

Aromatic profile of Macedonian and Bulgarian red wines from local variety Vranec and hybrid variety Kaylashki Rubin

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Abstract

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Introduction. The aim of the present study was to define the aromatic profile of Bulgarian and Macedonian red wines obtained from the local variety Vranec and the hybrid variety Kaylashki Rubin.

Materials and methods. Gas chromatographic (GC-MS) study to define the aromatic profile of red wines from the local variety Vranec (grown in the Republic of Macedonia) and the hybrid variety Kaylashki Rubin (grown in the Republic of Bulgaria) was conducted.

Results and discussion. 1-pentanol was dominated in the fraction of higher alcohols in both wines. Other aroma compounds identified were 1-propanol, 2-propanol, 1-butanol, 1-hexanol, and 3-methylthio -1-propanol. The wine of the Vranec variety showed greater complexity in terms of this fraction, as in it 3-hexen-1-ol was identified, which was not present in the wine of Kaylashki Rubin. High amount of the aromatic alcohol – phenylethanol – was identified in both wines. This compound had great importance for their floral aroma. The ester fraction of the two wines was diverse, represented by isopentyl acetate, ethyl caprylate, ethyl hexanoate, ethyl decanoate and diethyl malate. The Vranec wine showed greater ester complexity, as in it two more ester representatives were identified – ethyl-2-hydrobutyrate and 2-hydroxy-3-methyl-diethyl ester. In both wines, one fatty acid was identified – heptanoic acid, in very low concentrations. According to the panelist both wines were very harmonious in their own way and had their typical notes as expected for the both varieties. In overall, the descriptive analyses confirmed the components determined by the GC-MS and gave a clear view about the aroma profile of both varieties.

Conclusions. Both wines showed a diverse, balanced aromatic profile, each of which, based on the peculiarities of its volatile composition. Meanwhile, each wine had individual aromatic properties.

Introduction

The aromatic profile of the wines is a descriptor for their quality. It is determined by the presence, concentrations, ratio and distribution of specific volatile compounds.

Vranec is the main variety for the production of red wines in R. N. Macedonia. It is also widespread in Montenegro, Serbia, Croatia and Bosnia and Herzegovina. The variety was brought to R. Macedonia in the distant 1950 by prof. Dragan Nastev in the experimental vineyard of the Institute of Agriculture in Skopje (Nastev, 1985). Nowadays, the Vranec variety is one of the main red grapevine varieties used for the production of quality red wines in the Republic of Macedonia. It occupies the largest share of vineyards in the Republic. Ivanova et al. (2013) studied the volatile composition of Macedonian and Hungarian wines. In this study the team found a total amount of volatile compounds of $41.318 \pm 56.30 \mu\text{g}/\text{dm}^3$ in the red wine from the Vranec grapevine variety. The ester fraction of this wine had a total quantitative presence of $2631 \pm 21.90 \mu\text{g}/\text{dm}^3$. The team did not establish the presence of terpenes in the studied wine. Bogoeva et al. (2018) studied the influence of different oenological practices on the aromatic composition of wines from Vranec. They identified 63 aromatic compounds from different volatile groups: esters, alcohols, fatty acids, aldehydes, ketones and sulfur compounds.

