ANTHOCYANIN MARK OF LOCAL VARIETIES OF RED WINES

AMPRENTA ANTOCIANICĂ A VINURILOR ROŞII DIN SOIURI AUTOHTONE

OBADĂ Leonora[1], RUSU E.[1], CIBUC Mariana[1], GOLENCO Lidia[1]
e-mail: oenologie_vdo@mail.ru

Abstract. *Significant for red wines is their colors, which participate in the formation of phenolic compounds extracted from the peel, the main anthocyans. Research interest the profile of anthocyans of red wines made from local varieties in relation to cosmopolitan Merlot variety. Research have undergone red wines produced from 11 local varieties (Fetească Neagră, Rară Neagră, Codrinschi etc.), of cosmopolitan vintage Merlot variety harvest 2011. Anthocyans profile was determined by high performance liquid chromatography (HHPC).For each chromatogram were identified and calculated the relative proportions of anthocyans mono glycoside following: malvidol, petunidol, peonidol, delfinidol and cianidol. Similarly, was calculated the amount of anthocyans glycosides and the amount of free and of acylated anthocyans. It was found that red wines from local varieties are distinguished, as they over wine - Merlot witness through a different of anthocyans profile. Color of local varieties of red wines subject to investigations consists mainly of anthocyanins glycosides, when the wine Merlot is dominated by acylated anthocyanins and free forms, which are more stable and contribute to wine color intensity.*
Key words: *anthocyanin mark, chromatogram, local varieties, monoglicozide*

Rezumat. *Important pentru vinurile roşii este culoarea lor, la formarea căreia participă compuşii fenolici extraşi din pieliță, principalii fiind antocianii. Prezintă interes cercetarea profilului antocianilor vinurilor roşii obținute din soiuri autohtone în raport cu soiul cosmopolit Merlot. Au fost supuse cercetărilor vinurile roşii obținute din 11 soiuri autohtone (Fetească Neagră, Rară Neagră, Codrinschi ş.a.), soiul cosmopolit Merlot din recolta anului 2011. Profilul antocianilor a fost determinat prin metoda cromatografiei lichide de înaltă performanță (HHPC). Pentru fiecare cromatogramă s-au identificat şi calculat proporțiile relative ale antocianilor monoglicozidici ai: malvidolului, petunidolului, peonidolului, delfinidolului şi cianidolului. La fel, s-a calculat suma antocianilor glicozilați, precum şi suma antocianilor liberi şi acilați. S-a constatat, că vinurile roşii din soiurile autohtone se disting între ele, precum şi în raport cu vinul martor Merlot, printr-un profil al antocianilor diferit. Culoarea vinurilor roşii din soiuri autohtone supuse investigărilor este formată cu preponderență din antociani glicozilați, pe când cea a vinului din soiul Merlot este dominată de formele de antociani acilați şi liberi, care sunt mai stabile şi contribuie la intensitatea culorii vinului.*
Cuvinte cheie: *amprenta antocianică, cromatogramă, soiuri autohtone, monoglicozide*

[1] Scientifico-Practical Institute of Horticulture and Food Technologies, Chişinău, R. Moldova

INTRODUCTION

Color is an important caracteristics of red wines. The phenolic compounds extracted from skin by maceration-fermentation process, wich main of them are anthocyanins give to the wine red color. However, extracted anthocyanins are not stable, they participate in various reactions, as a result their content decreases in the process of the storage of wine. In the first year of storage anthocyanins content is halved after that they become stable. (Pomohaci et al., 2001). The structure of anthocyanins consists of anthocyanidins, anthocyanins that form the coloring matter and carbohydrates. In grapes, must and wine two anthocyanins are met, which are distinguished from each other by the number of hydroxyl groups on the benzene ring side, known as cyanidin and delphinidin, and their methyl esters - peonidin, petunidin and malvidin.

Anthocyanidins are relatively unstable substances, some of them combined with sugars, as a result the dynamic balance is created between the two nonglycosylated forms (anthocyanidins) and the glycosylated (anthocyans). Depending on the number of carbohydrate residues are known anthocyanins monoglycoside and diglycoside. Both categories of anthocyanins can contain in their molecule acylated sugars with one, rarely two scraps of p-coumaric acid, p-hydroxybenzoic acid, p-hydroxy cinnamic acid or acetic acid (Cotea D. V. et al., 2009).

In other words, the formation of color of grapes and red young wine participate various forms of anthocyanins - anthocyanidins, antocyanosides and acylated anthocyanins. Accumulation of anthocyanins in grapes is influenced by many factors, the main being the biological capacity of the variety and climatic conditions of the year (Cotea D. V. et al., 2009). On the other hand, according to Coşofreț et al. (2005), identification the variety from which a red wine can be producted is made through relationships of anthocyanins which is free form or as aglycone, which are specific to each variety. In this context, research interest fingerprints of anthocyanins of red wines made from local red varieties against Merlot cosmopolitan variety.

