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STUDY OF THE ANTHOCYANIC POTENTIAL OF GRAPES VARIETIES FOR RED WINES IN DRANIC WINE CENTER

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Abstract

The Dranic plantation is one of the youngest in Dolj county and was founded in 2010 through the process of reconversion and restructuring of the wine sector in our country. Under the favorable ecologically conditions for viticulture in the Oltenia area, the varieties for red wines besides the superior potential of glucidic accumulation, have a remarkable ability for biosynthesis of anthocyanins. The chromatic structures of the anthocyanin extracts represented by the yellow, red and blue pigments are balanced, attractive and fully in line with current requirements. They are dimensioned by colour intensity values, but especially by the qualitative chromatic indicators: the colour tone and the proportions of the flavylium cations. This study may be the start for the suitability of this area for obtaining high-quality red wines.

Key words*: anthocyanin, grape maturity, red, wines, extractability, chromatic structure.*

INTRODUCTION

The Dranic plantation is one of the youngest in Dolj county and was founded in 2010 through the process of reconversion and restructuring of the wine sector in our country. In the absence of clear data from the literature showing the direct relationship between natural factors and the evolution of the red wine grape ripening process, this detailed study was needed. This study may be the start for the suitability of this area for obtaining high-quality red wines (Muntean et al., 2017).

Phenolics, such as flavonoids, phenolic acids, and tannins, are considered to be the main antioxidants in fruits and vegetables (Mnari et al., 2016).

Phenolic compounds, such as phenols, phenolic acids, flavonoids, tannins, and anthocyanins, have received considerable attention for their high antioxidant activity (Karakaya et al., 2001; Rice-Evans et al., 1996). Phenolic compounds are free radical scavengers because they are nucleophiles that inhibit lipid peroxidation and chelators of metal ions that induce oxidation (Han and Baik, 2008).

Anthocyanins, the pigments responsible for the red colour of grapes, are widely used to carry out classification and chemotaxonomic studies in flavonoid metabolism.

Anthocyanins are contained in the grape skin, except in the case of a few cultivars whose pulp is also pigmented. Thus, a close relationship can be expected between anthocyanin composition and visual appearance (Fernandez-Lopez et al., 1998). The International Office of the Vine plants (OIV) has a descriptor list for grape vine varieties and *Vitis* species which classifies the grape varieties in seven groups according to their external colour: 1 (green-yellow), 2 (pink), 3 (red), 4 (red-grey), 5 (red-dark violet), 6 (blue-black) and 7 (red-black) (OIV, 1988).

Anthocyanins are gradually accumulated in berry skins from veraison through grape ripening (Gomez-Plaza, 2006; Fournand et al., 2006) malvidin-3-glucoside being the most abundant anthocyanin in almost all red grape varieties. However, the anthocyanin concentration may decline just before harvest and/or during over-ripening (Rolle et al., 2011). The relationship between cell wall composition and extractability of anthocyanins from red grape skins was assessed in Tempranillo grape samples harvested at three stages of ripening (pre-harvest, harvest and over-ripening) and three different contents of soluble solids (22, 24 and 26 °Brix) within each stage (Hernandez-Hierro et al., 2014).

The extractability of anthocyanins from wine-grapes with different skin hardness at two different ripening stages was evaluated by Role et al (2009). Significant interactions between ripening stage and skin hardness were found in the composition of individual anthocyanins present in the extract.

Some researchers Romero-Cascales et al., in 2005, were studying the differences in anthocyanin extractability from grapes to wines according to variety. The anthocyanin concentration of *Vitis vinifera* L. cvs. 'Cabernet Sauvignon', 'Merlot', 'Syrah' and 'Monastrell' grape skins was determined together with anthocyanin extractability at the exact time of harvest (measured by an extractability assay based on the comparison of the anthocyanin concentration of two different solutions obtained after macerating the grapes for four hours at two different pH values). These data were compared with the anthocyanin concentration and chromatic characteristics of the resulting wines.

The purpose of this study was to investigate the evolution of anthocyanin content during grapes maturation and the degree of extraction in wines

MATERIALS AND METHODS

Grape and wine sample

This study was carried out with grapes of the three cultivars *Vitis vinifera* cv. 'Cabernet Sauvignon', 'Merlot' and 'Feteasca neagră' from the wine-growing center Dranic-Dolj.

Grape samples of three red cultivars (*V. vinifera* L.) were collected at full maturity (FM) and at different other date after full maturity, means FM+10 days and FM+15 days. The grapes was harvest at FM+10 days which corespond with technological maturity.

The wine was obtained under the same biotechnological conditions of red vinification which was SO_2 - 50 mg/l; ADY addition 15 g/hl; 7 days maceration time; maceration temperature 26-28^{0}C.

Determination of anthocyanins from grapes and wine, pigments structure and flavilium cation from grapes and also chromatic composition and intensity and tonality of wine was done.

