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Aromatic profiles of monovarietal raspberry Geists

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Abstract. The paper presents the results of gas chromatography-flame ionization detection-mass spectrometry (GC-FID-MS) analysis of volatile substances that form the aromatic profiles of raspberry Geists produced from Serbia's most common raspberry varieties ('Willamette', 'Meeker', and 'Tulameen'). Considering that raspberry Geist is a spirit drink obtained by maceration of unfermented fruits in ethanol, followed by distillation of the obtained macerate, the compounds that dominate the aromatic complex of this alcoholic beverage are volatile compounds originating mainly from raspberry fruits. A total of 134 compounds were quantified, of which 112 in Geist from the cultivar 'Willamette', 76 in Geist from the cultivar 'Meeker', and 99 in Geist from the cultivar 'Tulameen'. The identified compounds belonged to the classes of terpenoids, sesquiterpenoids, C13 norisoprenoids, ketones, aldehydes, alcohols, acetals, esters, acids, lactones, and others. Among the 60 compounds common to all 3 monovarietal Geists, 15 were represented in higher concentrations, especially (E)-β-ionone, α-ionone, 2-hexenal, and ethyl oleate.

Key words: 'Willamette','Meeker','Tulameen', spirit drinks, volatile compounds, GC-FID-MS

Introduction

Raspberries are an interesting raw material for the production of alcoholic beverages due to their pronounced, specific, and fine aroma (Bezerra et al., 2024). There are two groups of alcoholic beverages produced from raspberries. Raspberry wine, which contains less than 15 vol% ethanol, belongs to the first group. The second group includes spirit drinks, which, according to the current EU Regulation (2008), have a minimum of 15 vol% ethanol. Depending on the method of production, there are 4 types of spirit drinks made of raspberries (raspberry liquer, raspberry spirit, raspberry spirit obtained by maceration and distillation, and raspberry Geist). Raspberry liqueurs are produced by maceration of raspberry fruits or juice in ethanol of agricultural origin and/or some other fruit distillate. In the production of the other three raspberry spirit drinks, distillation is a mandatory technological operation. Raspberry spirit is obtained by alcoholic fermentation of fruits or juice, followed by distillation of fermented raspberry mash or juice. Raspberry spirit obtained by maceration and distillation is produced by maceration of partially fermented berries in ethanol or spirit and/or distillate deriving from the same fruit, followed by distillation of macerate. Raspberry Geist, according to the current Regulation, is obtained by maceration of unfermented raspberry fruits in ethanol of agricultural origin and then by distillation of the macerate, whereby the obtained distillate must contain less than 86 vol% ethanol. Final products for direct consumption have different amounts of ethanol; liqueurs can have less than 37.5 vol% ethanol, while spirits and Geist must have a minimum of 37.5 vol% ethanol.

One of the important reasons for the production of raspberry Geist is the fact that raspberries have a low sugar content (Leposavić et al., 2013), so the high yields of ethanol, i.e., distillate, cannot be obtained by the production process that includes alcoholic fermentation (Christoph & Bauer-Christoph, 2007). Beside the low sugar content, fresh raspberries often have an extremely high price, which makes them an expensive raw material for the production of spirit drink based on the alcoholic fermentation. However, due to the intense and fine aroma, the raspberry spirit drinks are very attractive to modern consumers. Thus producers, considering the economy of processing, often decide to produce raspberry Geist, which requires significantly less raw material than the production of raspberry spirit (Nikićević & Paunović, 2013). The mentioned authors emphasize that the best aroma of raspberry distillate is obtained by a process that includes only the maceration of the fruits and then the distillation of the macerate. The technological process of Geist production is based on these two steps.

Raspberries Geist is traditionally produced in Austria, France, Germany, Hungary, and northern Italy (Christoph & Bauer-Christoph, 2007). Schwarzwälder Himbeergeist with Geographical indication (with a minimum ethanol content of 40 vol%), which is produced in Germany, is the most famous raspberry Geist in the world. However, there are few studies on the aroma of raspberry Geists. The studies mainly analyzed the contents of the major volatile components (methanol, higher alcohols, acetaldehyde, ethyl acetate, and ethyl lactate) of raspberry Geist with the aim of differentiating these products from other spirit drinks (Lachenmeier & Musshoff, 2004), that is, for their differentiation from raspberry spirit and raspberry spirit obtained by maceration and distillation (Dubinina et al., 2018).

Serbia is one of the world's leading producers of raspberries, which are mainly (about 90%) exported as frozen fruits (Leposavić, 2023). Changes in the world market's demands resulted in new ways of using and processing raspberries. As a consequence of these new trends, the production of raspberry spirit drinks has become more important. The quality of raspberry spirit drinks depends on the raw material (cultivar) and the processing method. Due to the specific and delicate aroma, raspberries are a very interesting raw material for the production of spirit drink obtained by maceration of unfermented berries (Geist). Since in the production of Geist there is no alcoholic fermentation of the raw material, which significantly affects the composition of the final product, it remains that the choice of raw material, i.e., the raspberry cultivar used for its production, is of crucial importance for the aroma of the Geist. In our previous works, we found that raspberry cultivars grown in Serbia differ in the content of aromatic components, i.e., the aromatic profile (Leposavić et al., 2022).

