Sošić, S., Pajović-Šćepanović, R., Raičević, D., Popović, T. (2023): Quality of wines Vranac and Kratošija in the vintage 2021. Agriculture and Forestry, 69 (1): 127-137. doi:10.17707/AgricultForest.69.1.11

DOI: 10.17707/AgricultForest.69.1.11

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QUALITY OF WINES VRANAC AND KRATOŠIJA IN THE VINTAGE 2021

SUMMARY

Wine production in Montenegro is based on the autochthonous grape varieties Vranac and Kratošija that make Montenegro recognizable in the wine world.

The quality of grapes and wine is influenced by numerous factors, but varietal potential in combination with environmental factors mostly determine quality. Our research refers to the examination of the polyphenolic composition and quality of wine obtained from grapes of the autochthonous varieties Vranac and Kratošija in the 2021 vintage. The chemical composition of the wine was analyzed by OIV methods, and several phenolic groups were determined by spectrophotometric methods. The obtained results showed a good chemical composition of the tested wines, characterized by a high content of alcohol and extracts, while the other values were within the expected level. Vranac wine showed a medium to high content of polyphenols and high content of anthocyanins. The components of colored substances showed a high proportion of red and yellow color. The wines of Kratošija had a moderate content of total polyphenols, an expectedly lower content of anthocyanins, and a high content of parameters related to the components of colored substances (color intensity, proportion of red and blue colors). Variations in the parameters of chemical and polyphenolic composition were found in both tested varietal wines from different producers. Statistical analysis showed statistically significant differenece for some parameters of the polyphenolic composition between Vranac and Kratošija wine, but not for components of chemical composition.

The polyphenolic content of the analyzed wines, including other chemical characteristics, indicates that these Montenegrin autochthonous varieties can produce wines of exceptional properties and very good quality.

Keywords: polyphenol composition, chemical composition, Montenegrin autochtonous red wines

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Notes: The authors declare that they have no conflicts of interest. Authorship Form signed online.

Recieved:09/02/2023 *Accepted:20/03/2023*

INTRODUCTION

Due to increasing climate variability and extreme weather condition, it is not easy for producers to maintain continuity in the quality of their wines. Climate changes in the last 50 years have led to significant warming in most of the world's wine-growing areas. According to the climate forecasts, increase in the average air temperature during the growing season is expected in wine-growing regions until 2049 (Blancquaert *et al*., 2019). All this changes require continual studies of the components of the chemical and polyphenolic composition of wine. Polyphenols are the most studied group of compounds, which contribute to the final complexity of wine. Their structure and concentration vary depending on the variety, climatic factors, environmental condition and pathogens, as well as the technological production process. Polyphenolic compounds present in grape berries determine their taste, smell and color (Williams, 2019). They especially contribute to the organoleptic characteristics of wine because these are responsible for some of the sensory properties such as aroma, color, taste, bitterness and astringency (Ribéreau-Gayon *et al.*, 2006). Sensory properties, chemical and polyphenol composition of wine determine its quality.

Studies of the phenolic composition of some varieties of grapes and wines, produced in different years and in several locations, were conducted in Montenegro (Minić, 2021). The influence of some seasonal variations in temperature and rainfall is reflected in the content of total polyphenols in red variety wines (Pajović *et al*., 2014; Šućur *et al.,* 2016; Raičević *et al.*, 2017; Radonjić *et al*., 2019). The presence of some individual phenolic compounds in wines reflects its varietal specificity, and shows little difference in relation to the wine region where the vines were grown (Pajović-Šćepanović *et al*., 2018). Oscillations in weather conditions, and especially the amount of precipitation and its distribution, strongly influence the different content of polyphenols in commercial wines of the Vranac variety (Pajović-Šćepanović *et al*., 2019b). It is generally accepted that the reduction of yield in Vranac vine contributes to the achievement of better phenolic maturity, sugar accumulation, and an increasinge the content of polyphenols and anthocyanins (Košmerl *et al*., 2013). The content of flavan-3-ol in grapes is determined by environmental factors in the region where grapes are grown, and enables the use this parameter as a regional marker (Pajović-Šćepanović *et al*., 2019a). The presence of a wide range of phenolic compounds was determined when examining the phenolic composition of leaves, grapes and wine of the Vranac variety (Šuković *et al*., 2020). The main indicators of quality of wine are sugar concentration and total acidity in grapes (Pajović *et al*., 2013).

