THE INFLUENCE OF RED YOUNG WINES OXIDATION ON THE ANTHOCYANINS SPECTRUM

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Abstract
In this paper is studied the oxidation process of some Romanian red wines, during two months after the bottles of wine were opened. For this, the absorbance spectra were drawn, the colour (the density, the intensity and the hue) was appreciation, the anthocyanin and sulphur dioxide content was determined. The studied wines were: Cabernet Sauvignon, Merlot and Pinot Noir, produced in 2009 by a local producer from the Valea Calugareasca area. The wine colour is determined by the spectrophotometric methods and the SO_2 content was assayed by titration with iodine solution. It was remark that, during the oxidation process of wines, the decreasing of SO_2 content is produced in the same time with the decreasing of anthocyanin content. They are correlated with the increase of the wine colour intensity. The research clearly showed the existence of correlations between the anthocyanins content and SO_2 content, during the oxidation process of wine.

Keywords: wine, oxidation, anthocyanins, colour intensity, SO_2

1. INTRODUCTION

According to the Romanian language dictionary, wine is an alcoholic drink obtained by fermentation of grape or other fruit. This definition is rather general and incomplete, even misleading because it includes in the category of wine and drinks made from fruit. A more complete definition is given in Law of Vine and Wine no. 244/2002, which says that "wine is the drink produced exclusively by alcoholic fermentation, all or partial of the fresh grapes, broken or crushed, or the grape must".

There is no chemical formula for the composition of wine, being over 1500 organic molecules and minerals derived from the grapes, mostly formed during the alcoholic fermentation and during the wine aging. Taking into account the concentration and their role in the wine, the chemical substances from the composition of wine are divided into three categories (Ţârdea [1]):

- The main substances (alcohols, acids, sugars, glycerol, minerals, etc.), with a content more than 1 g/l, which define the quality of wine;
- The secondary substances (aldehydes, esters, aminoacids, anthocyanins, phenols, etc.), with content of milligrams order, which determine the authenticity and typicity of wine;
- The substances present in trace amounts in wine (mycotoxins, pesticide residues, chemical pollutants, etc.), which are determined only in special cases.

The chemically speaking wine is a polydispersive hydroalcoholic solution, which contains several organic and mineral substances.

By the Law of Vine and Wine no. 244/2002, Romania has a national legislation in line with the resolutions of International Organisation of Vine and Wine and the EU regulations. These documents establish the characteristics of wines admitted before putting features in consumption and the methods of analysis and technology control of their quality.

The authenticity and typicity of wine are the basic attributes which guarantee the quality of a wine (Ţârdea [1]).

The paper seeks to study the oxidation process of three young red wines (2009) produced by a local producer in the Valea Calugareasca area, based on the content of anthocyanins. The wines were opened in early September 2010 and the chemical analysis was done immediately after the opening of bottles. To follow the effect of oxidation of samples, we studied the variation in colour, the anthocyanin content and the sulphur dioxide content for two months.

2. MATERIAL AND METHODS

The studied wines are: Cabernet Sauvignon, Merlot and Pinot Noir, produced in 2009 by a local producer from the Valea Calugareasca area.
The analyses of wines have followed the appreciation of colour (the density, the intensity and the hue) and the determination of anthocyanin content and sulphur dioxide content, for two months.
The absorbance spectra were studied with a Perkin Elmer UV-Vis spectrophotometer Lambda 25, with double-beam.
The wine colour is due to phenolic compounds from the wine. The colour of red wines is due to the polyphenols (antocyans and tannins), flavones and phenolic acids. The most important are antocyans that determine the blue-red colour of the wine (Ţârdea [1]).
The wine colour is determined by the spectrophotometric methods as: is measured the absorbencies of the wine samples at the wavelengths of 420, 520 and 620 nm and is calculated (Sudraud [2], Somers [3]):
- The wine colour density (D_C):

$$D_C = A_{420} + A_{520} \quad (1)$$

- The wine colour hue (N_C):

$$N_C = \frac{A_{420nm}}{A_{520nm}} \quad (2)$$

- The wine colour intensity (I_C):

$$I_C = A_{420} + A_{520} + A_{620} \quad (3)$$

The absorbance measurement at 420 nm provides an estimate of the yellow brown pigments present in wine. The absorbance measurement at 520 nm provides an estimate of the anthocyanins and other red coloured compounds present in wine.
The quantitative determination of anthocyanins from the red wines aims to track the evolution of the phenolic ripening process of the grapes and the establishing of the anthocyanins content. This determination is made by the visible spectrophotometry and is based on the colour change of antocyanins function of pH (Ţârdea [1]). The absorbance variation for the antocyanins colour is measured, at two pH values, namely 0.6 and 3.5, compared with the distilled water. The measurements are taken at the wavelength of 520 nm, the absorbance of the samples being proportional to the antocyanins content.
The sulphur dioxide (SO_2) content was determined using volumetric method. The SO_2 content was assayed by titration with iodine solution. The main problems encountered in analysis of sulphur compounds in wine are low concentration levels and the highly reactive nature of these compounds (Mestres [4]).

