THE IMPACT OF THE HARVESTING YEAR ON CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE VRANEC WINE

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Abstract. This paper defines chemical and physical characteristics of Vranec wine, grown in region of Povardarie, particular Tikvesh wine region. Vranec is a Montenegrin autochthonous grape variety and also it is one of most widespread red wine varieties in Macedonian vineyard regions. Due to grape localized geography it produces a dry red wine of unique taste that is synonymous with Balkans. The samples differ between each other by year of harvest: 2009, 2010 and 2011. All samples have finished fermentation in a bundle and then were stored in a storage tank for finished wine. The physical–chemical properties of tested wines (total acid, pH, lactic acid, acetic acid, malic acid, citric acid, reducing sugars, total sugars, volatile acids, alcohol, total and free SO₂, polyphenols, anthocyanins, colour intensity and shade) were determined by using traditional and advanced analytical techniques. Also, correlation of variation of climatic parameters during different harvest years with characteristics of produced wines was assessed.

Keywords: Vranec, Republic of Macedonia, wine, physico–chemical characteristics.

Introduction
The wine represents a product obtained exclusively by full or partial alcoholic fermentation of fresh grapes and grape must, suppress or unsuppressed [NASTEV, 1984; YOUSFI et al., 2012].

The plantations with vines in Macedonia, for protection of geographical origin of wine, are divided into three wine regions: “Povardarski, Pchinski–Osogovski and Pelagonisko–Poloshkii” and regions themselves are divided into sub–regions or vineyards.

In scope of “Povardarie” is Tikvesh wine region where it is grown to about one–third of total production on vineyards. In this region interact Mediterranean and continental climates, and is driest area of Balkan Peninsula. Vranec wine is produced from grape Vranec, which is most important for production of red wines in Macedonia.

Vranec is native Montenegro variety, but is present in all vineyards in Vardar region and lesser extent in other vineyards [HRISTOVSKI, 2009; RUBIO et al., 2009; PRadelles et al., 2008].

Materials and methods
There were examined three samples of wine Vranec, with finished fermentation in tank in grapes of same variety–Vranec, in Stobi Winery, located in Tikvesh wine region. Vranec wine is vintage 2009, 2010 and 2011 th.

Parameters for weather conditions (minimum and maximum temperature, wind–strength in bofors, cloudy and rainfall in mm) are taken, during growing of grapes to winery’s own plantations for period from March to June for above years.


The determination of total acids and volatile acids is done also with reference methods of International organization of wine (O.IV–MA–AS313–01, O.IV–MA–AS313–02).
Reduced sugars like glucose and fructose were determined by method of Rebelein, while amount of alcohol is determined with ebullioscopy using method of Malligand.

Total polyphenols were determined according to reference method O.IV–MA–AS2–10 also examined and intensity and hue of wine and presence of sulphur dioxide by reference method O.IV–MA–AS323–04V).

### Results and discussion

The climatic conditions are one of most important parameters during cultivation of vines, under which is determined quality of grapes and further quality of wine.

Higher temperatures lead to greater amounts of sugars, which are further converted into alcohol.

In table 1 are presented parameters for climatic conditions in 2009, 2012 and 2011.

<table>
<thead>
<tr>
<th>Year</th>
<th>Minimum temperature</th>
<th>Maximum temperature</th>
<th>Wind–strength in bofors</th>
<th>Cloudy</th>
<th>Rainfalls in mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009</td>
<td>11.86</td>
<td>24.16</td>
<td>1.88</td>
<td>5.16</td>
<td>1.68</td>
</tr>
<tr>
<td>2010</td>
<td>11.80</td>
<td>23.44</td>
<td>1.46</td>
<td>5.38</td>
<td>1.68</td>
</tr>
<tr>
<td>2011</td>
<td>11.72</td>
<td>23.5</td>
<td>1.48</td>
<td>5.28</td>
<td>0.74</td>
</tr>
</tbody>
</table>

From table 1 it can be seen that highest maximum temperature and lowest value of cloudiness are in 2009, and according to that it could be expected, sugar quantity in this year to be highest.

Red and black grapes require more sunlight to be able to develop.

Red wines are specialty of warm and sunny regions, where it is not difficult to achieve adequate maturity.

The grapevines need greater amounts of sunlight in order to produce phenolic compounds.

When grapevine is planted in cold areas, then red wine will not be able to achieve full potential of texture, because epidermis mature little.

In figure 1 are presented values of tested samples of wine Vranec for pH, total acid and volatile acids.

![Figure 1. pH, total acid and Volatile acids](image)

There are two ways of expressing acidity of wine: total acidity (acid titration) and real acidity (pH). The total acidity includes organic and inorganic acids and their salts and their other components that can be titrated with base.