The aim of this research is to determine wine quality (chemical and polyphenolic composition) of the autochthonous wines Vranac and Kratošija in the vintage year 2021 in the Podgorica subregion in order to determine whether the current climate changes have affected the investigated characteristics of the wine.

MATERIAL AND METHODS

Wine samples

In this experiment, red variety wines Vranac and Kratošija from Montenegrin region of Skadar Lake, Podgorica sub–region: Doljani (2 and 7), Šipčanik (3, 4, 8 and 9) and Lješkopolje (5 and 10), and Piperi subregion: Rogami (1 and 6) were analysed.

Table 1. Data on the analysed wines

Wine	Winery/Producer	Subregion/Region	Locality
1. Vranac-Zenta	Vučinić	Piperi/ MRSL	Rogami
2. Vranac	Đukić	Podgorica/ MRSL	Doljani
3. Vranac	13.jul Plantaže	Podgorica/ MRSL	Ćemovsko polje
4. Vranac	13.jul Plantaže	Podgorica/ MRSL	Ćemovsko polje
5. Vranac	Biotechnical faculty	Podgorica/ MRSL	Lješkopolje
6. Kratošija-Zenta	Vučinić	Piperi/ MRSL	Rogami
7. Kratošija	Đukić	Podgorica/ MRSL	Doljani
8. Kratošija	13.jul Plantaže	Podgorica/ MRSL	Ćemovsko polje
9. Kratošija	13.jul Plantaže	Podgorica/ MRSL	Ćemovsko polje
10. Kratošija	Biotechnical faculty	Podgorica/ MRSL	Lješkopolje

*MRSL-Montenegrin region of Skadar Lake

The following meteorological factors were determined: average monthly and average vegetation temperatures, average monthly and average vegetation precipitation, relative humidity and average cloudiness. Meteorological data were obtained from the Institute of Hydrometeorology and Seismology, Podgorica.

Physico-chemical analyses

Wine analyses were performed in the laboratory of the Biotechnical faculty. The following parameters of the physico-chemical composition of the wine were examined: alcohol, extract, total acids, pH, volatile acids and residual sugar in the wine. Analyzes were performed in accordance with the Compendium of International Methods of Wine Analysis and beyond (OIV, 2011).

Total polyphenols

Total polyphenols (TP) were determined by reduction of Folin-Ciocalteu reagent to blue pigments in alkaline solution. Sample cleaning was adone according to Di Stefano & Guidoni, (1989). When the absorbance was between 0.3 and 0.6 AU, the results were expressed as Total polyphenols, (+) catechins mg/l= (186.5*A*d)/V; A-absorbance; d-sample dilution; V-volume of sample taken (1ml).

Total phenolic index (TPI)

The index of total phenols (index A_{280}) was determined spectrophotometrically according to the method of Ribereau-Gayon (1971). So that the absorbance at 280 nm was measured in a quartz cuvette (after diluting the wine with water) and the value was calculated according to the formula Index $A_{280}=A_{280}\times100$.

Total anthocyanins

Total anthocyanins (TA) were determined based on the maximum absorbance in the visible range (536 to 542 nm) in a 1 cm cuvette. A blank was performed with distilled water (Di Stefano et al., 1989). When the absorbance was between 0.3 and 0.6 AU. The results were expressed through the following formula: total anthocyanins mg/l=A×26.6×R×4; A-absorbance; R-sample dilution.

Determining the color of wine

The color of wine is composed of three components: yellow (λ=420 nm), red (λ=520 nm) and blue (λ=620 nm). By measuring the absorbance at these three wavelengths, the values of the following parameters are obtained: color intensity, color shade (Recueil d OIV, 1990), the proportion of yellow, red and blue colors and the shape of the spectrum (Glories, 1984).

