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ХЕМИСКИ СОСТАВ НА ЦРВЕНИ ВИНА ОД СОРТАТА ВРАНЕЦ ОД РАЗЛИЧНИ ЛОКАЦИИ

Жанета Нечева[1], Виолета Иванова Петропулос[1*]

Краток извадок

Во ова истражување беа произведени вина од сортата на грозје *вранец* (берба 2014), одгледувано на различни локации: Барово, Дисан, Градско и Битола. Винаа беа произведени со иста технологија, применувајќи традиционален начин на производство. Притоа беа определени следните основни хемиски параметри коишто го одредуваат квалитетот на виното: вкупна киселост, pH, испарлива киселост, алкохол, SO_2 (слободен и вкупен) и редуцирачки шеќери. Винаа содржеа вкупни киселини од 4,9 до 7,1 g/L, а испарливата киселост беше во граници од 0,4 до 0,52 g/L. Содржината на алкохол беше од 8,78 до 14,3%. Сите вина беа добро заштитени од оксидација со доволна содржина на SO_2. Во однос на концентрацијата на редуцирачки шеќери, кај винаа од Барово и Дисан беше целосно завршена алкохолната ферментација, а винаа од Градско и Битола содржеа недоферментиран шеќер (4,5 g/L). Беше заклучено дека произведените вина имаат сличен хемиски состав и параметри кои се во границите на дозволените вредности. Локацијата не влијае значително на квалитетот на виното. Поголемо влијание на квалитетот има технологијата на производство на вино.

Клучни зборови: *основни хемиски параметри, вино, вранец, вински региони*.

CHEMICAL COMPOSITION OF RED VRANEC WINES FROM DIFFERENT LOCATIONS

Zaneta Neceva[2], Violeta Ivanova Petropulos[3]

Abstract

In this study, red Vranec wines (vintage 2014) were produced from grapes grown at different locations: Barovo, Disan, Gradsko and Bitola. Wines were

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produced with same technology, applying traditional way of production. In addition, following chemical parameters which influence the wine quality were determined: total acidity, pH, volatile acidity, alcohol, SO_2 (free and total) and reducing sugars. Wines contained total acids in range from 4.9 to 7.1 g/L and the volatile acidity was in range from 0.4 to 0.52 g/L. The alcohol content was between 8.78 to 14.3 %. All wines were well protected from oxidation containing enough content of SO_2. Concerning the reducing sugars concentration, alcoholic fermentation was finished in the wines from Barovo and Disan, while wines from Grasko and Bitola contained small amount of reducing sugars (4,5 g/L). It was concluded that the produced wines presented similar chemical composition and all parameters were in the range of allowed values. Locality did not influence the wine quality. Higher influence on the wine quality has the technology of winemaking.

Keywords: *SO_2, reducing sugars, wine, titration*

1. Introduction

Macedonia has a very long tradition in winemaking. In 2010 there were 86 registered wineries in Macedonia with a total capacity of ca. 2 million hectolitres per year. The total capacity of bottling is around 0.65 million hL per year [1]. The wineries are mainly located in the region of the river Vardar valley, in particular in Skopje, Tikveš, and Gevgelija-Valandovo. Red wine represents approx. 60% of the national production and includes both autochthonous (Stanušina) and international grape varieties such as Cabernet Sauvignon, Syrah and Merlot [1]. Vranec is the most important grape variety used for red wine production in R. Macedonia since it represents about 50 % of the total red wine production in the country. It is grown in all vineyards, mostly in the Tikveš wine region, where more than 80% of the Macedonian vineyards are located. The wine produced from this variety has an intense dark red colour, aroma of plum, sour cherry and wild berries, rich in polyphenols.

Wine contains two main components, water (~ 80%) and alcohol (~12%). But, the overall aroma and taste of the wine depends on the other compounds (~8%) present in the wine. In fact, wine is a complex mixture of a large number of compounds including carbohydrates, alcohols, aldehydes, esters, acids, proteins and vitamins. It also contains a number of elements, polyhydroxy aromatic and polyphenolic compounds, such as tannins, anthocyanins and flavonols, which contribute highly to colour and taste [1-6].

Ethanol is the most important alcohol in wine. The primary source of ethanol in wine is yeast fermentation. Under standard fermentation conditions, ethanol can accumulate at up to about 14–15%. Organic acids are other important components for the wine chemical and microbiological stability.