Bearing all this in mind, as well as the fact that until now there have been no works examining the aromatic profile of Geist produced from raspberries originated from the Serbian raspberry growing regions, the aim of the work was to determine the aromatic profiles of raspberry Geists produced from the cultivars most commonly grown in Serbia ('Willamette', 'Meeker', and 'Tulameen') in order to characterize and determine the quality and authenticity of this spirit drink.

Materials and Methods

Raspberry Samples and Geists Production. For the production of monovarietal raspberry Geists, on a pilot scale, fully ripe raspberries of the 'Willamette' (W), 'Meeker' (M), and 'Tulameen' (T) cultivars from a commercial orchard in Krstac (Arilje raspberry growing area) were used.

The production of raspberry Geist (G) was carried out according to the procedure described by Nikićević & Paunović (2013). Briefly, hand-crushed raspberries were macerated in refined ethanol (in a ratio of 2.5:1

w/v) in closed vessels, at room temperature, for 24 h. Three separate macerations were performed for each cultivar (in polyethylene vessels with a volume of 30 l). The macerates were then distilled in a pilot-scale alembic (volume 25 l) of traditional construction, made of copper, whereby distillates with an ethanol content of 60 vol% were obtained. Three distillates from the same raspberry cultivar were then mixed and stored in full glass flasks until analysis. For analyses, samples were diluted with deionized water to 40 vol% ethanol.

Geist Samples Preparation. Aroma compounds of raspberry Geists samples were determined by gas chromatography-flame ionization detection-mass spectrometry (GC-FID-MS) analysis. The extraction of aroma compounds for GC-FID-MS analysis was started by diluting an aliquot of 100 ml of sample with 100 ml distilled water, followed by adding of 15 ml of 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.

GC-FID-MS Analysis. The GC-FID-MS analysis of aroma compounds were performed on Agilent 7890A GC system (Agilent Technologies, Santa Clara, CA, USA) equipped with a 5975C mass selective detector (MSD) and a flame ionization detector (FID) connected by capillary flow technology through a two-way splitter. A non-polar HP-5MSI capillary column (30 m × 0.25 mm, 0.25 µm film thickness) was used. Column temperature was programmed linearly in the range of 60°C to 270°C at a rate of 3°C/min, then at a rate of 20°C/min to 310°C with final 8 min hold. Helium was used as carrier, auxiliary and make up gas; inlet pressure was constant at 19.7 psi (flow 1.0 ml/min at 210°C), auxiliary pressure was 3.8 psi and FID make up flow was 25 ml/min. FID temperature was 300°C, split ratio was 5:1 and injection volume was 1 µl for all analysis. Mass spectra obtained by electron ionization with 70 eV at 200°C. Quadrupole temperature was set to 150°C and MS range was 40–550 amu. Transfer line temperature was 315°C. The identification of the aroma compounds was based on comparison with the reference spectra (Wiley and NIST databases). The percentages of the identified compounds are obtained from the electronic integration of the GC-FID peak areas.

Results and Discussion

Volatile compounds that formed the aroma profiles of raspberry Geists produced from the most represented varieties in the assortment of Serbia were quantified for the first time (Table 1). A total of 134 compounds were quantified, of which 112 in Geist from the cultivar 'Willamette' (WG), 76 in Geist from the cultivar 'Meeker' (MG), and 99 in Geist from the cultivar 'Tulameen' (TG). Regarding the classes of chemical compounds, 30 esters (27 in WG, 16 in MG, and 16 in TG), 17 aldehydes (13 in WG, 13 in MG, and 15 in TG), 17 C13-norisoprenoids (13 in WG, 11 in MG, and 13 in TG), 12 acetals (11 in WG, 8 in MG, and 11 in TG), 11 terpenoids (10 in WG, 8 in MG, and 9 in TG), 6 ketones (5 in WG, 2 in MG, and 5 in TG), 4 alcohols (3 in WG, 2 in MG, and 4 in TG), 4 acids (4 in WG, 0 in MG, and 0 in TG), 3 lactones (3 in WG, 1 in MG, and 2 in TG), and 2 sesquiterpenoids (1 in WG, 1 in MG, and 2 in TG) were quantified in raspberry Geists. Also, 3 compounds clasified as Others (2 in WG, 1 in MG, and 3 in TG), as well as 25 unidentified (NI) compounds (20 in WG, 13 in MG, and 19 in TG) were quantified. Nikićević et al. (2004) quantified 74 aromatic components (25 esters, 9 acids, 8 aldehydes, 8 C13 norisoprenoids, 7 terpenoids, 6 sesquiterpenoids, 5 alcohols, 3 acetals, and 3 other compounds) in raspberry spirit produced by distillation of 'Willamette' fermented mash.