Kaylashki Rubin variety is an interspecific hybrid obtained by crossing of (Pamid x Hybrid VI 2/15) x (Game noir x *Vitis amurensis*). It was created by the scientists of the Institute of Viticulture and Enology, Bulgaria in 2009 and was patented in 2010 (Ivanov, 2016). It is characterized by high resistance to low winter temperatures. In Bulgaria, the aromatic profile of wines from this variety have been studied, mainly by the GC-FID method or classical chemical analysis, which provides information on components, in larger quantities (mg/dm^3). A study (Dimitrov et al., 2018) on the aromatic profile of red wines of several varieties grown in the region of Central Northern Bulgaria found high total final concentrations of volatile compounds in red wine of the variety Kaylashki Rubin ($693.97 \text{ mg}/\text{dm}^3$). The study identified 4 higher alcohols, 5 esters, 1 aldehyde and 3 terpene alcohols in the wine of Kaylashki Rubin. Yoncheva et al. (2016) conducted a technological study of some varieties and clones of vines. The study also includes Kaylashki Rubin. It was concluded that the wines of Kaylashki Rubin are characterized by the highest concentration of total esters and aldehydes. Yoncheva et al. (2019) in a study on the chemical composition of Bulgarian wines of hybrid varieties found a total concentration of esters, aldehydes and higher alcohols in wines of Kaylashki Rubin respectively $228.80 \text{ mg}/\text{dm}^3$, $46.20 \text{ mg}/\text{dm}^3$ and $314.00 \text{ mg}/\text{dm}^3$. Dimitrov and Iliev (2021) studied the influence of different vine rootstocks on the volatile composition of wines from Kaylashki Rubin from three harvests (2017, 2018 and 2019). The team established a diverse volatile composition, represented mainly by 2-methyl-1-butanol, 3-methyl-1-butanol, 1-butanol, 1-hexanol, 4-methyl-2-pentanol, 1-propanol, 2-butanol (higher alcohols fraction), ethyl acetate (esters fraction), geraniol (terpenes fraction). The application of the GC-MS method in the present study provides a new information on the aromatic profile, identifying components of the aromatic composition in minor concentrations ($\mu\text{g}/\text{dm}^3$). This will enrich the scientific literature and provide new data on the potential of the variety to accumulate aromatic components in its wines, reflecting its qualities. Study was focused on identification and quantification of volatile compounds (quality wine descriptor) from the main aromatic groups, that were established in a lot of wine studies worldwide: esters, higher alcohols, aldehydes, terpenes, fatty acids (Bakharev et al., 2021; Itu et al., 2011; Kim et al., 2018; Manolache et al., 2018; Mateo et al., 2000; Meng et al., 2011; Nan et al., 2021; Rapp et al., 1986; Rusjan et al., 2008; Tardea, 2007; Tomasino et al., 2020; Yankov et al., 2000).

The aim of the present study was to define the aromatic profile of Bulgarian and Macedonian red wines obtained from the local variety Vranec and the hybrid variety Kaylashki Rubin. The significance of the purpose is based on the fact that the data obtained from the study will provide information on the characteristics of the qualities of regional wines (terroir influence) obtained from varieties with different genetic origin.

Materials and methods

Grapevine varieties

The study was conducted in 2017. The wines were obtained from two red grapevine varieties (Vranec and Kaylashki Rubin) from harvest 2016, different by their genetic origin and grown in two different locations – R. Macedonia and R. Bulgaria.

Climatic conditions of the area of cultivation

The vines of the Vranec variety used for this study were grown in the region of Veles. According to Nedelkovski (2017) this region is characterized by a typical continental climate with the following indicators: temperature sum during the vegetation period – 4626.5– 4942.6 °C; the average monthly temperature during the vegetation period is 18.1 °C; the min. temperature -12.9 °C and maximum temperature is 40.7 °C; duration of the vegetation period bud break to harvest 142–157 days; beginning of vegetation – 12.04 to 22.04; frequency of spring frosts up to 10%; annual precipitation amount – 355–663 mm/dm³.

The experimental vines of the Kaylashki Rubin variety were grown in the Experimental Base of Institute of Viticulture and Enology (IVE) – Pleven, Bulgaria. The region of the town of Pleven is characterized by a typical continental climate with the following indicators: temperature sum during the vegetation period – 3130–4003 °C; duration of the vegetation period – 190–210 days; duration of frost-free period – 178–223 days; beginning of vegetation – 02.04 to 14.04; frequency of spring frosts up to 20%; annual precipitation amount – 532–753 mm/dm³ (Katerov et al., 1990; Pandeliev et al., 2005).

Vinification

The Vranec grapes were harvested at technological grape maturity and processed in the experimental wine cellar of the Institute of Agriculture – Skopje. The production of the wines was carried out according to the classic scheme for production of red dry wines: Hand harvesting of the grapes → Crushing and destemming of the grapes → Adding 50 mg/dm³ SO₂ → Inoculation of wine yeast (*Saccharomyces cerevisiae*) → Fermentation for 12 days at temperature 22±3 °C → Raking → Wine filtration → Bottling → Storage.