Statistical analysis

The data were processed by ANOVA statistical analysis, and for the parameters significant differences were detected, an additional LSD test was applied at the significance level of $p<0.05$. Statistical analysis was performed using the Statgraphics Centurion XVI program (Manugistics Inc., Rockville, MD, USA).

RESULTS AND DISCUSSION

Table 2 shows the following climatic parameters: total precipitation, air temperature, relative humidity and mean cloudiness, in the examined vintage year (2021).

Table 2. Climatic parameters in 2021

2021	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	at	avt
Mean air temperature (°C)	7.1	9.5	10.0	13.0	19.9	26.6	29.4	28.5	23.2	15.5	13.6	8.2	17.0	23.9
Total rainfall (mm)	436.1	193.5	103.4	129.2	44.7	10.8	19.6	45.0	33.2	93.6	191.6	89.8	1390.5	376.1
Relative humidity (%)	75	67	62	63	58	46	42	43	49	61	76	68	59	51
Medium cloudiness	7.4	4.6	5.1	5.5	5.1	3.3	2.2	2.3	3.5	4.3	6.5	6.1	4.7	3.7

*at- annual temperature *avt-average vegetation temperature

During the examined year (2021) the mean annual temperature was 17.0˚C, and the mean vegetation temperature was 23.9˚C. There is an oscilation of mean monthly temperatures, mean annual and mean vegetation temperatures compared to the thirty-year average 1985-2014. An increase in average annual temperatures as well as average vegetation temperatures is observed in relation to the mentioned period for this area (Minić, 2021). During 2021 the total amount of precipitation (1390.5 mm) is less than the multi-year average (1679.7 mm). Also, the vegetation sum of precipitation in the examined year (376.1 mm) is slightly lower than the multi-year average (700.5 mm). In 2021, the mean relative air humidity was approximately the same both at the annual level and during the growing season, with a small deviation of the values compared to the thirty-year period. In the year when the survey was conducted, the average annual cloud cover was 4.7 tenths. During the growing season, an average value of 3.7 tens was recorded.

Chemical composition of wines

The results of the analysis of the examined parameters in the wines of the Vranac and Kratošija varieties are presented in the table 1. The density ranged from 0.9924 g/ml to 0.9963 g/ml. All analysed wines had the expected high alcohol content, over 13 vol%, except for wine No. 8. The alcohol content in the samples of varietal wines analised is higher than the values published by Pajović-Šćepanović *et al.*, (2016), what can be explained by higher temperatures in the analyzed year of analysis. Oscillation in the acid content of Vranac wine between producers is significant, greater than in Kratošija wine, probably due to different style of wine production in terms of ajusting acidity. The high value of total acids has a positive effect on microbiological stabilization and contributes to the freshness of the wine (Ivanova Petropulos *et al.*, 2015). Volatile acids ranged from 0.61 g/l to 0.98 g/l. The values of the total extract and the pH values of the tested varietal wine samples is in line with range reported by Pajović-Šćepanović *et al.*, (2016). The values of the other parameters were within the expected values of Vranac and Kratošija varietal wines.

From table 3 it is noted that the parameters of the chemical composition were different in the tested varietal wines. Statistical analysis (ANOVA) was performed to determine statistical difference in the two varietal wines Vranac and Kratošija. The results showed that there was no statistically significant difference ($p<0.05$) in any parameter of chemical composition: density, alcohol, total and volatile acids, pH, extract, reducing sugar, total and free sulfur.

The values of total polyphenols in the Vranac wines were in range from 1.02 g/l to 2.14 g/l. Kratošija wine had interval of the content of polyphenolic substances in the range from 0.80 g/l to 1.71 g/l. The average total polyphenol content of 1.63 g/l for the Vranac wine in our study falls within the range of 1.59-2.23 g/l, which Alexandre Tudo (2017) categorize as wines with medium to high polyphenol content. However, some of Vranac wines had a lower content of total polyphenols what was in the category of wines with a medium to low content of polyphenols. Kratošija wines, according to the same author, belonged to the category of wines with medium to low polyphenol content (1.04-1.59). Statistical analysis-LSD test, however, did not show a statistically significant difference between these wines.