According to some scientists pH in red wine varies in range from 3.0 to 3.8 which depends on contact of skin and juice before or during fermentation.

Studies conducted in Montenegro to wine Vranec produced on Biotechnical Faculty
show that calculated values are almost identical to our obtained (pH 3.41) [MILASHEVICH, 2012]. Total acids are defined as concentration of organic acids present in wine.

It represents a measure of concentration of hydrogen ions plus concentration of potassium and sodium ions.

The total acidity in red wines ranges from 6–9 g/L [GAMP et al., 2009; MILASHEVICH, 2012; OIV.INT]. Comparing results of wine Vranec of Biotechnical Faculty at University of Podgorica (6.96) confirms fact that regardless country that produces wine, values of volatile acids in wine Vranec are moving within limits prescribed by OIV.

Volatile acidity is generated during fermentation activity of acetic–acid bacteria that converts alcohol into acetic acid and ethyl acetate.

All table wines have a certain level of volatile acidity which is not observed below a certain level [HALIDAY and JOHNSON, 2011].

The values of volatile acidity of wine Vranec of biotechnical Faculty in University of Podgorica are larger than obtained (0.76 mg/L) [MILASHEVICH, 2012].

Table 2 gives quantities of acids in tested samples of wine Vranec.

Table 2.

<table>
<thead>
<tr>
<th>Acid</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malic acid mg/L</td>
<td>1.21</td>
<td>0.14</td>
<td>0.65</td>
</tr>
<tr>
<td>Lactic acid mg/L</td>
<td>0.02</td>
<td>0.69</td>
<td>0.2</td>
</tr>
<tr>
<td>Citric acid g/L</td>
<td>1.1</td>
<td>0.19</td>
<td>0.38</td>
</tr>
<tr>
<td>Acetic acid g/L</td>
<td>0.22</td>
<td>0.35</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The difference in acidity titration due to conversion of malic acid into lactic acid is easily visible in taste. The effects on aroma of red wine caused by malic–lactic fermentation are subtle and noticed only in strict tasting conditions [BISON et al., 2012].

Lactic acid is a result of malic–lactic acid fermentation, where malic acid turns into lactic acid, diacetyl and carbon dioxide gas [LINTON et al., 2012].

From table we can see that in wine of year 2009 there was hardly conversion of malic acid into lactic acid, i.e. almost no flow Malic–lactic fermentation.

Citric acid represents organic acid which supports stabilization, i.e. wines not to create condensates [LINTON et al., 2012].

In presence of oxygen, acetic acid bacteria convert alcohol into acetic acid, which together with water, that is naturally present in wine, produce vinegar [KALUPAJA].

From results in Table 2 it can be seen that acetic acid has smallest quantity in wine from vintage 2011, which is understandable since very lodging of wine increases contact of acetic acid bacteria in air, i.e. wine in 2011 has shortest time to provide contact of acetic acid bacteria in air.

Wine acid has very little noticeable taste. Malic acid tastes like green apple, milk butter and cheese, until acetic acid tastes like vinegar [LINTON et al., 2012].

**Carbohydrates**

Carbohydrates are polyhydric aldehydes, ketones and their derivatives.

This compounds it consisting of the C, N and O in the ratio of Cn(H2O).

In wine where we have complete alcoholic fermentation total amount of sugar is relatively small 1 to 2 g/L, no greater quantity of sugar is left if alcohol fermentation runs to end.

Glucose and fructose are both present in grapes, as each of them contributes by 10g/100g.

Susrose is one of three most common sugars.

According to some authors dry table wines have 0 % reducing sugars, but practice most of analyzed samples of dry wines has reducing sugars less than 2.0 g/L [GAMP et al., 2009].
In figure 2 are given values for total sugar and amount of reducing sugar.

![Figure 2](image)

**Figure 2.** Amount of total sugar and reducing sugars expressed as glucose–fructose

By comparing results shown in figure with specified values of reducing sugars, it can be easily seen that values of studied samples range in specified frame to 2.0 g / L.

**Alcohol**

The stability of wine depends on percentage of alcohol that wine contains. In many countries wines are taxed exactly by percentage of alcohol they contain. According to specified standards of International organization of vine and wine (OIV) it is required wine to contain at least 8.5 % vol. so that a product can be characterized as wine.

In figure 3 are given determined quantities of alcohol in tested samples.

![Figure 3](image)

**Figure 3.** Quantity of alcohol expressed as % vol.

Wines that have a percentage of alcohol more than 14 % vol. are characterized by hot climate in areas where vines are grown for their issuance, have a high degree of maturity, and amount of sugar in grape juice is more than 26% by weight, while in relation of body of these wines, they are full–bodied, rich in texture.

**Polyphenols and antocyanins**

Table wines are composed of 85 % water, 12 % ethyl alcohol and only 3 % belong to color fragrancy and body.

