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CHEMICAL COMPOSITION OF GRAPES AND WINE OF SMEDEREVKA VARIETY

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ABSTRACT

Examination of Smederevka cv was performed in area of Belgrade region. Analysis of grapes and wine was performed in laboratory of Faculty of Agriculture and Chemistry University of Belgrade. The aim of research was qualitative and quantitative determination of aromatic compounds in grapes and wine. Aromatic compounds in grapes and wine were detected by SPME GC/MS method. Presence of main herbaceous aromatic grape compounds as aldehydes, primarily n-hexanals and (E)-2-hexenals was detected. Terpenes (linalool, geraniol, α-terpineol), higher alcohols (isoamyl alcohol, 1-hexanol, 1-octen-3-ol, etc.), and ketones were also detected. In wine was determined presence of: esters, higher alcohols, terpenes, aldehydes, acids and ketones. Most of detected compounds belong to esters (ethyl acetate, ethyl butanoate, isoamyl acetate, ethyl octanoate, ethyl 9-octanoate, 2-methylbutyl octanoate, ethyl palmitate, etc.) which form fruit aromas (apple, banana, pear, almond, pineapple).

Key words: Smederevka, chemical composition, grapes, wine, aroma.

INTRODUCTION

Smederevka belongs to the *Proles pontica* ecological-geographical group. It is variety from the Balkan region, which is grown in Bulgaria, Russian Federation, Moldova, North Macedonia, Greece and Turkey. In Serbia, it is present in all vineyard areas (Žunić & Garić, 2010). Considering its growing area, it is found under many synonyms: Dimyat (Bulgaria), Dimiat (Romania), Galan (Russian Federation, Ukraine, Moldova), Szemendriai zold (Hungary), Belina krupna (Serbia). The first time it was mentioned in professional written sources in 1855, when the Austrian ampelographer Trumer published a systematic classification in which "Weiser Szemendrianer" (in German: white Smederevka) is mentioned as a variety of grapevine widespread in Hungary, and in 1876 he mentioned it and Hermann Goethe as the variety Bela Smederevka, which is widespread in Hungary and Serbia. Bearing in mind the multitude of synonyms of this variety, the said synonym is related to name of variety described by Pliny the Elder in a book from the 1st century AD. Characteristics of description from that part are close to ampelographic description of Smederevka variety. Considering the adaptation of this cosmopolitan Balkan variety to the regions of Serbia, Greece, Minor Asia, Bulgaria, North Macedonia, it can be assumed that it is a very archaic variety.

Smederevka is a variety for production of table and quality wines (Zirojević, 1983). Grape juice (must) is with out color, with a neutral taste and weakly expressed aromas, while wine is typically varietal with mildly pronounced herbal, floral tones and fruit aromas.

According to the origin, aroma of grapes and wine can be: primary (original or varietal), secondary-created during primary processing (grape crushing, enzyme activity), fermentative-created during alcoholic fermentation and the aroma of storage or lager

bouquet-created during wine aging. The total content of aromatic substances in wine ranges from 0.8 to 1.2 g/l, with 50% of higher alcohols that are produced during alcoholic fermentation. The odor detection of various aromatic substances ranges between 10^{-4} and 10^{-12} g/l (Rusjan, 2010; Pržić, 2014).

Formation of the primary wine aroma begins in vineyard under the influence of soil, climate, ampelotechnical measures and grape variety (Nakalamić & Marković, 2009; Marković, 2012; Radivojević & Marković, 2020). Characteristic compounds for primary aroma are aldehydes, terpene compounds, norisoprenoids and methoxypyrazines. The main fermentative aromas come from higher alcohols and esters (Molina et al., 2007).

Over 800 aromatic compounds have been detected in grapes and wine, which are 30-40 the most aromatically active. These compounds are found in their free-volatile form and non-volatile form where they are bound to sugars. The most important aromatic compounds are found in form of aglycones and are belongs to the group of terpenes, higher alcohols, benzene derivatives, C13-norisoprenoids, esters and volatile phenols (Winterhalter et al., 1990; Ribereau-Gayon et al., 2006).

MATERIALS AND METHODS

The research was carried out on grapes and wine sample of Smederevka variety sampled from Belgrade region, Grocka vineyard-"Janko" winery. The aim of this paper is to determine presence of different groups of compounds of aromatic complex in grapes and produced wine from Smederevka variety.