The Kaylashki Rubin grapes were harvested after reaching of technological maturity, in the amount of 30 kg, and processed in the Experimental Wine Cellar of Institute of Viticulture and Enology – Pleven, in the conditions of microvinification, following the classic scheme for the red dry wines production: Crushing and destemming → Sulphitation (50 mg/kg SO₂) → Inoculation with pure culture dry yeasts *Saccharomyces cerevisiae* Siha Rubio Cru (EATON Begerow) –20 g/100 L → Fermentation (temperature of fermentation – 28 °C) → Separation from solids → Further sulphitation → Storage (Yankov, 1992).

Chemicals and reagents

For the extraction of volatile components in the wine samples, dichloromethane was used, purchased by Sigma Aldrich (USA); Reference standard diethyl succinate, 2-phenyl ethanol, ethyl hexanoate, 1-hexanol, 1-heptanol purchased by Merck (Germany); Isoamyl acetate, purchased from Aldrich Chemicals (USA); The 1-octanol used as an internal standard was purchased from Sigma Aldrich (USA).

Extraction procedure and gas chromatography (GC-MS) analysis

The volatile components were extracted by liquid-liquid extraction (Ivanova et al., 2012). We transfer 50 ml of the wine sample in 500 ml Erlenmeyer flask and add 50 ml of the extragent (dichloromethane), as internal standard 25 μ l 1-octanol was added. The Erlenmeyer flask was sealed and was placed on a magnetic stirrer for 1 hour. After one hour the mixture was centrifuged at 3000 rpm for 10 min. The separated dichloromethane phase was then evaporated under a stream of nitrogen until dryness. Then the evaporated sample was rehydrated with 100 μ l of dichloromethane and it was injected into the GC-MS. The gas chromatograph used was Varian 3900 (Middelburg, The Netherlands). The mass spectrometer was Varian Saturn 2100T (Middelburg, The Netherlands). Parameters of gas chromatographic determination were: injector temperature – 240 °C, MS source – 230 °C, MS quad from 150 °C and 280 °C transfer line. The initial temperature was 40 °C for 3 min and then rises to 180 °C at a level of 3 °C/min. The temperature then rose further to 260 °C at 20 °C/min and hold at 260 °C for 10 min. The carrier gas was He with flow rate 1.5 ml/min.

Sensory evaluation

The sensory evaluation of both wines was performed by the descriptive method described by Mario Ubini (2004). The wine panelists (4 experts in the field of enology) first had to degustate both wines and then purpose descriptors that will describe both the aroma and taste of the analyzed wines. Four panelists were involved in the analysis. According to them 11 descriptors were proposed to describe these wines: red fruits, black fruits, flower aromas, herbal aromas, acidity, astringency, structure, harmony, typicity, bitterness and body.

Statistical analysis

Statistical analysis of the analyzed parameters between the two wine samples was performed with the computer statistical program SPSS 14.0. For the comparison of the results Pater Samples Statistic of T-Test was performed with significant differences of 0.05.

Results and discussion

The data on the quantitative presence of volatile compounds are presented in Table 1. The results were statistically analyzed with the statistical tool T-test guided by the fact that we wanted to make a comparison of each aromatic component between the examined wines. According to the statistical test statistical proven differences were found for aroma components like 1-propanol, 1,5-hexadien-3-ol, 1-pentanol, 2-propanol, 1-hexanol, 2,3-butanediol, ethyl decanoate, diethyl succinate, and 3-(methylthio)-1-propanol. For the phenylethanol in all samples statistical differences was not proven.

Table 1
Identified volatile compounds in red wines of local variety Vranec and hybrid variety Kaylashki Rubin