It is interesting that in the aromatic complex of raspberry spirit analyzed in the work of the mentioned authors (Nikićević et al., 2004), quantitatively the most represented (47.94%) were ethyl esters of saturated fatty acids with an even number of C atoms (from ethyl hexanoate to ethyl octadecanoate). The total content of these esters in the experimentally produced raspberry Geists was significantly lower (3.22% in WG, 4.6% in MG, and 2.9% in TG, respectively). A similar pattern of results were obtained for acetate esters of 2/3-methyl-1-butanol (their content in raspberry spirit was 1.44%, while they were not found in monovarietal Geists), as well as for saturated fatty acids with an even number of carbon (C) atoms, from C8 to C16 (6.15% in raspberry spirit, while in the analyzed Geists only WG contained 0.5% of these acids, and MG and TG did not). The mentioned compounds are mainly sinthetized by yeasts during alcoholic fermentation (Christoph &

Table 1. The content of the volatile compounds in monovarietal raspberry Geists
Tabela 1. Sadržaj isparljivih komponenata u monosortnim Geistevima od maline

Compound *Jedinjenje*	RT* (min)	Area/*Površina* (%) WG**	 MG	 TG
Terpenoids/*Terpenoidi* (11)		**6.4**	**5.1**	**6.6**
α-Pinene/*α-Pinen*	5.72	1.0	0.5	1.0
Myrcene/*Mircen*	7.31	0.3	–	0.1
p-Cymene/*p-Cimen*	8.49	0.3	0.2	0.2
β-Phellandrene/*β-Felandren*	8.60	0.5	0.3	0.4
Linalool/*Linalol*	11.25	2.2	2.8	3.3
Ocimenol/*Ocimenol*	13.95	–	0.1	–
4-Terpineol/*4-Terpineol*	14.51	0.3	0.2	0.2
α-Terpineol/*α-Terpineol*	15.12	1.5	0.9	1.2
β-Cyclocitral/*β-Ciklocitral*	16.39	0.1	0.1	0.1
Piperiton/*Piperiton*	17.88	0.1	–	0.1
Phellandral/*Felandral*	18.80	0.1	–	–
Sesquiterpenoids/*Seskviterpenoidi* (2)		**0.3**	**0.1**	**1.7**
(E)-Caryophyllene/*(E)-Kariofilen*	25.15	–	–	1.0
α-Humulene/*α-Humulen*	26.61	0.3	0.1	0.7
C13 norisoprenoids/*C13 norisoprenoidi* (17)		**40.5**	**43.4**	**44.5**
Metastigma-3,7,9-triene/*Metastigma-3,7,9-trien*	16.16	–	–	0.1
Ionene/*Jonen*	17.77	–	–	0.1
Vitispirane/*Vitispiran*	18.92	0.1	–	–
Ionene/*Jonen*	20.11	0.9	0.1	–
Edulan I/*Edulan I*	21.25	0.8	0.4	2.9
Metastigma-4,6,8-triene (isomer)/*Metastigma-4,6,8-trien (isom.)*	21.65	–	–	0.1
Dehydro-ar-ionene (TDN)/*Dehidro-ar-jonen (TDN)*	22.17	0.3	0.2	0.3
Metastigma-4,6,8-triene (isomer)/*Metastigma-4,6,8-trien (isom.)*	22.62	0.2	–	0.7
Metastigma-4,6,8-triene (isomer)/*Metastigma-4,6,8-trien (isom.)*	23.31	3.4	1.5	2.3
(E)-α-Ionol/*(E)-α-Jonol*	23.80	0.1	0.2	0.4
α-Ionone/*α-Jonon*	25.50	15.5	17.2	8.4
7,8-Dihydro-β-ionone/*7,8*-Dihidro-β-jonon	25.85	0.4	0.6	1.5
(E)-β-Ionone/*(E)-β-Jonon*	27.95	18.0	22.6	27.1
7,11-Epoxymegastigma-5(6)-en-9-one/ *7,11-Epoksimegastigma-5(6)-en-9-on*	32.05	0.3	0.2	0.4
4-Oxo-β-ionone/*4-Okso-β-jonon*	35.37	0.4	0.2	–
4-(2,4,4-Trimethyl- cyclohexa-1,5-dienyl)-but-3-en-2-one/ *4-(2,4,4-Trimetil- cikloheksa-1,5-dienil)-but-3-en-2-on*	35.77	–	0.2	0.2
2,5,5,8a-Tetramethyl-6,7,8,8a-tetrahydro-5H-chromen-3-one/ *2,5,5,8a-Tetrametil-6,7,8,8a-tetrahidro-5H-hromen-3-on*	37.12	0.1	–	–
Ketones/*Ketoni* (6)		**1.2**	**0.3**	**0.7**
2-Heptanone/*2-Heptanon*	4.76	0.3	–	0.1
2-Nonanone/*2-Nonanon*	10.85	0.2	0.1	0.2
2-Undecanone/*2-Undekanon*	19.64	0.2	–	0.1
3-(Prop-2-en-1-onyl)-2,4,4-trimethylcyclohex-2-en-1-one/ *3-(Prop-2-en-1-onil)-2,4,4-trimetilcikloheks-2-en-1-on*	28.80	0.4	0.2	0.2
6-Methyl-6-(5-methylfuran-2-yl)heptan-2-one/ *6-Metil-6-(5-metilfuran-2-il)heptan-2-on*	36.02	–	–	0.1
6,10,14-Trimethyl-2-pentadecanone/ *6,10,14-Trimetil-2-pentadekanon*	41.72	0.1	–	–
Aldehydes/*Aldehidi* (17)		**17.9**	**13.4**	**21.5**
2-Furfural/*2-Furfural*	3.70	1.5	–	1.1
2-Hexenal/*2-Heksenal*	4.06	9.3	1.9	12.1

