylethanol); **Ad-Aldehydes** (**Ad55**-nonanal; **Ad5**-furfural; **Ad25**-benzaldehyde); **Ac-Acids** (**Ac6**-3-metylbutanoic acid; **Ac30**-hexanoic acid; **Ac43**-2-hydroxy-4-methylpentanoic acid; **Ac68**-octanoic acid; **Ac107**-decanoic acid); **At-Acetals** (**At23**-1,1-diethoxy-3-methylbutane; **At49**-1,1,3-triethoxypropane; **At51**-1,1-diethoxyhexane); **E-Esters** (**E1**-ethyl butanoate; **E33**-ethyl hexanoate; **E73**-ethyl octanoate; **E95**-ethyl nonanoate; **E111**-ethyl decanoate; **E130**-ethyl dodecanoate; **E158**-Ethyl hexadecanoate; **E8**-ethyl 2-methylbutanoate; **E14**-3-methylbutyl acetate; **E84**-2-phenylethyl acetate; **E2**-ethyl lactate; **E64**-ethyl benzoate; **E121**-ethyl-(*E*)-cinnamate; **E7**-ethyl-2-(*Z*)-butenoate; **E67**-diethyl succinate; **T-Terpenoids** (**T50**-(*E*)-linalool oxide (furanoid); **T54**-linalool);

REFERENCES

1. S. Ivanović, K. Simić, V. Tešević, L.; L. Vujisić, M. Ljekočević, D. Gođevac, *Molecules* **26** (2021) 1391 (https://doi.org/10.3390/molecules26051391)
2. T. E. Coldea, C. Socaciu, Z. Moldovan, E. Mudura, *Not. Bot. Horti. Agrobo.* **42** (2014) 530 (https://doi.org/10.15835/nbha4229607)
3. V. Tešević, N. Nikićević, A. Jovanović, D. Djoković, L. Vujisić, I. Vučković, M. Bonić, *Food Technol. Biotech.* **43** (2005) 367 (http://www.ftb.com.hr/images/pdfarticles/2005/October-December/43-367.pdf)
4. K. Misselhorn, *Branntweinwirtschaft*, **1** (1992) 74
5. L. Nykänen, I. Nykänen, *Distilled beverages*, in *Volatile Compounds in Food and Beverages*, H. Marse, Ed., Marcel Dekker, Inc., New York, NY, 1991, p. 547 (https://doi.org/10.1002/food.19910351027)
6. W. Brandes, M. Karner, R. Eder, *Mitt. Klosterneuburg* **57** (2007) 63.