Volatile compounds	Aromatic descriptor	Kaylashki Rubin, $\mu\text{g}/\text{dm}^3$	Vranec, $\mu\text{g}/\text{dm}^3$	T-Test	Sig.
1-Propanol		905.32 ± 5.66	700.96 ± 12.05	55.436	.000
1,5-hexadien-3-ol		9972.91 ± 74.91	4747.42 ± 59.59	590.592	.000
Isoamylacetate	Banana	105.33 ± 13.76	120.49 ± 9.41	-6.034	.026
1-Butanol	Medical, Alcohol	460.35 ± 14.65	452.08 ± 13.00	8.681	.013
1-Pentanol	Flowery	23519.08 ± 288.9	11968.72 ± 208.7	249.386	.000
ethyl hexanoate	Green apple, strawberry	178.38 ± 13.35	185.41 ± 14.00	-18.887	.003
2-Propanol		1078.90 ± 78.91	668.48 ± 30.35	14.639	.005
1-Hexanol	Green, Grassy	1076.30 ± 66.54	1300.63 ± 49.42	-22.693	.002
3-hexen-1-ol	Green, Flowery	ND	134.04 ± 15.65		
Ethyl caprylate	Pineapple, Pear, flowery	202.95 ± 14.42	233.48 ± 13.81	-86.703	.000
Ethyl -2-hydroxybutyrate		ND	124.16 ± 13.08		
2,3-Butanediol	Butter, Creamy	1152.06 ± 46.25	934.93 ± 26.19	18.748	.003
1-Octanol (IS)		1397.86 ± 30.25	1447.41 ± 39.33		
Ethyl decanoate	Vegetable, Anise	174.28 ± 25.19	45.65 ± 8.37	13.246	.006
Diethyl succinate	Fruity	7623.03 ± 52.97	1348.55 ± 50.55	4500.085	.000
3-(methylthio)-1-propanol	Boiled potatoes, rubber	1149.80 ± 59.91	749.63 ± 26.32	8.039	.015
2-phenyl ethyl acetate		ND	TRACES		
Vinyl butyrate		TRACES	ND		
Phenylethanol	Flower, pollen, perfume	17864.31 ± 155.00	20076.12 ± 88.02	-57.192	.000
Diethyl malate		55.00 ± 5.00	63.12 ± 6.12	-12.557	.006
Heptanoic acid		1209.76 ± 51.25	1297.00 ± 70.01	-8.055	.015
2-hydroxy-3-methyl-diethylester		ND	105.13 ± 8.05		
Ethyl palmate		ND	TRACES		
Ethyl cinnamate		ND	259.01 ± 11.22		

T-test with statistically significant difference ($p < 0.05$)

Identified alcohols

1-propanol is one of the main higher alcohols of the volatile wine fraction. In the wine of the local variety Vranec it was identified in an amount of $700.96 \pm 12.05 \mu\text{g}/\text{dm}^3$. In Kaylashki Rubin this representative was found in a higher concentration – $905.32 \pm 5.66 \mu\text{g}/\text{dm}^3$. The aromatic descriptor of 1-propanol is a flower bouquet and a ripe fruit. Characteristic of propanol is that it participates in transformational changes during the wine's aging, forming volatile esters with propionic, acetic and caprylic acids (Chobanova, 2012). A study of changes in the aromatic compounds of Cabernet Sauvignon red wines aged in stainless steel tanks (Meng et al., 2011) found a variation of this compound from $2554.87 \mu\text{g}/\text{dm}^3$ to $5091.44 \mu\text{g}/\text{dm}^3$. In the young wine (before the aging process) the team (Meng et al., 2011) found a concentration of this higher alcohol of $3058.80 \mu\text{g}/\text{dm}^3$. The presence of 1-propanol in the studied wines of Vranec and Kaylashki Rubin was significantly lower. This could be attributed to the characteristic features where the grapes were grown and harvested. Both varieties were grown in different geographical locations under different soil and climatic conditions.

The highest concentration of higher alcohols in the studied wines was found for the 1-pentanol. In the wine of the Vranec variety it was identified in an amount of $11968.72 \pm 208.70 \mu\text{g}/\text{dm}^3$, while in Kaylashki Rubin its concentration was almost twice as high – $23519.08 \pm 288.90 \mu\text{g}/\text{dm}^3$. Its threshold of aromatic perception (with a characteristic aroma of flowers) is $30.00 \mu\text{g}/\text{dm}^3$. In both wines it was found above this threshold, which was reflected in its special sensory expression. In a study on the volatile composition of Macedonian (Vranec, Merlot, Cabernet Sauvignon, Tamianka and Chardonnay) and Hungarian (Kefrankos and Tokaji) wines was found that in red wines 1-pentanol and 2-phenylethanol were the main components of the volatile fraction (Ivanova et al., 2013).