Aromatic complex compounds in grapes and wine were detected by SPME GC-MS method. The samples were prepared using microextraction on solid phase and using polydimethylsiloxane (PDMS) as a sorbent. An Agilent 6890 Network GC system gas chromatograph connected to an Agilent 5973 MSD selective mass detector was used for GC/MS analysis. The separation was performed on an Agilent 19091S-433 HP-5MS capillary column, 30 m long, 0.25 mm internal diameter, and 0.25 μm film thickness. Helium was used as carrier gas with a flow rate of 1 ml/min measured at 210°C. The column temperature was linearly programmed from 60°C to 285°C and increased by 4.3°C/min. Mass measurement was performed in the range of 40-250 Daltons, with 11.47 scans per minute. The resulting mass spectra were compared with Wiley and NIST library spectra. The relative shares (in %) of the identified components were calculated based on the peak areas in the gas chromatogram, where 1-chlorodecane was added at a concentration of 4ppm as an internal standard due to the quantification of other compounds.

RESULTS AND DISCUSSION

Grape analysis (GC/MS analysis) detected primary aroma compounds of Smederevka feom which 35 compounds belonging to alcohols, aldehydes, acids, terpenes and ketones.

Two aldehydes had the largest share in the varietal aroma of Smederevka grape: (E)-2-hexenal (41.15%), which gives a green-fruity aroma and n-hexanal (29.13%), which forms herbaceous, sometimes bitter aromas. Both compounds (n-hexanal and (E)-2-hexenal) belong to C6 aldehyde group and are typical represent of herbaceous aroma. Compounds that are represent of citrus and other fruit aromas (n-heptanal, 1-pentanol, 2-heptenal, (E,E)-2.4-heptadienal, *trans*-2-octenal, *cis*-linalool oxide) were detected in minimum concentration. Unlike them, compounds that give pronounced herbal tones ((Z)-2-hexen-1-ol, 1-hexanol) were detected far above the detection threshold. The compounds with floral aromas Smederevka grape are: 1-octanol, phenethyl alcohol, *cis*-linalool oxide (furanoid), linalool (it was detected far above the detection threshold), linalool oxide (pyranoid), α-terpineol. Geraniol is represent of rose aroma and it was detected in a high enough concentration that it can also be find in wine. Also, above the threshold of sensitivity, compounds that give the

coffee and cocoa aroma (n-pentanal) and almond aroma (benzaldehyde) were detected. Also free forms of monoterpenes, geraniol, α-terpineol, linalool oxide and linalool were detected. Monoterpenes are used for varietal characterization of wine, they do not change during alcoholic fermentation and they do not change under the influence of yeast metabolism.

Table 1. Aromatic compounds of Smederevka grapes

Compound	Aroma description	Detection-minimum µg/ml	c (ppm)	Rel. %	Group of compounds
Isoamyl alcohol	ripe fruit	0.03	0.057	0.1	Alcohols
1-pentanol	marzipan, fruitiness	/	0.269	0.45	Alcohols
(E)-2-Penten-1-ol	/	/	0.069	0.12	Alcohols
(Z)-2-hexene-1-ol	herbal tones	/	0.995	1.68	Alcohols
1-hexanol	herbal tones, flowers	0.0008	5.558	9.4	Alcohols
1-octane-3-ol	mushrooms	0.02	0.297	0.5	Alcohols
(S)-3-etil-4-metil pentanol	/	/	0.069	0.12	Alcohols
2-etil-1-hexanol	herbal and flower tones, citrus	0.008	0.387	0.65	Alcohols
Benzyl alcohol	smoked, fried	0.00062	0.131	0.22	Alcohols
(Z)-2-octane-1-ol	/	/	0.103	0.17	Alcohols
1-octanol	roses smell, citrus	/	0.05	0.08	Alcohols
Phenetyl alcohol	roses smell, honey	/	0.186	0.32	Alcohols
cis-linalol oxide	flower and fruit aroma	0.1	0.1	0.17	Terpenes
Linalol	roses smell, citrus	0.025	0.415	0.7	Terpenes
Camphor	menthol	/	0.027	0.05	Terpenes
Terpinen-4-ol	nutmeg	/	0.046	0.08	Terpenes
α-terpineol	white flowers	0.4-0.5	0.151	0.26	Terpenes
Geraniol	roses smell, citrus	0.03	0.036	0.06	Terpenes
Geranyl aceton	sweet aroma, pear	/	0.017	0.03	Terpenes
2,2 dimethyl-propane	pungent smell	8.1	0.039	0.07	Acids
Hexanoic acid	rancid, cheese smell	0.42	4.084	6.91	Acids
trans-2-hexanoic acid	raspberry, strawberry, aple	/	0.607	1.03	Acids
Geranic acid	bitter orange	/	0.049	0.08	Acids
n-pentanal	coffee, cocoa, fruit	/	0.291	0.49	Aldehydes
n-hexanal	green aroma, bitter	/	17.227	29.13	Aldehydes
(E)-2-hexenal	green and fruit	/	24.332	41.15	Aldehydes
n-heptanal	Citrus and green	/	0.025	0.04	Aldehydes
2-heptenal	fruit and green	/	0.374	0.63	Aldehydes
Benzaldehyde	almond	0.0002	0.077	0.13	Aldehydes
(E,E)-2.4-heptadienal	orange and tangerine	/	0.032	0.05	Aldehydes
Benzeneacetaldehyde	/	/	1.183	2	Aldehydes
trans-2-octanal	tangerine	/	0.083	0.14	Aldehydes
3-hidroxy-2-butanon	/	/	0.016	0.03	Ketones
6-methyl-5-hepten-2-on	/	/	0.073	0.12	Ketones