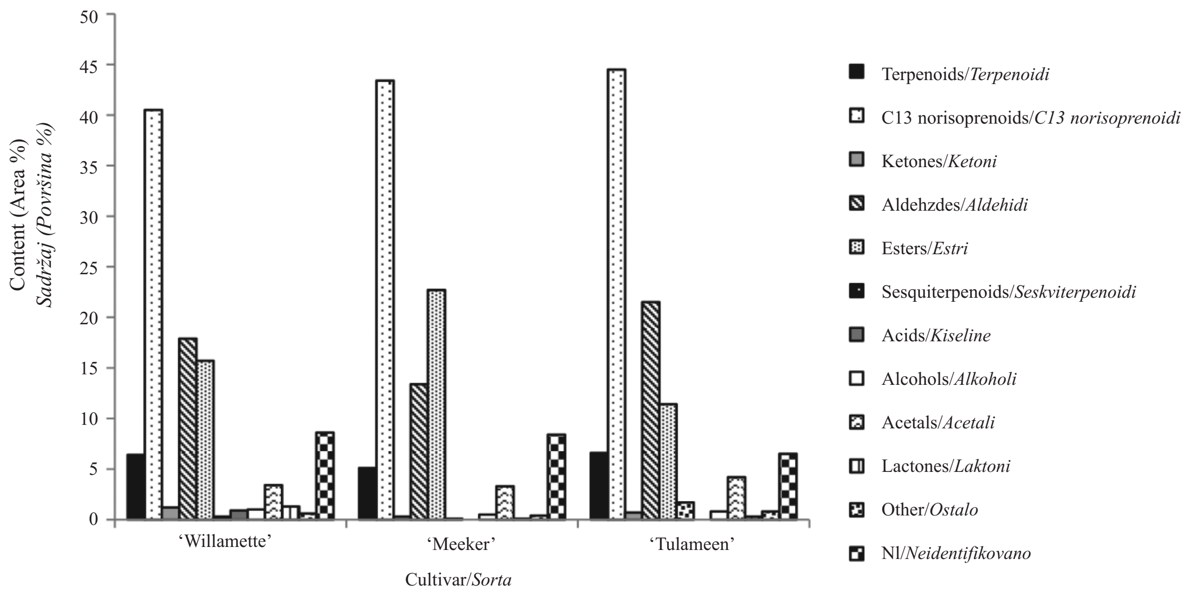
Heptanal/*Heptanal*	5.04	0.4	0.3	–
Benzaldehyde/*Benzaldehid*	6.55	0.2	–	0.2
Octanal/*Oktanal*	7.74	0.5	0.6	0.5
2-Phenylacetaldehyde/*2-Fenilacetaldehid*	9.20	0.1	–	0.1
Nonanal/*Nonanal*	11.45	1.8	1.4	1.8
Decanal/*Dekanal*	15.73	1.7	1.3	1.6
Undecanal/*Undekanal*	20.22	–	0.7	0.6
2-Undecenal/*Undecenal*	22.75	0.2	–	0.2
Dodecanal/*Dodekanal*	24.72	–	1.2	–
Tridecanal/*Tridekana*l	29.05	0.7	0.8	0.8
Tetradecanal/*Tetradekanal*	33.15	0.9	2.9	1.1
Pentadecanal/*Pentadekanal*	37.01	0.5	0.8	0.3
Hexadecanal/*Heksadekanal*	40.71	–	1.0	0.8
Heptadecanal/*Heptadekanal*	44.22	–	0.4	0.2
Octadecanal/*Oktadekanal*	47.56	0.1	0.1	0.1
Alcohols/*Alkoholi* (4)		**1.0**	**0.5**	**0.8**
(E)-3-Hexenol/*(E)-3-Heksenol*	4.12	0.3	0.1	0.1
1-Hexanol/*1-Heksanol*	4.38	0.6	0.4	0.2
2-Heptanol/*2-Heptanol*	4.84	–	–	0.4
1-Octanol/*1-Oktanol*	10.20	0.1	–	0.1
Acetals/*Acetali* (12)		**3.4**	**3.3**	**4.2**
1,1-Diethoxybutane/*1,1-Dietoksibutan*	4.28	0.1	–	–
1,1-Diethoxy-3-methylbutane/*1,1-Dietoksi-3-metilbutan*	6.27	0.4	0.4	0.5
1,1-Diethoxypentane/*1,1-Dietoksipentan*	7.50	1.1	1.1	1.1
1,1,3-Triethoxypropane/*1,1,3-Trietoksipropan*	10.43	0.1	0.2	0.1
1,1-Diethoxyhexane/*1,1-Dietoksiheksan*	11.00	0.6	0.4	0.8
1,1-Diethoxyheptane/*1,1-Dietoksiheptan*	18.26	–	–	0.1
1,1-Diethoxyoctane/*1,1-Dietoksioktan*	19.31	0.2	–	0.3
1,1-Diethoxynonane/*1,1-Dietoksinonan*	23.68	0.3	0.7	0.5
1,1-Diethoxydecane/*1,1-Dietoksidekan*	27.86	0.3	0.1	0.2
1,1-Diethoxytridecane/*1,1-Dietoksitridekan*	39.30	0.1	0.2	0.2
1,1-Diethoxytetradecane/*1,1-Dietoksitetradekan*	42.76	0.1	0.2	0.2
1,1-Diethoxyhexadecane/*1,1-Dietoksiheksadekan*	49.16	0.1	–	0.2
Esters/*Estri* (30)		**15.7**	**22.7**	**11.4**
Ethyl hexanoate/*Etilheksanoat*	7.55	0.2	0.1	0.5
Ethyl (3E)-hexenoate/*Etil-(3E)-heksenoat*	7.67	0.3	–	0.3
Ethyl 2-furoate/*Etil-2-furoat*	9.50	0.2	–	0.1
Methyl octanoate/*Metiloktanoat*	12.25	0.1	–	–
Ethyl benzoate/*Etilbenzoat*	14.23	0.2	0.1	0.4
Ethyl octanoate/*Etiloktanoat*	15.37	0.2	0.1	0.2
2-Phenylethyl acetate/*2-Feniletilacetat*	18.00	0.1	–	–
Ethyl nonanoate/*Etilnonanoat*	19.83	0.1	–	–
Ethyl decanoate/*Etildekanoat*	24.18	–	0.2	0.1
3-Methylbutyl octanoate/*3-Metilbutiloktanoat*	26.06	0.2	0.2	–
Ethyl cinnamate/*Etilcinamat*	27.14	0.1	–	–
Methyl 10-oxodecanoate/*Metil-10-oksodekanoat*	30.08	0.1	–	–
Methyl 10-oxodecanoate/*Metil-10-oksodekanoat*	30.36	0.1	–	0.1
Ethyl dodecanoate/*Etildodekanoat*	32.45	0.5	1.0	0.3
Methyl 11-oxo-9-undecenoate (isomer)/ *Metil-11-oxo-9-undecenoat (izomer)*	36.39	0.2	–	–
Methyl 11-oxo-9-undecenoate (isomer)/ *Metil-11-oxo-9-undecenoat (izomer)*	36.62	–	0.7	–
Ethyl tetradecanoate/*Etiltetradecenoat*	39.94	0.4	0.4	0.3
Ethyl tetradecenoate (isomer)/*Etiltetradecenoat (izomer)*	40.14	0.1	–	–
Ethyl tetradecenoate (isomer)/*Etiltetradecenoat (izomer)*	40.61	0.5	–	–
Isopropyl myristate/*Izopropilmiristat*	41.06	0.1	–	0.1