The data obtained in the present study correlate with the study of the above team. After 1-pentanol, 1,5-hexadien-3-ol was ranked by concentration. This compound was found in a higher amount in the wine of the Kaylashki Rubin variety ($9972.91 \pm 74.91 \mu\text{g}/\text{dm}^3$), compared to that of Vranec ($4747.42 \pm 59.59 \mu\text{g}/\text{dm}^3$).

3-hexen-1-ol was identified only in Vranec wine. It was available in an amount of $134.04 \pm 15.65 \mu\text{g}/\text{dm}^3$. A characteristic aromatic nuance that this compound imparts is green, grassy (Newcomb et al., 2010). However, its threshold of aromatic perception is higher ($400.00 \mu\text{g}/\text{dm}^3$) than its established concentration. This was reflected in the lack of aromatic expression of 3-hexen-1-ol in its identified amount in the red wine of Vranec.

2,3-butanediol is a compound – a product of yeast metabolism. Its concentration is highly dependent on the type of yeasts (Romano et al., 1998; Ng et al., 2012). It was identified in both wines studied. In the wine of Kaylashki Rubin it was present in an amount of $1152.06 \pm 46.25 \mu\text{g}/\text{dm}^3$, and in that of Vranec – $934.36 \pm 26.19 \mu\text{g}/\text{dm}^3$. A characteristic aroma that gives this compound is butter, creamy. In both wines it was identified above its threshold of aromatic perception ($120.00 \mu\text{g}/\text{dm}^3$), which significantly determined the participation of its influence on the wine aromatic profile.

Another major representative of the higher alcohols fraction was 2-propanol (isopropyl alcohol). In the wine of Kaylashki Rubin it was identified in a higher concentration ($1078.90 \pm 78.91 \mu\text{g}/\text{dm}^3$), compared to that found in Vranec ($668.48 \pm 30.35 \mu\text{g}/\text{dm}^3$).

1-butanol was found in very similar amounts in the two wines studied. Its concentration in Kaylashki Rubin was $460.35 \pm 14.65 \mu\text{g}/\text{dm}^3$, and in the red wine of Vranec it was contained in an amount of $452.08 \pm 13.00 \mu\text{g}/\text{dm}^3$. A study on the volatile fraction of ten wines from north-western Spain obtained from varieties from *Vitis vinifera* (Vilanova et al., 2013) found a variation of 1-butanol from $8.96 \pm 1.23 \mu\text{g}/\text{dm}^3$ (Riesling) to $76.98 \pm 9.13 \mu\text{g}/\text{dm}^3$

(Gewürztraminer). On the other hand, Meng et al. (2011) in a study of Cabernet Sauvignon wines aged in stainless steel tanks found the content of 1-butanol in young wine – $3058.80 \mu\text{g}/\text{dm}^3$. It could be seen that the concentration presence of 1-butanol varies between wines obtained from grapes grown in different geographical locations.

1-hexanol is a higher alcohol present in the volatile fraction of wine and imparting a characteristic grassy aroma (Abrasheva et al., 2008). It was identified in both studied wines, and in that of Vranec its quantity was higher ($1300.63 \pm 49.42 \mu\text{g}/\text{dm}^3$), in comparison with Kaylashki Rubin ($1076.30 \pm 66.54 \mu\text{g}/\text{dm}^3$). This component of the volatile fraction was also found in red wine from Cabernet Sauvignon ($4017.70 \mu\text{g}/\text{dm}^3$) from Xiangning County, China (Jiang et al., 2010). Another study (Tao et al., 2009) again on the volatile composition of Cabernet Sauvignon wine, Changli County region (China), identified it at a significantly higher concentration (average $17300.00 \mu\text{g}/\text{dm}^3$). 1-hexanol has been identified as a major component of the higher alcohols volatile fraction in the study of the aromatic profile at the aging process (6 and 12 months; respectively in concentrations varying quantitatively from $139.04 \pm 3.25 \mu\text{g}/\text{dm}^3$ – $529.77 \pm 0.39 \mu\text{g}/\text{dm}^3$ and from $183.79 \pm 0.22 \mu\text{g}/\text{dm}^3$ – $570.89 \pm 8.04 \mu\text{g}/\text{dm}^3$) of red wines from Cabernet Sauvignon, Fetească neagră, Pinot Noir and Merlot from different regions of Romania (Manolache et al., 2018).