Their total content in wine ranges between 5.5 and 8.5 mg/L, expressed in tartaric acid equivalents. White wines contain higher concentration compared to the red wines. A pH range between 3.1 and 3.4 is considered as suitable for most white wines, and between 3.3 and 3.6 for most red wines.

The use of SO_2 in winemaking is due to its ability of an effective antoxidant, preventing the activity of the oxidases. Also, it has significant activity as antimicrobial agent, as well as potential for bleaching the pigments and elimination of unpleasant odours (as a result of oxidation). Because yeasts are very sensitive to SO_2 (also, to other stress factors), it can selectively act against the wild yeasts, which come from the grape skin or equipment in the winery, and stop their activity. Sulphur dioxide can be added in a form of a salt, potassium metabisulphate ($K_2S_2O_5$), which can be ionized in acid media, releasing gaseous SO_2 [7, 8].

Volatile acidity is also very important parameter which determines the wine quality. Acetic acid is the main volatile acid, which is a product of the yeast and bacteria metabolism. Other carboxylic acids such as formic, butyric, and propionic acids may also be involved in volatile acidity. Sugars, glucose and fructose can be present in the wines, even dry wines usually do not contain these carbohydrates or contain small amounts of unfermented glucose and fructose. In dry wines, the residual sugar content consists primarily of pentose sugars, such as arabinose, rhamnose, and xylose.

Harvesting the grapes from the vineyards is the first step in red winemaking process, followed by transportation to the winery whereas the process of young red wine production begins. There are several stages of red winemaking, including grape crushing, fermentation of the juice in presence of skins, maceration, alcohol fermentation, decantation, racking, stabilization, aging and bottling.

This study is focused on the production of wines from Vranec grapes grown at four locations in the Republic of Macedonia: three of them were located in the Povardarie wine-growing region (locations: Barovo, Disan and Gradsko) and one was located in the Pelagonija-Polog wine-growing region (location: Bitola). The aim of the work was to study the influence of location on the principal chemical parameters, such as alcohol content, SO_2 (free and total), total acidity, volatile acidity, reducing sugars and pH.

2. **Materials and methods**

2.1. Chemicals and Reagents

Standard solution of SO_2 and standards of glucose and fructose were purchased from Sigma Aldrich (St. Louis, MO). All other reagents used were with analytical grade of purity. Ultra-pure deionized water (LC-MS Chromasolv®) was obtained from Fluka (Buchs, Switzerland).

2.2. Winemaking

Grapes from *Vitis vinifera* L., *cv.* Vranec were grown at vineyards located at four wine locations in R. Macedonia (Barovo, Disan, Gradsko and Bitola). Grapes were manually harvested (20 kg) at optimal technological maturity (18-24ºBrix) in September/October, 2014 and transported to the wine cellar of BOVIN Winery, Negotino, R. Macedonia. Grapes from each location were processed separately applying the same technology. Thus, grapes were mechanically pressed using a mechanical inox crusher/destemmer, and treated with sulphur dioxide (50 mg/L) prior to the undergoing skin fermentation at 22-24°C. Sulphur dioxide was added in a form of 5 % sulphurous acid. After the addition of SO_2, a commercial pectolitic enzyme preparation (Endozym Rouge, AEB, Italy) was applied in order to obtain higher concentration of coloring compounds, skin tannins and varietal aromas (1 g/hL). After two-three hours, wines were inoculated with *Saccharomyces cerevisiae* yeast (Fermol Medterranee, AEB, Italy). Yeast was prepared by rehydration (20 g/hL) in must, followed by the addition of nutrients, 10 g/hL (Fermol Plus starter, obtained from AEB, Italy, containing 59.8 % diammonium phosphate, 39.52% cellulose and 0.6 % thiamine hydrochloride). Grape mash was macerated for 7 days and during that period, the cap was mechanically punched down two times a day until it remained submerged. After the maceration period, wine was separated from the pomace by mechanically pressing and stored in 10-L vessels in at room temperature. After ten days of conservation, wines were racked and again were treated with sulphur dioxide (30 mg/L). The second racking was performed after two months of storage, when wines were bottled and stored in a cellar at 8-10°C for about 8 months until analyzed.

2.3. Principal chemical composition

The following parameters: total acidity, volatile acidity, total and free SO2, alcohol, reducing sugars and pH, were analyzed according to the official methods of analysis of wines [9].