Ethyl hexadecenoate (isomer)/*Etilheksadecenoat (izomer)*	46.04	0.3	0.4	0.3
Ethyl hexadecenoate (isomer)/*Etilheksadecenoat (izomer)*	46.58	0.5	0.5	0.4
Ethyl hexadecanoate/*Etilheksadekanoat*	46.76	1.8	2.8	1.4
Ethyl hexadecadienoate (isomer)/*Etilheksadekadienoat (izomer)*	48.30	0.2	0.1	–
Ethyl hexadecadienoate (isomer)/*Etilheksadekadienoat (izomer)*	48.72	0.1	–	–
Ethyl hexadecadienoate (isomer)/*Etilheksadekadienoat (izomer)*	48.80	0.1	0.1	–
Ethyl hexadecadienoate (isomer)/*Etilheksadekadienoat (izomer)*	48.95	–	0.1	–
Ethyl linoleate/*Etillinoleat*	51.96	1.4	2.1	1.5
Ethyl oleate (isomer)/*Etiloleat (izomer)*	52.15	7.5	13.8	5.3
Ethyl octadecanoate/*Etiloktadekanoat*	52.94	0.1	–	0.1
Acids/*Kiseline* (4)		**0.9**	**–**	**–**
Decanoic acid/*Dekanska kiselina*	24.01	0.2	–	–
Tetradecanoic acid/*Tetradekanska kiselina*	38.83	0.3	–	–
Hexadecenoic acid/*Heksadecenska kiselina*	44.09	0.2	–	–
Palmitoleic acid/*Palmitooleinska kiselina*	45.00	0.2	–	–
Lactones/*Laktoni* (3)		**1.3**	**0.1**	**0.3**
5-Ethyl-2(5H)-furanone/*5-Etil-2(5H)-furanon*	6.46	0.4	–	–
δ-Decalactone/*δ-Dekalakton*	28.40	0.4	–	0.2
γ-Dodecalactone/*γ-Dodekalakton*	35.68	0.5	0.1	0.1
Others/*Ostalo* (3)		**0.6**	**0.4**	**0.8**
10,10-Dimethyl-4-acetyl-tricyclo[5.2.1.0(1,5)]decane/ 10,10-Dimetil-4-acetil-triciklo[5.2.1.0(1,5)]dekan	29.26	0.1	–	0.1
5,6,7,7a-Tetrahydro-4,4-7a-trimethyl-2-(4H)- benzofuranone/ 5,6,7,7a-Tetrahidro-4,4-7a-trimetil-2-(4H)- benzofuranon	29.77	0.5	0.4	0.6
Heneicosane/Heneikozan	50.15	–	–	0.1
Not identified compounds/*Neidentifikovana jedinjenja* (25)		**8.6**	**8.4**	**6.5**
NI/*NI*	7.35	–	–	0.2
NI/*NI*	7.84	0.6	0.6	0.5
NI/*NI*	8.15	0.3	–	0.1
NI/*NI*	15.95	0.7	0.7	0.6
NI/*NI*	20.66	0.1	–	–
NI/*NI*	22.22	0.1	–	–
NI/*NI*	22.37	0.1	0.1	0.2
NI/*NI*	22.81	–	0.1	–
NI/*NI*	24.40	0.7	0.3	0.7
NI/*NI*	24.62	1.0	–	–
NI/*NI*	24.65	–	–	0.7
NI/*NI*	25.70	1.0	0.2	0.1
NI/*NI*	25.92	0.2	–	–
NI/*NI*	26.15	–	–	0.5
NI/*NI*	30.60	–	–	0.2
NI/*NI*	30.87	0.2	0.3	0.2
NI/*NI*	31.03	0.2	0.5	0.2
NI/*NI*	31.16	0.3	–	0.1
NI/*NI*	31.53	1.2	–	–
NI/*NI*	31.61	0.1	1.7	1.5
NI/*NI*	31.85	0.1	0.4	0.1
NI/*NI*	32.85	0.3	1.5	0.2
NI/*NI*	33.07	0.3	–	–
NI/*NI*	34.44	0.4	0.9	0.1
NI/*NI*	34.61	0.7	1.1	0.3
Total/*Ukupno* (134)		**97.8**	**97.7**	**99.0**