An aromatic alcohol – phenylethanol – was identified in the wines of Vranec and Kaylashki Rubin. It was identified in high concentration presence in the aromatic matrix of the two wines. In the wine of Vranec it was found in a higher amount ($20076.12 \pm 88.02 \mu\text{g}/\text{dm}^3$), compared to that of Kaylashki Rubin ($17864.31 \pm 155.00 \mu\text{g}/\text{dm}^3$). The characteristic aroma that this alcohol gives is floral, in particular rose (Etievant, 1991). Our data on the content of 2-phenylethanol were in agreement with the data of Manolache et al. (2018), which found this alcohol in high quantities by the GC-MS study of 4 red wines from the varieties Cabernet Sauvignon, Fetească neagră, Pinot Noir and Merlot from regions of Romania. This alcohol also has been found to be dominant quantitatively in the study of the volatile fraction of Italian red wines from the Negroamaro and Primitivo varieties (Tufarriello et al., 2012; Capone et al., 2013). A study of the volatile composition of wine from two harvests of three varieties of *Vitis vinifera* grown in Spain (Vilanova et al., 2008) found a variation of phenylethanol on average for both harvests from $8321.20 \pm 5065.90 \mu\text{g}/\text{dm}^3$ to $10116.90 \pm 3323.40 \mu\text{g}/\text{dm}^3$. In Cabernet Sauvignon wines from China, phenylethanol was identified in an amount of $14504.80 \mu\text{g}/\text{dm}^3$ (Jiang et al., 2010). The data obtained in our study for phenylethanol correlated with the results in the cited studies.

Other higher alcohol identified in the two wines studied was 3-methylthiol-1-propanol. It was found in a higher concentration in the wine from Kaylashki Rubin ($1149.80 \pm 59.91 \mu\text{g}/\text{dm}^3$), compared to Vranec ($749.63 \pm 26.32 \mu\text{g}/\text{dm}^3$). 3-methylthiol-1-propanol has an aromatic perception threshold of $500.00 \mu\text{g}/\text{dm}^3$ and imparts a characteristic aroma of boiled potatoes. In both studied wines it was identified in concentrations above its threshold of aromatic perception.

Identified esters

Of the ester fraction, the highest quantitative presence in both wines was found for diethyl succinate ester. It gives a fruity aroma. It was found in a very high concentration in the wine of the Kaylashki Rubin variety ($7623.03 \pm 52.97 \mu\text{g}/\text{dm}^3$). It exceeded almost six times that found in Vranec ($1348.55 \pm 50.55 \mu\text{g}/\text{dm}^3$). According to Chobanova (2012), diethyl succinate is an important ester, the presence of which in wine is observed in the range of 20.00 – $400.00 \text{ mg}/\text{dm}^3$. The data in the present study confirmed the main presence of this ester in the two wines studied.

Isopentyl acetate was identified with a small quantitative difference between the two wines. In Vranec its amount was slightly higher ($120.49 \pm 9.41 \mu\text{g}/\text{dm}^3$), compared to Kaylashki Rubin ($105.33 \pm 13.76 \mu\text{g}/\text{dm}^3$). The ester is a major contributor to the fruity aroma of wines (Li et al., 2008), with its characteristic descriptor being the banana aroma (Vilanova et al., 2013). Data on the presence of isopentyl acetate in the wines of Vranec and Kaylashki Rubin were correlated with Vilanova et al. (2008), which identified it in Spanish red wine of the Seradelo variety in an average quantity for two harvests (2006 and 2007) of $301.00 \pm 225.80 \mu\text{g}/\text{dm}^3$. Our results for this ester were correlated with data of Ivanova et al. (2013), which established it in nine studied Hungarian and Macedonian wines, with concentrations ranging from $136.00 \pm 1.89 \mu\text{g}/\text{dm}^3$ to $1320.00 \pm 0.35 \mu\text{g}/\text{dm}^3$.