Out of this 3 % highest is presence of phenols which were once called phenolic substances i.e. tannins.

The whole group of phenolic compounds can be called polyphenols. They are mostly found in seeds, then vine, and less in skins, but in seeds at least. Polyphenols are divided into two groups: flavonoids and non–flavonoids.

Red, blue, pink, violet, and pink–purple color due to presence of anthocyanins. Along with other polyphenolic substances they occur as glycosides and aglycones, which are known as antocyanidynes.

In nature there are only six antocyaninidynes, but depending on process of glycosylation and pilgrimages, encountered numerous anthocyanins are known which are containing antocyanidynes.
Out of six known antocyanidynes in grapes is present just pelargonidyn [COULAT, 2011].

In Figure 4 are given quantities of polyphenols and anthocyanins in wine samples of Vranec.

![Figure 4](image)

**Figure 4. Amount of anthocyanins and polyphenols**

From enclosed results it can be said that with keeping for longer period wine, i.e. storage, amount of polyphenols and anthocyanins is reduced, i.e. highest amount of polyphenols and anthocyanins is noticeable in wines made from grapes from vintage in 2011, while lowest value of polyphenols and anthocyanins is noticeable in wine from vintage 2009. According to studies made by [GRINNICI et al., 2010] values of polyphenols/anthocyanins of wine Vranec produced in 2003 from Tikvesh wine region, is smaller than all three tested samples (polyphenols 1382±38.2 mg L⁻¹, anthocyanins 239±14.8 mg L⁻¹) [OLD and GIGLIO, 2012].

**Intensity and shades**

Among red wines there are 20 shades of red color. The splendour of colours decreases with increasing pH value of wine, and also a low pH is with addition of little sulphur dioxide, that slightly affects color of red wine.

![Figure 5](image)

**Figure 5. Results of tests for color intensity of Vranec**

The life span of red wine colors goes from purple to brown, from dark to light color, and these changes are caused by polymerization of antocyanins and colored tannins, which turn out in end as sediment [HOLIDAY and JOHNSON, 2011].

In figures 5 and 6 are
presented results of survey of color intensity and tint (coloration). According to obtained results, it can be said that with extension of, keeping time intensity and color shade are decreasing.

![Results of tests for shade (wine coloration)](image)

**Figure 6.** Results of tests for shade (wine coloration)

**Sulphur dioxide**  
Sulphur dioxide can be found free and bound, and sum of free and linked SO\(_2\) gives total amount of SO\(_2\) content.  
Bound SO\(_2\) binds bisulphite ion with aldehydes, anthocyanins, proteins and aldo–sugars.

The maximum permitted level for sulphur dioxide allowed by OIV is 350 mg / L [GAMP et al., 2009].

In figure 7 are shown values for total sulphur dioxide and free sulphur dioxide expressed in mg / L.

![Amount of total and free SO\(_2\)](image)

**Figure 7.** Amount of total and free SO\(_2\)

The results in figure 7 compared to maximum permitted values of free SO\(_2\) by OIV, show that values of tested samples are far from maximum values.

**Conclusion**  
Climatic conditions suggest that 2009 has best potential for production of grapes, and further to obtaining quality wine.

In relation to concentration of hydrogen ions (pH), all samples are moving in limit of 3.3 to 3.8, as pH value. The largest quantity of total acids is noticed in wine of vintage 2011 with complete fermentation and transferred and kept in tank.

The largest quantity of lactic acid is noticed in wine from vintage 2010, while largest amount of malic acid recorded in wines of vintage 2009, which indicates fact that during malic–lactic fermentation in this wine there is almost no conversion of malic acid into lactic acid.
As for citric acid, it is recorded that her highest values are in wines of vintage 2009. Volatile acids include all acids which are present in wine, and are diluted with steam. Volatile acidity ranges between 0.2–0.4 g / L. This shows that analyzed wines are moving exactly in that interval. Acetic acid largest values are recorded in wines from vintage 2011 (0.20 mg / L).

The greatest amounts of sugars in wine are noticed in vintage 2009 (5.4 g / L), out of which amount of analyzed reducing sugars, glucose and fructose, by enzymatic method represents 0.75 g / L. Phenol compounds–polyphenols and anthocyanins compared with extension of storage time are decreasing, so highest values are noticed in wine from vintage 2011 and lowest from 2009. The same conclusion can be made for color intensity and shade i.e. colouration. The presence of SO₂ can be double–edged sword. On one hand, increased presence of SO₂ leads to inactivation of undesirable microorganisms (which is desirable), while on other hand increased amount of SO₂ by a number of scientific studies indicates a potential health problem for a certain class of individuals, such as asthmatics. Since maximum total content of SO₂ by OIV (350 mg / L), in tested samples are observed three times smaller values.

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