A large number of domestic and foreign authors (Downey et al., 2003; Mathieu et al., 2005; Lenk et al., 2007; Jackson, 2014; Marković et al., 2015; Pržić, 2015) state that in grapes and wine of white wine varieties have been identified about 70 monoterpenes, which represent floral aromas with a fragrant note of rose, and the most important representatives are: geraniol, linalool, α-terpineol, nerol and citronellol. From it linalool and citronellol have the most intense smell (Ribéreau-Gayon et al., 2006).

In addition to floral, fruity and chocolate tones, analysis also revealed presence of hexanoic acid, which gives a rancid and cheese smell, then, benzyl alcohol, which gives a smoky, fried smell, and 2,2 dimethyl-propanoic acid, whit sharp smell.

According to Rusjan (2010), the compounds concentration in wine determines aroma that is felt during sensory assessment. At lower concentrations, floral, light and gentle tones are detected, with increasing concentration, fruity and spicy tones.

In table 2 are presented aromatic complex compounds of Smederevka wine. By chemical analysis of wine it is founded presence of acids, higher alcohols, terpenes, aldehydes, esters and ketones.

Table 2. Aromatic compounds of Smederevka wines

Compound	**Aroma description**	**Rel. %**	**Group of compounds**
Octane acid	cheese and sweet smell	1.66	Acids
n-decan acid	wood smell, dry	0.31	Acids
2-methylbutil decan acid	rancid	0.03	Acids
Isoamyl alcohol	ripen fruit	7.08	Higer alcoholes
n-hexanol	fruit, sweet, green flower	0.18	Higer alcoholes
Octanol	roses and citrus smell	0.01	Higer alcoholes
Phenetyl alcohol	roses and honey	1.52	Higer alcoholes
Mircen	green aroma	0.04	Terpenes
Cimen	citrus, lemon	0	Terpenes
Limonene	orange	0.06	Terpenes
trans-Ocimen	green and sweet aroma	0.02	Terpenes
Isoterpinolen	/	0.02	Terpenes
Linalol	roses, lavanda, citrus	0.22	Terpenes
α-terpineol	flower and citrus aroma	0.05	Terpenes
Damascenone	peach, aple and pear	0.05	Terpenes
Dodecanal	flower, green and almond	0.04	Aldehydes
Ethyl acetate	fruit, ananas and pear	0.77	Esters
Ethyl butanoat	sweet fruit, banana, aple	0.09	Esters
Isoamyl acetate	fruit aroma, banana, pear	3.53	Esters
Ethyl hexanoate	aple and almond	3.75	Esters
Hexyl acetate	fruit, aple, pear	1.03	Esters
Ethyl-2-hexanoate	fruit aroma, ananas	0.01	Esters
Ethyl octanoate	ripen fruit, sweet, pear	29.08	Esters
Isoamyl hexanoat	fruit aroma	0.04	Esters
β-phenyl ethyl acetate	flower smel, honey aroma	2.31	Esters
Ethyl nonaoate	Aple and banana	0.04	Esters
Isobuthyl octanoat	fruit aromas	0.01	Esters
Ethyl-9-decenoat	fruit aromas	0.44	Esters
Ethyl decanoat	fruit and grape aroma	42.23	Esters
2-methylbutyl octanoate	aple and ananas	0.05	Esters
Ethyl dodecanoatae	flower and honey	3.62	Esters
Isopenthyl decanoate	/	0.13	Esters
Ethyl tetradecanoate	flower and honey	0.24	Esters
Isopropyl miristat	/	0.11	Esters
Ethyl palmitate	sligthly waxy aromas	0.53	Esters
Nerol oxide	/	0.01	Ketones