Ethyl caprylate was identified in close concentrations between the two wines. A slightly higher amount of this ester was found in Vranec wine ($233.48 \pm 13.81 \mu\text{g}/\text{dm}^3$) compared to Kaylashki Rubin ($202.95 \pm 14.42 \mu\text{g}/\text{dm}^3$). The ester gives a characteristic fruity aroma (pineapple and pear). Its threshold of aromatic perception is very low ($2.00 \mu\text{g}/\text{dm}^3$). In both wines it was identified in a concentration 100 times higher than the threshold, which determined its important influence on their aroma. This ester was identified in higher amounts ($5107.90 \mu\text{g}/\text{dm}^3$) in Cabernet Sauvignon wine from China (Jiang et al., 2010).

Ethyl hexanoate was identified in both wines studied. In the wine of Vranec it was present in an amount of $185.41 \pm 14.00 \mu\text{g}/\text{dm}^3$, and in that of Kaylashki Rubin it was present in a slightly lower concentration ($178.38 \pm 13.35 \mu\text{g}/\text{dm}^3$). This ester is also one of the main ones present in the wine aromatic matrix. It was also found in another study in wines from Merlot ($167.55 \pm 1.05 \mu\text{g}/\text{dm}^3$) and Cabernet Sauvignon ($195.42 \pm 8.72 \mu\text{g}/\text{dm}^3$) (Vilanova et al., 2013). Our data were correlated with those established by this team. A characteristic aroma that gives ethyl hexanoate is of green apple, fruity, strawberry (Tao et al., 2009). Our data also correlated with the research of Manolache et al., (2018), which also found this ester in red wines aged for the periods of 6 months ($86.44 \pm 5.38 \mu\text{g}/\text{dm}^3$ – $164.10 \pm 1.92 \mu\text{g}/\text{dm}^3$) and 12 months ($124.30 \pm 3.47 \mu\text{g}/\text{dm}^3$ – $434.53 \pm 6.82 \mu\text{g}/\text{dm}^3$).

Ethyl decanoate was found in a higher concentration in the wine of Kaylashki Rubin ($174.28 \pm 25.19 \mu\text{g}/\text{dm}^3$), compared to Vranec ($45.65 \pm 8.37 \mu\text{g}/\text{dm}^3$). This ester belongs to the group of fatty acid ethyl esters, which is one of the important for this fraction (Francis et al., 2005). A typical descriptor of this compound is vegetable aroma.

Ethyl-2-hydrobutyrate and ethyl cinnamate were identified only in Vranec red wine in concentrations of $124.16 \pm 13.08 \mu\text{g}/\text{dm}^3$ and $259.01 \pm 11.22 \mu\text{g}/\text{dm}^3$, respectively. They were absent in the aromatic matrix of Kaylashki Rubin.

Diethyl malate was identified in both wines studied. In the wine of Vranec it was present in a slightly higher concentration ($63.12 \pm 6.12 \mu\text{g}/\text{dm}^3$), compared to that of Kaylashki Rubin ($55.00 \pm 5.00 \mu\text{g}/\text{dm}^3$). This ester is also one of the main representatives of the fraction, normally present in wines in concentrations of 10.00 – $100.00 \text{ mg}/\text{dm}^3$ (Chobanova, 2012).

2-hydroxy-3-methyl-diethyl ester was identified only in Vranec wine ($105.13 \pm 8.05 \mu\text{g}/\text{dm}^3$).

Identified fatty acids

Fatty acids originate from yeasts and bacterial biosynthesis and have an important contribution to wine aroma (Etievant, 1991). In the present study, only one fatty acid was identified – heptanoic acid. In Vranec wine it was found in a slightly higher concentration – $1297.00 \pm 70.01 \mu\text{g}/\text{dm}^3$. In the wine of Kaylashki Rubin it was available in an amount of $1209.76 \pm 51.25 \mu\text{g}/\text{dm}^3$. Jiang and Ziang (2010) found traces of heptanoic acid in red wines from Cabernet Sauvignon. Añón et al. (2014) investigated the influence of different

oenological practices on the fermentation aroma of Menica red wines and found the presence of heptanoic acid in the variants in the range from 2.00 to 20.00 $\mu\text{g}/\text{dm}^3$. In the present study, this fatty acid was found in higher concentrations.

Sensory evaluation of red wines

The results obtained from the panelists (4 experts in the field of enology) were calculated and transferred into spider diagram (Figure 1) that showed us the two different wine profiles that the wines from these varieties had.