Table 3. Chemical composition of the investigated red wines

WINE	Density (g/ml)	Alcohol (% v/v)	Total acidity (g/l)	Volatile acidity (g/l)	pH	Extract (g/l)	Free SO_2 (mg/l)	Total SO_2 (mg/l)	Residual sugar (g/l)
VRANAC	0.9940	14.77	6.75	0.72	3.92	33.60	34.23	112.75	2.40
	0.9944	14.36	5.47	0.67	3.57	33.50	39.07	96.60	2.20
	0.9931	15.38	6.07	0.88	3.48	33.00	30.95	138.37	1.22
	0.9936	15.08	4.50	0.61	3.48	33.70	31.00	129.40	3.18
	0.9949	13.30	7.0	0.83	3.66	31.69	20.86	110.55	1.79
	0.9940±0.007	**14.57±0.8**	**6.0±1.0**	**0.74±0.1**	**3.62±0.18**	**33.09±0.8**	**31.22±6.7**	**117.53±16.5**	**2.15±0.7**
KRATOŠIJA	0.9942	13.72	5.92	0.75	3.62	31.1	26.77	118.30	2.60
	0.9924	14.07	5.77	0.98	3.44	35.60	23.06	117.23	2.25
	0.9963	11.69	5.02	0.65	3.82	30.06	39.71	168.87	2.11
	0.9941	15.77	6.07	0.84	3.51	37.00	32.67	109.34	3.25
	0.9958	14.10	5.2	0.77	3.81	35.54	34.52	113.84	2.40
	0.9945±0.015	**13.87±1.5**	**5.59±0.5**	**0.79±0.1**	**3.64±0.17**	**33.86±3.1**	**31.34±6.6**	**125.51±24.5**	**2.52±0.5**

*ANOVA was used to compare the data between varietal wines ($p < 0.05$)

The obtained values of total polyphenols for the wines of the Vranac variety in our research fall into the range of values for the Podgorica sub-region stated by: Pajović-Šćepanović *et al*., (2019c) from 1.83 g/l to 2.18 g/l (2015 year) and from 1.55 g/l to 2.06 g/l (2016 year) and Košmerl *et al.,* (2013) from 1.69 g/l to 2.07 g/l. The content of polyphenols in Serbian and Macedonian red wines reported by Mitić *et al*., (2014) is slightly higher than the range of our values and ranges from 2.38-2.85 g/l.

When it comes to the Kratošija wines, values for total polyphenols were in the range reported for Montenegrin wines by Pajović-Šćepanović *et al*., (2019c) in 2015.1.40-2.06 g/l and in 2016. 1.20-1.83 g/l and Košmerl *et al.*, (2013) from 1.26 g/l to 1.85 g/l.

The measured interval of phenol index ranged from 95.94 to 56.03 for Vranac wines.and from 37.07 to 73.12 for Kratošija. It is in line with the average value of the Vranac wine of the Podgorica sub-region presented by Minić (2021) for the vintage year 2019; 65.62 and 65.60 for vintage 2020. For Kratošija wines same author stated higher values: 70.89 for 2019 and 66.32 for 2020. A statistical test (ANOVA) showed a statistically significant difference in the content of the A_{280} index in the investigated samples of the Vranac and Kratošija red varieties.

Based on the data shown in table 4 it can be observed that the variation of the value of anthocyanins in the both examined wines ranged from 244.45 mg/l to 1005.48 mg/l. The value of total anthocyanins in Kratošija wine ranged from 244.4 mg/l to 409.6 mg/l, respectively and Vranac wine from 425.6 mg/l to 1005.5 mg/l, respectively.

The values for the wines Vranac in our study fall within the range of 0.47-2.24 g/l, which Alexandre Tudo (2017) categorizes as wines with a high anthocyanin content.