*RT – retention times/*retenciona vremena*; **WG – 'Willamette' Geist/*Geist od sorte Willamette*; MG – 'Meeker' Geist/*Geist od sorte Meeker*; TG – 'Tulameen' Geist/ *Geist od sorte Tulameen*; NI – not identified compounds/*neidentifikovana jedinjenja*;

Bauer-Christoph, 2007), which explains the appearance of these significant differences in the composition of two types of spirit drinks made of raspberry. In other words, alcoholic fermentation is one of the basic steps in the production of fruit spirits, while in the production of Geist, the fruits are only macerated in ethanol without alcoholic fermentation. This implies that the aromatic complex of raspberry Geist is dominated by ingredients that come from fruits, which numerous authors (Klesk et al., 2004; Aprea et al., 2009; Aprea et al., 2015; Leposavić et al., 2022) have identified in the fruits of different cultivars of raspberries. These aromatic components of raspberry fruits are transferred to distillate through maceration and distillation. The results of the experiment found that monovarietal Geists contain total C13 norisoprenoids (40.5–44.5%), terpenoids (5.1%–6.6%), sesquiterpenoids (0.1%–0.7%), ketones (0.3–1.2%), and lactones (0.1–1.3%). Also, other classes of chemical compounds were present in Geists in the following ranges: esters (11.4–22.7%), aldehydes (13.4–21.5%), alcohols (0.5–1.0%), and acids (0.9% in WG, while in MG and TG they were not found). Interestingly, numerous acetals (e.g., 1,1-diethoxyoctane, 1,1-diethoxynonane, 1,1-diethoxydecane, 1,1-diethoxytetradecane, etc.) were also present in the obtained raspberry Geists. Acetals are not found in raspberry fruits (Aprea, 2015). They are formed during distillation (Nykänen & Nykänen, 1991) by the reaction of aldehydes (in the case of Geist – aldehydes originating from fruits, such as octanal, nonanal, decanal, tetradecanal, etc.) and the ethanol used for maceration. The amount of unidentified compounds (NI) in the experimentally produced Geists was 6.5–8.6%. Aromatic profiles of monovarietal Geists, based on the main classes of volatile compounds, are shown in Graph 1. The results showed that WG was characterized by the highest contents of total ketones, lactones, and acids, MG by the content of total esters, and TG by the content of total sesquiterpenoids, while the total contents of other classes of chemical compounds were quite uniform.

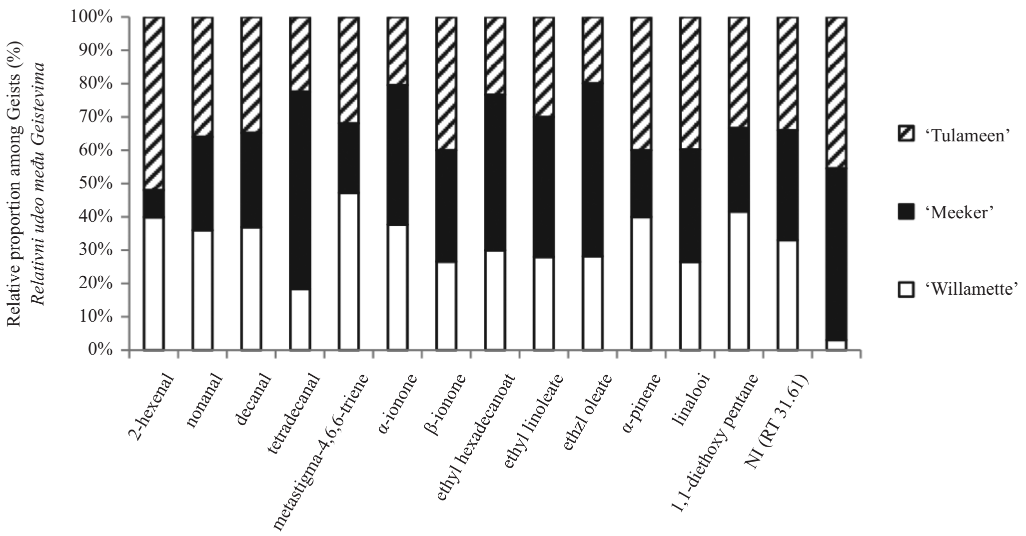
60 compounds were common to all three monovarietal Geists (WG, MG, and TG), of which 7 belonged to the class of terpenoids, 1 to sesquiterpenoids, 8 to C13 norisoprenoids, 2 to ketones, 8 to aldehydes, 10 to esters, 2 to alcohols, 8 to acetals, and 1 to lactones, as well as 1 compound from the group of other compounds and 12 unidentified compounds (NI). Among these compounds, 15 were represented in significant