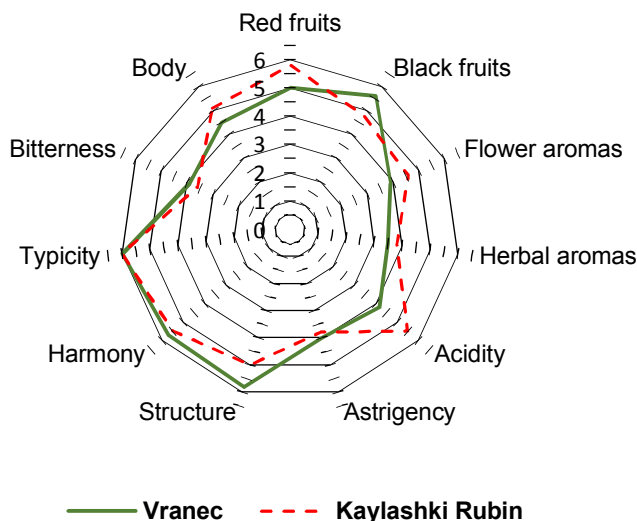


Figure 1. Sensory evaluation of red wines obtained from Vranec and Kaylashki Rubin varieties

According to this diagram we can see that the wine obtained from Vranec variety had more body and structure than Kaylashki Rubin, also the content of tannins was higher that could be noticed from the descriptor for bitterness and astringency. Vranec wine had less acidity and more black (dark) fruit aromas, lower freshness and less flowery notes in the wine. On the other hand, the wine from Kaylashki Rubin had higher level of acidity, more freshness which could be noticed from the descriptors flower and herbal aromas, also the wine had very intensive fresh red fruits aromas. According to the panelist both wines were very harmonious in their own way, both wines had their typical notes as expected for the both varieties. In overall the descriptive analyses confirm the analyzed components from the GC-MS analysis and gave us clear view about the aroma profile of both varieties.

The data regarding the sensory profile of the wine from Kaylashki Rubin were correlated with the research of Yoncheva et al. (2016, 2019), which defined the wine of this variety as harmonious, balanced and with pronounced varietal aroma, good color characteristics, dense and extractive. The data regarding the Vranec wine correlated with the study of Milanov et al. (2019), which determine the astringency and bitterness as dominant sensory characteristics in the wine from this variety.

Conclusions

The following conclusions can be made from the study conducted to define the aromatic profile of red wines from the local variety Vranec and the hybrid variety Kaylashki Rubin:

1. The fraction of higher alcohols in both wines consisted of 1-pentanol, 1-propanol, 2-propanol, 1-butanol, 1-hexanol, and 3-methylthio-1-propanol. 1-pentanol had the highest quantitative presence of this fraction. In the wine of the Vranec variety, 3-hexyl-1-ol was also identified, which was not present in that of Kaylashki Rubin.
2. One aromatic alcohol – phenylethanol – was identified. This compound was found in very high concentrations in both wines, with predominance in Vranec (20076.12±88.02 µg/dm³), compared to Kaylashki Rubin (17864.31±155.0 µg/dm³). Phenylethanol was an important component influencing the floral aroma of wines.
3. The main representative of the ester fraction in both wines was diethyl succinate. It occupied the highest concentration. Important ester compounds were identified – isopentyl acetate, ethyl caprylate, ethyl hexanoate, ethyl decanoate and diethyl malate. Ethyl-2-hydrobutyrate and 2-hydroxy-3-methyl-diethyl ester were identified only in Vranec wine. They were absent in the aromatic matrix of Kaylashki Rubin. This made the ester complexity of Vranec higher.
4. In the two studied red wines, only one fatty acid was identified, namely heptanoic acid in almost the same amounts.
5. The performed sensory evaluation showed that the Vranec wine had a better body and structure than that of Kaylashki Rubin. Vranec showed lower freshness and floral notes in the aroma, compared to Kaylashki Rubin. In Vranec the aromas of black fruits dominated, while Kaylashki Rubin showed a pronounced floral and herbal aromas, as well as fresh red fruits aroma. Both wines showed a diverse, balanced aromatic profile, each of which, based on the peculiarities of its volatile composition. Each wine has an individual aromatic capacity.

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