Table 4. Content of polyphenolic substances and values of colorimetric parameters in red wines, vintage 2021.

WINE	WINARY/ PRODUCER	TOTAL PHENOLS (mg/l)	INDEX 280	TOTAL ANTHOCYANINS (mg/l)	COLOR INTESITY	COLOR HINT	% RED COLORS	% YELLOW COLORS	% BLUE COLORS	SPECTRUM SHAPE (da%)
VRANAC	1.Plantaže 13. Jul	1020,90	56.09	1005.48	1.49	0.57	57.12	32.54	10.33	72.46
	2.Plantaže 13. Jul	1982.12	86.91	885.24	1.41	0.56	57.11	33.00	9.86	74.94
	3.Đukić	1255.14	56.03	425.6	1.47	0.68	51.42	35.47	13.10	72.99
	4.Vučinić	2145.49	95.94	953.34	1.43	0.55	58.02	32.27	9.69	74.94
	5.Biotechnical faculty	1780.55	75.92	757.56	1.26	0.61	53.33	32.86	13.79	79.97
		1638.7±481.24	**61.77±16.44^{A}**	**805.44±231.75^{A}**	**1.41±0.09^{A}**	**0.59±0.05**	**55.32±2.81**	**33.18±1.29^{A}**	**11.47±1.83**	**75.06±2.96**
KRATOŠIJA	6.Plantaže 13. Jul	966.81	51.87	366.54	0.45	0.71	52.91	37.98	9.09	83.78
	7.Plantaže 13. Jul	953.57	42.71	395.80	0.60	0.64	55.24	35.79	8.95	71.93
	8.Đukić	807.73	37.07	244.45	0.62	0.70	51.36	36.28	12.35	69.88
	9.Vučinić	1710.57	73.12	409.64	0.73	0.58	56.97	33.48	9.54	59.14
	10. Biotechnical faculty	1117.10	52.21	395.80	0.79	0.62	54.57	36.28	9.14	68.70
		1121.9±353.64	**41.99±5.48^{B}**	**362.45±67.80^{B}**	**0.63±0.13^{B}**	**0.65±0.05**	**54.21±13.11**	**35.96±10.39^{B}**	**9.81±3.54**	**70.68±8.81**

*ANOVA was used to compare the data between varietal wines ($p < 0.05$)
*different letters in the row indicating the average value for the varieties show the statistical significance of the difference ($p < 0.05$)

The average total anthocyanin content of 0.36 g/l for Kratošija wine in our study, according to the same author, falls within the range of 0.31-0.47 g/l categorizing all wines in medium to high anthocyanin content cathegory. However, some Kratosija wines due to the lower anthocyanin content were in the category of wines with medium to low content of anthocyanins.

The values in this research for the content of total anthocyanins in the Vranac wines were in the range of values for the same Montenegrin wine variety stated by Pajović-Šćepanović *et al*., (2019b) and ranged from 462-690 mg/l for 2008, 404-672 mg/l for 2009, and 321-611 mg/l for 2010, Raičević *et al*., (2017) 600-870 g/l for 2008, and 640-790 mg/l for 2009 vintage year. In the research of Pajović-Šćepanović *et al*., (2019c) presented values for the Vranac variety in 2015 ranged from 800 mg/l to 815 mg/l and in 2016 from 738 mg/l to 883 mg/l. The results of the anthocyanin content of Vranac wine correspond to the values for this varietal wine from Macedonia. Ivanova Petropulos *et al*., (2015) for the examined samples of Vranac indicated values of total anthocyanins from 395 mg/l to 1530 mg/l, Milanov *et al*., (2014) showed lower values of total anthocyanins content (375.05 mg/l to 580.25 mg/l), whereas Mitrevska *et al*., (2020) presented much lower values: 121.15-273.06 mg/l.