3. RESULTS AND DISCUSSION

The colour of wine is the first sensory impression perceived in the glass during tasting. The depth of colour for the red wine is accepted as being correlated to quality. Thus, the deeper coloured red wines are normally considered of higher quality than their lighter coloured counterparts.

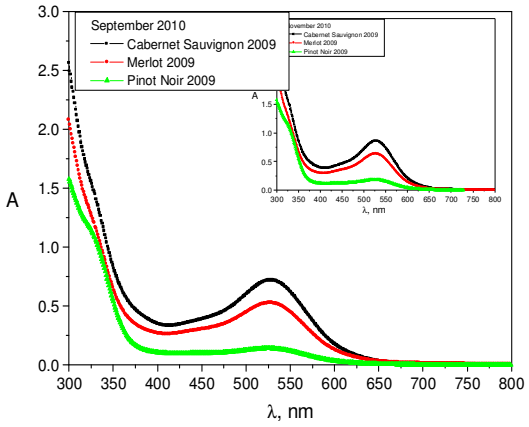

Figure 1. Absorption spectra of the young wines recorded at the bottle opening; Inset: after two months of the opening of the bottle

In basis of the methods described by Sudrand [2] and Somers [3], the absorption spectra for the three young wines (Figure 1) were recorded

and the colour parameters of wines (Table 1) were calculated.

Figure 2 shows the increased of the spectra intensity in the time for two months. This intensity increase for the absorption bands in time is consistent with results for the colour parameters of the wines showing a slight oxidation of their own.

Table 1. Colour parameters of the wines from Valea Calugareasca area

Wine	Month	D_C	N_C	I_C
Cabernet Sauvignon	September	1.04	0.48	1.14
	November	1.23	0.46	1.35
Merlot	September	0.78	0.51	0.86
	November	0.93	0.48	1.01
Pinot Noir	September	0.24	0.71	0.26
	November	0.29	0.65	0.32

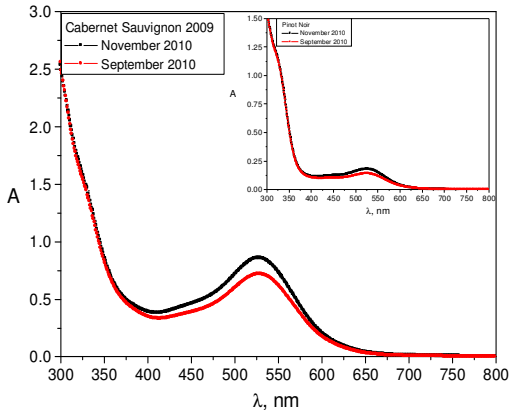

Figure 2. Absorption spectra of two wines, Cabernet Sauvignon and Pinot Noir (inset), recorded in the time for two months

As a result of the wine colour, the chemical compounds related to wine colour are of great importance and are continually investigated. Anthocyanins, a group of phenolic compounds, are primarily responsible for the red colour of grapes and wines (Singleton [5]).

The anthocyanin concentration of grapes, musts and red wines are highly correlated with wine colour intensity (Somers [3], Marais [6], Iland [7]).

Anthocyanins, pigments responsible for the red colour of grapes and wines, are located primarily in the lower epidermis of grape skins (Asen [8], Singleton [5]).

The red wines contain the monomers anthocyanins (anthocyanidins) monoglucosides and diglucosides. The monoglucosides anthocyanins predominate, containing between 200 and 900 mg/l of wine: malvidin 50-60 %, petunidin 10-15%, peonidin 8-10%, delphinidin 5-8% and cyanidin 1.5-3.5%. The diglucosides anthocyanins are missing or present in trace amounts, up to a maximum of 5-15mg/l. The hybrid wines contain only diglucosides anthocyanins, malvidin being the most representative (Favretto [9], Kong [10], Ţârdea [1]).

The anthocyanins are glycosidic compounds, polyhydroxy and/or methoxyl, characterized by a core of 2-phenylbenzopyrilium that are attached one or two sugar molecules (glucose, galactose, rhamnose). Usually, the sugar is glucose. Hydroxylation occurs at positions $3'$, $4'$, $5'$ and methoxylation at positions $3'$ and $5'$, most frequently at positions $5'$ and 7 (Figure 3) (Ţârdea [1], Mazza [11]).