Of higher alcohols with highest degree of present (7.08%) in tested wine, isoamyl alcohol stands out. The mentioned higher alcohol is represent of fruity aroma in wine. Phenethyl alcohol, which is present in wine at 1.52%, is represent of floral aroma in wine, primarily roses. Hexanol is a higher alcohol that passes unchanged from grapes to wine and is represent floral aromas of green flowers. This also applies to octanol, which is present in a very small percentage and forms rose aroma.

Terpenes were represented in a small percentage in wine. All identified terpenes are represented by less than 1%. Representatives of floral aromas which are detected in wine are: linalool (aroma of rose, lavender) and α-terpineol (white flowers smell). Also, terpenes that represent fruity aromas were detected: cymene, limonene and damascenone. Myrcene and trans-ocimene were detected as representatives of herbaceous aroma in wine.

Esters are tgroup with the largest number of individually detected aromatic compounds in wine. With 20 detected compounds, they make up more than half of detected aromatic compounds. Esters are important in aroma formation for less aromatic varieties, and fruity character of esters is significant for young white wines aroma (Ferreira, et al., 1995).

Ethyl esters represent pleasant fruity aroma, which originated from ethanol and unsaturated fatty or organic acids (Jackson, 2014). The main representatives are ethyl hexanoate, ethyl octanoate and ethyl decanoate (Ferreira, 2010). Ethyl decanoate, as the represent of fruity aroma with grapes smell, is the most abundant aromatic compound (42.23%). At second place in terms of representation is ethyl octanoate (29.08%), which forms ripe fruit aroma, with a dominant pear tone. Ethyl hexanoate is the third most abundant (3.75%) and is also represent fruity aromas, but with apples and almonds smell. A slightly higher percentage is represented by isoamyl acetate (3.53%), which form bananas and pears aroma and hexyl acetate (1.03%), which form apples and pears aroma. Ethyl tetradecanoate (0.24%), ethyl dodecanoate (3.62%) and β-phenylethyl acetate (2.31%) are responsible for honey taste of floral aromas. A large number of esters did not exceed 1% presence, and they are mainly represent fruity aromas in wine. From aldehydes, only dodecanal (green fruit, almond) was detected, and of the ketones, neroloxide.

In wine are dominantly present three acids: octanoic acid (1.6%) which gives dryness to wine, n-decanoic acid (0.31%) which smells like wood and 2-methylbutyl ester of decanoic acid (0.03%) which is responsible for rancid aroma.

CONCLUSIONS

By analysis of aromatic composition of Smederevka grapes founded that aroma represents with the largest percent (41.15%) is aldehyde (E)-2-hexenal, which gives a green and fruity aroma. With a large relative percent (29.13%), aldehyde n-hexanal is also represented, which also gives an aroma with pronounced herbal tones. From group of alcohols, 1-hexanol with a large relative percent (9.4%) stood out, which gives herbaceous or green flowers aroma and (Z)-2-hexen-1-ol (1.68%) as a represent of herbal tones. From terpenes, linalool and geraniol are the dominant represent rose flower. Hexanoic acid is represented by 6.91% and is represent of cheese smell, among acids with a strong and sharp smell, the presence of trans-2-hexenoic acid stands out.

The chemical analysis of wine show presence of following groups of aromatic compounds: acids, higher alcohols, terpenes, aldehydes, esters and ketones. In wine, for the dominant fruit aromatic tones are responsible esters, especially ethyl octanoate and ethyl decanoate. Both compounds together make up over 70% of all detected compounds of the wine's aromatic complex.

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