Wines of Kratošija variety showed expected lower content of total anthocyanins in our research, which fits in with the previous conclusion about the lower content of colored substances compared to Vranac in research done for these two wines of the Podgorica subregion. Namely, Pajović-Šćepanović *et al*., (2019c) state values from 253 mg/l to 407 mg/l in vintage 2015 and 220 mg/l to 484 mg/l in vintage 2016; Radonjić (2020) 219-305 mg/l for and 198-282 mg/l for vintage 2012 and 2013, respectively. Slightly lower values presented Košmerl *et al*., (2013) from 146-158 mg/l. Differences in literature data maybe can be explained by the different methods used to determine anthocyanins. Statistical analysis showed a statistically significant difference in the content of total anthocyanins between the examined varietal wines Vranac and Kratošija.

Vranac variety wine had the highest color intensity 1.49 and the lowest with a value of 1.26. The color hue of Vranac wines ranged from 0.68 to 0.55. For Kratošija wine interval of color intensity ranged from 0.79 to 0.45. The highest value of the color hue was 0.71 and the lowest at 0.58.

The values in our research correspond to the color intensity values stated by Bogićević *et al*., (2015) for Montenegrin wines research for the 2011 vintage (1.85-2.06) and the range of hue values or the same varietal wines is 0.59-0.61. Košmerl *et al*., (2013) report higher intensity values of 5.33-6.01 and lower color hue values of 0.21-0.26 for the same varietal wine.

Values for the Kratošija wines, in this research, are slightly higher than the values stated by Minić (2021) for the hue of color in vintage 2019 (0.29) and for vintage 2020 (0.26) and lower in compare to the color intensity values of 1.49 (2019) and 0.92 (2020).

Color share (A420%, A520% and A620%) represents the share of each of the color components expressed in percentage and the shape of the spectrum refers to the "brightness" of the red color (dA%) (Puškaš, 2010).

The Vranac variety wine in our test had the highest percentage of red color and ranged from 58.02% to 51.42%. The proportion of yellow was in the range of 35.47% to 32.27%. The share of blue color was expectedly the smallest and ranged from 13.79% to 9.69%. The shape of the spectrum (dA) ranged 79.97% to 72.46%.

For Kratošija wines the range of red color was from 56.97% to 51.36%. The highest percentage of yellow was recorded at 37.98%, and the lowest at 33.48%. The lowest percentage of blue was 8.95%, while the highest was 12.35%. The shape of the spectrum ranged from 83.78% to 59.14%.

A slightly higher percentage of red color and a lower share of blue color is shown by Minic (2021) for Vranac from the territory of Montenegro. Namely, 58.2% red color, 30.3% yellow color, 11.3% blue color and for the shape of the spectrum 67.2% in 2019, and in 2020 59.2% (red), 31.1% (yellow), 9.7% (blue) and for the shape of the spectrum 70.1%.

The values in for wines Kratošija fall into the range of values shown by Minic (2021) for the proportion of red color (51.8%). yellow color (33.5%), blue color (14.7%) and for the shape spectrum (29.6%) in 2019, and 53.8% of red color, 35.1% of yellow color, 11.1% of blue color and for the shape of the spectrum 13.6% in 2020.

The statistical analysis revealed a statistically significant difference in the proportion of yellow color in the tested Vranac and Kratošija varietal wines.

CONCLUSIONS

In this research, the wines of the autochthonous Vranac and Kratošija varieties were analyzed, their polyphenolic composition and quality under the influence of meteorological condition for vintage year 2021. The chemical composition of the wine showed good values for all tested wines with high alcohol values. In addition extract values were also high, while other values were within the expected limits.

Vranac wine showed a medium to high content of polyphenols and a high content of anthocyanins, components of colored substances had a high proportion (red, yellow). The wines of Kratošija had a moderate content of total polyphenols, lower content of anthocyanins and a high content of parameters related to components of colored substances (intensity and proportion of red color).

The examined Vranac and Kratošija wines from the 2021 vintage year showed good results in terms of chemical and polyphenolic composition. However, both varietal wines showed significant variation in chemical composition and phenol content among different producers. This leads to the conclusion that it is possible to produce high quality wines only from excellent grape quality with timely harvesting and careful and proper management of technological procedures.

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