These analyzes were conducted in 3 consecutive viticultural years, 2015, 2016 and 2017.

Anthocynins extraction from grapes

Grape anthocyanins determined by the method of Poissant Leon. An average sample of 50 grape berries, weighed than the skin are carefully detached from the grape pulp. In order to remove excess moisture, the skins were wiped with filter paper and dried in a hot air source.

Dry skins are powdered quartz fine sand after which they are passed into a flask with ground glass stopper by repeated washing with 1% HCl solution (approx. 10 ml concentrated HCl/liter). In order to extract anthocynins first wash fraction (50 ml) to be in contact with the skins to about 12 hours. The reafter, the filtered or centrifuged extraction liquid is brought to a constant volume of 200 ml by mixing and the fractions resulting from repeated acid addition and kept in contact with the extract for at least one hour.

After obtaining the skin sample and the anthocynins extract, the filtered extract is read on a 1 cm cuvette spectrophotometer at the optical density (OD) of 520 nm. The amount of anthocynins is determined on the basis of the formula:

$$mg/kg\ grapes = \frac{OD520 \times 22.76 \times 0.4}{berries\ weight} \times 1000$$

Anthocynins from wines

Anthocyanins in wine are determined with spectrophotometer by pH difference (method Ribereau Gayon - Stonestreet - 1968). The difference between the optical densities read at 520 nm of a solution at two different pH is proportional to the amount of anthocynins contains the wine. From the optical density of the solution of pH 0.6, the optical density of the solution of pH 3.5 is decreased, thus obtaining the PA. The concentration in anthocynins is determined from the calibration curve, based on the data, and the expression is expressed in mg/l.

The colour of red wines (Glories, 1984) is determined with a T 70+UV/Vis spectrometer PG Instruments Ltd. in the visible field at wave lengths of 420, 520 and 620 nm.

After reading the yellow component at 420 nm (attributed to tannins and anthocyanin

degradation products), the red component at 520 nm (attributed mainly to the free anthocyanins as favylium cations and to the polymeric red pigments) and the blue component at 620 nm (attributed to anthocyanin quinoidal bases and copigmentation derived from a non-covalent complex copigment - anthocyanin), the colour intensity (Ic), the colour tone (Tc) and the flavylium cation-brilliance of red (dA%) ratios are calculated according to the following formulas:

$$Ic = OD420 + OD520 + OD620$$

$$Tc = \frac{OD420}{OD520}$$

$$dA\% = \left[OD520 - \frac{OD420 + OD620}{2} \right] \times \frac{1}{OD520} \times 100$$

RESULTS AND DISCUSSIONS

The anthocyanic potential and the chromatic structure of the grapes of the main varieties for high quality red wines grown in the center of the Winery are listed in Table 1.

By its genetic nature, the histological structure of the berry and the ability to harness the natural conditions superior to the 'Cabernet Sauvignon', accumulate the highest anthocyanin content, at the technological maturity ranging from 1394 - 1493 mg/kg of fresh berries. The second place is occupied by the Merlot variety, containing a concentration in anthocyanin ranging from 1205 to 1273 mg/kg of fresh berries. Modest contents of anthocyanin accumulates in grapes of 'Feteasc㠠neagră' variety being below 1200 mg/kg of fresh berries.

The chromatic structure, given by the proportions of the different categories of pigments, varies from one species to another and from one year to the next. Thus, in the anthocyanin complex of 'Cabernet Sauvignon' grapes, the yellow-orange pigments have the lowest values among the study varieties (31.5 - 33.9%) while the blue pigments are the most abundant (9.2 - 9.7%). The largest proportions of red and blue pigments have been accumulated, and the intensity of the anthocyanins extracts from the 'Cabernet Sauvignon' grapes is explained, as well as the values of the parameter for brilliance for red is high (dA% - 76.5 - 79.3). The 'Feteasc㠠naegră' variety showed the lowest anthocyanin content and the highest yellow pigments (39.5-41.7), while the blue component showed the lowest value (8.1-8.9%).

On the other hand Merlot variety, showed an intermediate characteristics, achieving a balanced chromatic structure with positive visual valences.

In the three years of study, the phenolic maturity was performed after full maturity, at about 10 days, between 15.X. and 25.X. for the 'Cabernet Sauvignon' variety, between 10.X. and 20.X. for the 'Merlot' variety. The maximum amount of anthocyanins in grapes does not correspond to the maximum amount of anthocyanins in wines. Correlated with phenolic maturity, the phenomenon is explained by the increase of extracts of anthocyanins from the skins to the over ripening of the grapes. At over-ripening, anthocyanin content in berries is lower, but wine has higher anthocyanin content.

Table 2 shows the evolution of anthocyanin content in grapes and their degree of extraction at full maturity and over-ripening in 2017, a year of excessively high temperatures.

In all 3 varieties observed, although total anthocyanin content decreases continuously, it increases, in turn, its extraction due to the degradation of the walls of the anthocyanin blasts of the hypodermis, under the action of its own pectolytic enzymes.