3. **Results and discussion**

Table 1 summarizes the chemical composition of Vranec wines produced from grapes grown in the Povardarie wine-growing region (locations: Barovo, Disan and Gradsko) and Pelagonija-Polog wine-growing region (location: Bitola).

In general, three wines (W2, W3 and W4) showed relatively high amount of total acidity (ranged from 6.2 to 7.1 g/L) as it was expected, that peaked

for Vranec wine (W2) produced from grapes grown in Disan. Only wine from Barovo location (W1) showed lower total acidity content (4.9 g/L), but this content is still enough to protect the wine from microbial spoilage. Obtained results were consistent with previous findings that found the Vranec wines (Macedonian as well as Montenegrin) characterized by high value of total acidity, typical for this variety [1, 10, 11]. Moreover, a high value of total acids helps the microbial stabilization and the freshness of these wines.

Table 1. Principal chemical composition of Vranec red wines from four locations (Barovo, Disan, Gradsko and Bitola).

Wines	**W1**	**W2**	**W3**	**W4**
Location	Barovo	Disan	Gradsko	Bitola
Total acidity (g/L)	4.9	7.1	6.7	6.2
pH	3.6	3.3	3.14	3.19
Volatile acidity (g/L)	0.48	0.52	0.40	0.52
Alcohol (%)	10.75	14.3	13.98	8.78
Free SO_2 (mg/L)	19.20	21.76	20.48	38.40
Total SO_2 (mg/L)	25.6	64	23.04	153.6
Reducing sugars (g/L)	1.6	2.9	4.5	4.5

Another factor that protects the wine and influences its stability is pH. The pH values ranged between 3.14 to 3.6, which were in the range typical for red wines. It is generally known that the lower the pH, the more difficult it is for microorganisms to survive. Wine W1 presented highest value of pH (3.6), which was in a correlation with the total acidity, presenting lowest value (4.9 g/L) between the wines. In fact, organic acids control the pH of wine, in which tartaric and malic acids are the two dicarboxylic acids that constitute more than 90 % of the acidity.

All wines presented low and similar values for the volatile acidity. Thus, the volatile acidity showed an overall average value of 0.48 ± 0.05 g/L with no influence on the quality of wines. All wines contained lower values than maximal allowed (1g/L) [10] which means that the wines had satisfactory quality.

The alcohol level was within the regulatory values of 20% for wines of area C III b (Reg. CE 606/2009). Wine W1 (from Disan location) presented highest value of alcohol (14.3 %), followed by the wine W3 (from Gradsko location) (13.98 %). Alcohol is produced during the alcoholic fermentation by the yeasts, which transform the sugars into ethanol and carbon dioxide. It presents inhibitory action, limiting the growth of microorganisms. This property of the ethanol, combined with the acidity of wine, permits wine to remain stable during the aging and bottling.

Wines were regularly protected from further oxidation and microbial contamination by the free SO_2 which was present in a sufficient level. Thus, the amount of free SO_2 ranged from 19.2 to 38.4 mg/L and the total SO_2 ranged from 23.04 to 153.6 mg/L (Table 1). These results were in a correlation to the legal regulations according to which the maximum allowed amount of SO_2 in red wines is 400 mg/L [10].

The content of reducing sugars was different between the wines (ranged from 1.6 to 4.5 g/L), which means that the rate of alcoholic fermentation was not similar in all wines where yeast cells were used to ferment glucose into ethanol. Therefore, wines from Barovo and Disan localities can be considered as dry wines (1.6 and 2.9 g/L reducing sugars, respectively) and wines from Gradsko and Bitola as semi-dry wines, both containing 4.5 g/L reducing sugars.

4. **Conclusion**

The chemical composition of Vranec wines from different locations, including Barovo, Disan, Gradsko and Bitola, was determined. Wines presented relatively high values of the total acidity (range: 4.9 - 7.1 g/L) and low values of the volatile acidity (range: 0.4 - 0.52 g/L). The alcohol content was between 8.78 to 14.3 %. This means that the wines had satisfactory quality, presenting good chemical and microbiological stability. Moreover, all wines were well protected from oxidation containing enough content of SO_2. Alcoholic fermentation was finished in the wines from Barovo and Disan, while wines from Grasko and Bitola contained small amount of reducing sugars (4,5 g/L). All wines presented similar chemical composition and locality did not have influence on the wine quality.

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