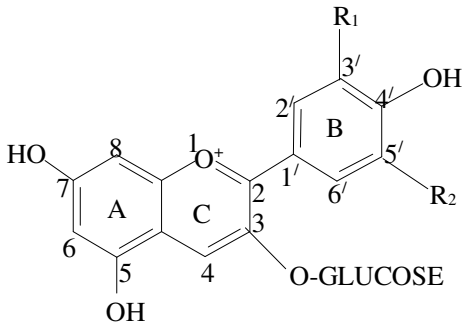

Figure 3. The anthocyanins structure (AC – core of benzopyrilium, B – phenyl rest, R_1 and R_2 – OCH_3, OH or H groups)

Anthocyanins are less soluble in water but soluble in alcohol, which is formed during the fermentation. In aqueous solution (the grape and the wine), they have two forms: the oxonium form (coloured) and the pseudobase form (colourless), caused by the oxygen atom from the benzopyrilium heterocyclic. Between the two forms (Figure 4) a balance is established, depending on the pH of medium. At acidic pH of wine (3 - 3.3), anthocyanins are in the equilibrium state between the oxonium

coloured form and the pseudobase colourless form. They are sensitive to oxidation and to protect the colour of the red wines, the sulphur dioxide (SO_2) is used yet from primary winemaking phase. When the free SO_2 in wine is lost, the wine regains its colour (Țârdea [1]).
In the young wines are prevalent the unacylates free anthocyanins, which give the wine a more intense colour. They quickly link at tannins, with formation of the addition complexes. In addition, in during the storage of wines, the anthocyanins undergo a series of reversible and irreversible changes that lead to a continuous decrease of their concentration in wine (Țârdea [1]).

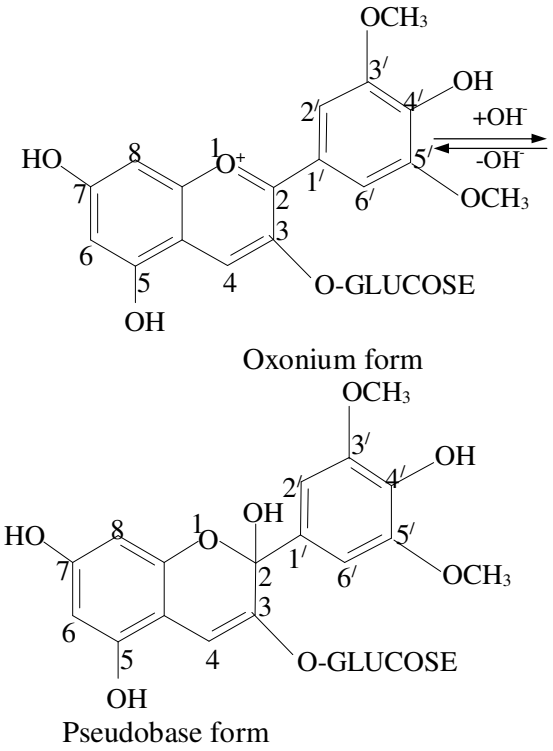

Figure 4. The forms of anthocyanins

During the vinification, SO_2 is primarily used for its antiseptic and antioxidative properties. The addition of SO_2 can result in the colour temporary reduction. This is the result of a reversible reaction between the red flavylium ion and sulphite (HSO_3^-) which forms a colourless sulphite-anthocyanin complex (Amerine [12]).

SO_2 decreases the anthocyanin polymerization in red wines (Dallas [13], Bakker [14]). Once formed, the polymerized anthocyanins or tanin-anthocyanin polymers are resistant to decolourization by SO_2 because the physical site of sulphite binding is the same site at which the polymerization reaction occur (Zoecklein [15]).
To obtain young red wines with good colour characteristics which will last during storage, addition of SO_2 at the moment of crushing is recommended (Gomez-Plaza [16-17]).
SO_2 protects the wines against the excessive browning during maturation (Bakker [14]).
The content in SO_2 and antocyanins obtained for three wines from Valea Călugărească area, Cabernet Sauvignon, Merlot and Pinot-Noir, is presented in Table 2.

Table 2. Content in SO_2 and anthocyanins of the wines from Valea Calugareasca area

Wine	Month	SO_2 total, mg/l	Anthocyanins, mg/l
Cabernet Sauvignon	September	168	568
	November	148	383
Merlot	September	120	487
	November	106	339
Pinot Noir	September	139	362
	November	117	138

The results obtained for the three wines from Valea Calugareasca area show a good correlation between the two parameters. Thus, in the same time with the decreasing of SO_2 content is produces the decreasing of anthocyanin content. Also, the colour intensity of wines increased.

4. CONCLUSIONS

The research clearly showed the existence of correlations between the anthocyanins content and SO_2 content, during the oxidation process of wine. It has been established that the anthocyanins and total SO_2 concentrations in wines are positively linked to the wine quality.
In addition, our study shows that it is possible to highlight the oxidation of the wine in time based on the colour measurements correlated with the anthocyanins and SO_2 content.

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