Thus, the proportion of extracted anthocyanins increases from the 41.5% to 54.1% ('Cabernet Sauvignon'), from the 41.7% to 52.5% ('Merlot') and from the 40.8% to 53.5% ('Feteasc㠠neagră').

In the wines obtained in 2017 the chromatic structure of the obtained wines has a different configuration (Table 3). As far as the over ripening of the grapes - raw material, in the anthocyanic complex extracted under the action of biotechnological factors, uniformly applied, they increase the proportions of yellow and red pigments and decrease the proportions of blue pigments, which is still a qualitative advantage of wine coloring, even when younger.

Values optical density at 420 nm wavelengths, 520 nm and 620 nm specific to different types

of pigments used to calculate the qualities chromaticity wines, listed in Table 3 reveals differences in some cases quite important. They are mostly of the genetic nature of variety and less of primary winemaking technology.

Yellow component showed the lowest value in wines produced from 'Cabernet Sauvignon', and the largest values in wines from 'Feteasca neagră' while the red component showed the highest values in wines of 'Cabernet Sauvignon' and the lowest value in wines of 'Feteasca neagră'. The blue component of wines is well and positively correlated with the red component.

An accurate image of the quantity and quality of material coloured wine is obtained from: absolute content of anthocyanins, the participation percentage of different types of pigments and values qualities chromaticity for their definition being considered optical density values (referred to in Table 4).

Table 1. Anthocyanin content and chromatic structure in grapes, technological maturity (Average 2015-2017)

Varieties	Antocyanin, mg/kg fresh berries		Yellow pigments OD 420 nm		Red pigments OD 520 nm		Blue pigments OD 620 nm		Brilliance of red, dA %	
	Variation	Average	Variation	Average	Variation	Average	Variation	Average	Variation	Average
Cabernet Sauvignon	1394.0 - 1493.0	1443.5	31.5-33.9	32.7	56.8-59.0	57.9	9.2-9.7	9.4	76.5-79.3	77.9
Merlot	1205.0 - 1273.0	1239.0	34.5-35.8	35.1	54.6-56.8	55.7	8.9-9.5	9.2	74.6-75.5	75.0
Feteasca neagră	1099.0 - 1140.0	1119.5	39.5-41.7	40.0	49.5-53.4	51.4	8.1-8.9	8.5	72.5-74.2	73.3

Table 2. Anthocyanin content of grapes and their degree extraction, depending on the harvesting period – 2017

Varieties	STAGE OF MATURITY								
	Full maturity (FM)			FM + 10 days			FM + 15 days		
	Total anthocyanin, mg/kg of fresh berries	Extractable anthocyanin, mg/kg of fresh berries	Degree of extr., %	Total anthocyanin, mg/kg of fresh berries	Extractable anthocyanin, mg/kg of fresh berries	Degree of extr., %	Total anthocyanin, mg/kg of fresh berries	Extractable anthocyanin, mg/kg of fresh berries	Degree of extr., %
Cabernet Sauvignon	1498.0	623.2	41.5	1493.0	744.5	49.8	1469.0	795.4	54.1
Merlot	1281.0	534.7	41.7	1273.0	598.0	46.9	1192.0	625.8	52.5
Feteasca neagră	1146.0	468.5	40.8	1140.0	584.6	51.2	1132.0	605.8	53.5

Table 3. The optical densities of red wines varieties 2017

Varieties	OD 420 nm (yellow pigments)	OD 520 nm (red pigments)	OD 620 nm (blue pigments)
Cabernet Sauvignon	0.489	0.832	0.140
Merlot	0.492	0.737	0.125
Feteasca neagră	0.522	0.658	0.115

Table 4. Chromatic composition of red wines 2017

Varieties	Composition of pigments %			Intensity of colour (Ic)	Tonality of colour (Tc)
	Yellow pigm. (OD 420 nm)	Red pigm. (OD 520 nm)	Blue pigm. (OD 620 nm)		
Cabernet Sauvignon	33.35	57.05	9.60	1.46	0.58
Merlot	36.50	54.30	9.20	1.35	0.67
Feteasca neagră	40.30	50.80	8.90	1.29	0.79

Data on participation of various types of pigment in composition of coloring matters and levels of characteristics chromatic of complex anthocyanins, show structures chromatic very

favorable to all wines and proportions of different types of pigments are able to provide levels of color corresponding total over the claims current.

CONCLUSIONS

The natural conditions that are particularly favorable to the vineyards in the Dranic vineyard and significantly mark the anthocyanin - rich content of the grapes of the 'Cabernet Sauvignon', 'Merlot' and even of the native 'Fetească neagră' variety.

During the over-ripening process of grapes - a condition that is generally required for the production of high class red wines, anthocyanin content decreases with the progress of process, but in the same time it was observed an increase of the extraction degree and, on the other hand, chromatic characteristics of the resulted wines are improved substantially.

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