Graph 1. Aromatic profiles of monovarietal raspberry Geists based on the volatile compounds classes
Grafikon 1. Aromatični profili monosortnih Geisteva od maline bazirani na klasama isparljivih jedinjenja

amounts in all three monovarietal Geists, and they practically constituted the basic aromatic skeleton of the Geists. These were the following compounds: α-pinene, linalool, α-terpineol, metastigma-4,6,8-triene (isomer), α-ionone, (E)-β-ionone, 2-hexenal, nonanal, decanal, tetradecanal, ethyl hexadecanoate, ethyl linoleate, ethyl oleate (isomer), 1,1-diethoxypentane, and NI (RT 31.61). Their relative shares in monovarietal Geists are shown in Graph 2. A similar conclusion was reached by Christoph & Bauer-Christoph (2007), who found that linalool, α-terpineol, α-ionone, β-ionone, benzyl alcohol, γ-lactones, and cis-3-hexenol significantly influenced the aroma of raspberry Geist. When considering the mentioned 15 compounds, it is interesting to note that, in addition to being present in high concentrations, they generally have low odor thresholds (OT), which results in their significant influence on the aroma of Geist. According to Zanghelini et al. (2024), their odor thresholds (determined in an ethanol:water matrix with about 40 vol%) are usually lower than 1 mg l^{-1} (from 0.0013 mg l^{-1} for (E)-β-ionones, i.e., 0.0018 for α-ionones, up to 0.87 mg l^{-1} for ethyl oleate). α-Terpineol has an OT of 1 mg l^{-1}, and the highest OT in this group of compounds common to all monovariety Geists has ethyl hexadecanoate (39.3 mg l^{-1}). Based on the aroma description of these compounds (given on the website www.thegoodscentscompany.com), it can be seen that only 3 compounds (α-ionone, (E)-β-ionone, and metastigma-4,6,8-triene) have the characteristics that are responsible for the raspberry-like aroma of Geist-type raspberry spirit drink. The aroma characteristics of the other most abundant ingredients are described as: α-pinene (woody, pine, camphoreous), linalool (floral, citrus), α-terpineol (terpenic, citrus), 2-hexenal (green, fruity), nonanal (aldehydic, orange peel), decanal (aldehydic, waxy, citrus, orange peel), tetradecanal (fatty, waxy), ethyl hexadecanoate (waxy, balsamic), ethyl linoleate (fatty, fruity, oily), ethyl oleate (fatty, oily, waxy), and 1,1-diethoxypentane (fruity).

In addition to the 60 ingredients common to all three Geists, there were also ingredients that were characteristic of only two Geists, and even those ingredients that were specific to only one monovarietal Geist. For example, 6 volatile aromatic compounds from different classes were found in WG and MG [2 C13 norisoprenoids – ionene, 4-oxo-β-ionone; 1 aldehyde – heptanal; 3 esters – 3-methylbutyl octanoate, ethyl hexadecadienoate (2 isomers)]; they were common to these two monovarietal Geists, but were not present in TG. 21 compounds were found in WG and TG, which MG did not contain. Also, MG and TG contained only 5 common compounds that were not found in WG.



Graph 2. Relative proportion of 15 volatile compounds in raspberry Geists obtained from different raspberry cultivars
Grafikon 2. Relativni udeli 15 isparljivih jedinjenja u Geistevima maline dobijenim od tri različite sorte maline

For the characterization of aromatic profiles, the presence of certain aromatic substances that are specific only for a certain monovarietal Geist is also important. Thus, WG contained as many as 25 compounds (1 tepenoid, 2 C13 norisoprenoids, 1 ketone, 9 esters, 4 acids, 1 acetal, 1 lactone, and 6 NI compounds) that were not found in MG and TG. In MG, 5 compounds (from different chemical classes) characteristic only for this raspberry Geist were found, while 12 compounds were found in TG that did not contain the other two monovarietal Geists.

It was observed that various aromatic profiles of varietal Geists affected the existence of fine differences in sensory characteristics of the products. All monovarietal Geists had a characteristic raspberry flavor. However, WG had an extra creamy note, MG had waxy, piney, terpenic character, while TG was very fruity and most resembled raspberries.

When considering the quality of the aroma of monovarietal raspberry Geists, one should take into account the fact that only one-year results are presented. These findings should serve as a basis for further research, especially if it is taken into account that the contents of individual aromatic volatile substances of raspberries can differ significantly depending on the variety, locality, and, especially, the year of harvest (Moore et al., 2002) that can cause the aromatic profile of monovarietal Geist to vary.

Conclusion

A total of 134 volatile compounds were quantified in three monovarietal raspberry Geists, produced from the three cultivars (‘Willamette’, ‘Meeker’, and ‘Tulameen’) most commonly grown in Serbia, which were classified into different classes of chemical compounds: esters (30), aldehydes (17), C13-norisoprenoids (17), acetals (12), terpenoids (11), ketones (6), alcohols (4), acids (4), lactones (3), and sesquiterpenoids (2). Also, 3 compounds from the group of others were quantified, as well as 25 unidentified (NI) compounds. Since there is no alcoholic fermentation in the production of Geist but only the maceration of the fruits in ethanol, most of these compounds originated from raspberry fruits. Sixty compounds were common to all three monovarietal Geists, while some compounds were characteristic of only two Geists, and some of them were exclusively in the composition of only one of the experimentally produced monovarietal Geists. The fine aroma of these spirit drinks, which resemble raspberries, originates from the characteristic components present among the 15 components found in them in significant amounts, such as metastigma-4,6,8-trienes (1.5–3.4%), α-ionone (8.4–17.2%), and (E)-β-ionone (18.0–27.1%).

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Aromatični profili monosortnih Geisteva od maline

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Rezime

Zbog izražene specifične i fine arome, maline su interesantna sirovina za proizvodnju alkoholnih pića. Postoje 4 vrste jakih alkoholnih pića od maline (liker, rakija, jako alkoholno piće dobijeno maceracijom i destilacijom, i Geist), koji se dobijaju na različite načine. Važan razlog za proizvodnju Geista od maline je zasnovan na činjenici da se plodovi maline odlikuju niskim sadržajem šećera, pa se njihovom preradom, koja uključuje alkoholnu fermentaciju, ne mogu dobiti visoki prinosi etanola, odnosno destilata. Pored toga, sveže maline često imaju i izuzetno visoku cenu, što ih čini skupom sirovinom za proizvodnju rakije koja podrazumeva i alkoholnu fermentaciju plodova. Međutim, zbog intenzivne i fine arome jakih pića od maline, koja postaju sve interesantnija modernim potrošačima, proizvođači se često odlučuju da, uzimajući u obzir i ekonomičnost prerade, proizvedu malinov Geist, za koji je potrebno znatno manje sirovine nego za proizvodnju rakije od maline. Tehnološki postupak proizvodnje Geista obuhvata samo maceraciju plodova, pa zatim destilaciju macerata, pri čemu se dobija destilat fine i izražene arome. S obzirom da u proizvodnji Geisteva nema alkoholne fermentacije sirovine, koja u značajnoj meri utiče na sastav finalnog proizvoda, presudni značaj za aromu Geista ima izbor sirovine, odnosno sorte maline. Cilj rada je bio da se utvrde aromatični profili Geisteva od maline, proizvedenih od sorata koje se najčešće gaje u Srbiji (Willamette, Meeker i Tulameen), u cilju karakterizacije, odnosno određivanja kvaliteta i autentičnosti ovih jakih alkoholnih pića.

Izmuljani plodovi tri ispitivane sorte maline su macerirani u rafinisanom etanolu, na sobnoj temperaturi, u toku jednog dana. Za svaku sortu izvršene su tri posebne maceracije. Macerati (zajedno sa plodovima) su zatim destilisani u pilot-scale alambiku tradicionalne konstrukcije, izrađenom od bakra, pri čemu su dobijeni destilati sa sadržajem etanola od 60 vol%. Po tri destilata od iste sorte maline su zatim mešana, i čuvana u staklenim balonima do analiza. Za analize, uzorci su razblaženi dejonizovanom vodom na 40 vol% etanola. Analiza aromatičnih materija monosortnih Geisteva od maline sprovedena je metodom gasne hromatografije spregnute sa plamen jonizacionim detektorom i masenim spektrometrom (GC-FID-MS).

U Geistevima od najzastupljenijih sorata maline u Srbiji, po prvi put su kvantifikovane aromatične materije koje presudno utiču na aromu ovih jakih pića. Ukupno je kvantifikovano 134 jedinjenja, od čega 112 u Geistu od sorte Willamette (WG), 76 u Geistu od sorte Meeker (MG) i 99 u Geistu od sorte Tulameen (TG). Posmatrano po klasama hemijskih jedinjenja, u Geistevima od maline nađeno je 30 estara, 17 aldehida, 17 C13-norizoprenoida, 12 acetala, 11 terpenoida, 6 ketona, 4 alkohola, 4 kiseline, 3 laktona, 2 seskviterpenoida, 3 jedinjenja iz ostalih klasa, kao i 25 neidentifikovanih (NI) jedinjenja. U eksperimentalno proizvedenim monosortnim Geistevima, kvantifikovano su bili najzastupljeniji C13 norizoprenoidi (40.5 – 44.5%), estri (11.4 – 22.7%), aldehidi (13.4 – 21.5%), i terpenoidi (5.1% – 6.6%). Ukupno 60 sastojaka je bilo zajedničko za sva tri monosortna Geista. Među ovim jedinjenjima, 15 je bilo zastupljeno u značajnoj količini u sva tri monosortna Geista, i praktično su činili osnovni aromatični skelet Geisteva. To su: α-pinen, linalol, α-terpineol, metastigma-4,6,8-trien, α-jonon, (E)-β-jonon, 2-heksenal, nonanal, dekanal, tetradekanal, etilheksadekanoat, etillinoleat, etiloleat, 1,1-dietoksipentan, NI (RT 31.61).

Ključne reči: Willamette, Meeker, Tulameen, jaka alkoholna pića, isparljiva jedinjenja, GC-FID-MS