MATERIAL AND METHOD

The researches was conducted on experimental red dry wines made from indigenous grapes varieties Seină, Rară Neagră, Brează, Negru de Akkerman, Ciorcuță neagră, Bătută neagră, Fetească neagră, Negru de Căuşeni, Kopceak, Busuioacă de Bohotin, Codrinschi (Stăuceni) and Merlot cosmopolitan variety, harvested from the central region of the Republic of Moldova and the variety Codrinschi - from the South of the Republic (Pleşeni). Experimental samples and control sample were prepared in the wine season of 2011 in the department microvinification of the Scientific- Practical Institute of Horticulture and Food Technologies using classic technology of fermentation maceration of the pulp at temperature 25-28 ° C.

Anthocyanins profile in the studied wine samples was determined by high performance liquid chromatography (HPLC) method MA-MD-AS315-11-ANCYAN in accordance with the technical regulations "Analytical methods for the wine production" (2011). Chromatograms were recorded using the chromatograph

Packard1100 Hewlett-type UV-VIS detector, with a Li Chrospher 100 RP 18 separation column.

For every chromatogram the relative proportions of following anthocyanins: delphinidin-3-monoglycoside, cyanidin-3-monoglycoside, malvidin-3 ,5-diglycoside, petunidin-3-monoglycoside, peonidin-3-monoglycoside , malvidin-3-monoglycoside was detected and calculated. Similarly, the amount of glycosylated anthocyanins and the amount of free and acylated anthocyanins for each wine sample are identified and then calculated.

RESULTS AND DISCUSSION

Table 1 reports the values of percentage of anthocyanins in red wines made from indigenous varieties and variety Merlot, which are calculated on the base of the obtained chromatograms. Chromatograms of colorants in wines producted from local varieties Fetească neagră, Codrinschi (Pleşeni) and control sample wine Merlot, are shown in Figure 1 (as an example).

Table 1

Values of reports of anthocyanins in wines made from black local varieties and cosmopolitan variety Merlot harvest of 2011,% of total

No.	Variety name	delphinidin-3-monoglycoside	cyanidin-3-monoglycoside	malvidin-3 ,5-diglycoside	petunidin-3-monoglycoside	peonidin-3-monoglycoside	malvidin-3-monoglycoside	∑ antocyanins free and acylated	∑ glycosylated antocyanins
1	Seină	2,7	<0,5	<0,5	5,6	4,6	64,5	21,4	78,4
2	Rară neagră	2,4	<0,5	<0,5	5,6	2,5	70,0	17,4	81,5
3	Brează	9,3	1,2	<0,5	12,7	4,7	51,7	18,4	80,1
4	Negru de Akkerman	2,2	0,5	0,6	1,9	3,5	36,4	46,8	45,1
5	Ciorcuță neagră	2,3	1,4	<0,5	4,6	2,0	59,4	28,9	70,2
6	Bătută neagră	1,9	<0,5	<0,5	3,4	3,6	52,9	37,1	62,8
7	Merlot	4,6	<0,5	<0,5	4,8	2,8	34,9	48,1	48,1
8	Fetească neagră	6,7	1,3	<0,5	11,2	5,3	53,6	17,6	78,6
9	Negru de Căuşeni	8,9	<0,5	<0,5	9,9	2,7	50,6	22,6	73,1
10	Codrinschi (Stăuceni)	6,9	1,2	2,8	6,8	2,9	48,3	21,4	68,9
11	Codrinschi (Pleşeni)	6,6	1,5	2,7	6,4	3,2	48,1	29,8	68,5
12	Kopceak	7,8	0,8	0,9	10,1	5,2	55,7	15,9	80,5
13	Busuioacă de Bohotin	2,3	2,2	1,6	2,9	10,5	56,2	20,5	75,7

Research shows that investigated wines are distinguished among themselves and in comparison with cosmopolitan variety Merlot, with a different profile of glycosylated anthocyanins. Malvidin-3-monoglycoside is the main component of anthocyanins determined in experimental wines and in cosmopolitan variety Merlot of harvest of 2011 and percentage ratio in sum of anthocyanins varies greatly depending on the variety. Thus, in wine Rară neagră

this index value consists 70.0%, in the wine Seină - 64.5%, Ciorcuță neagră - 59.4%, in Busuioacă de Bohotin - 56.2% and wine Kopceac-55,7%. Lower values of this index were determined in the samples of wine Negru de Akkerman (36.4%) and Codrinschi (48.3%) produced in both regions.

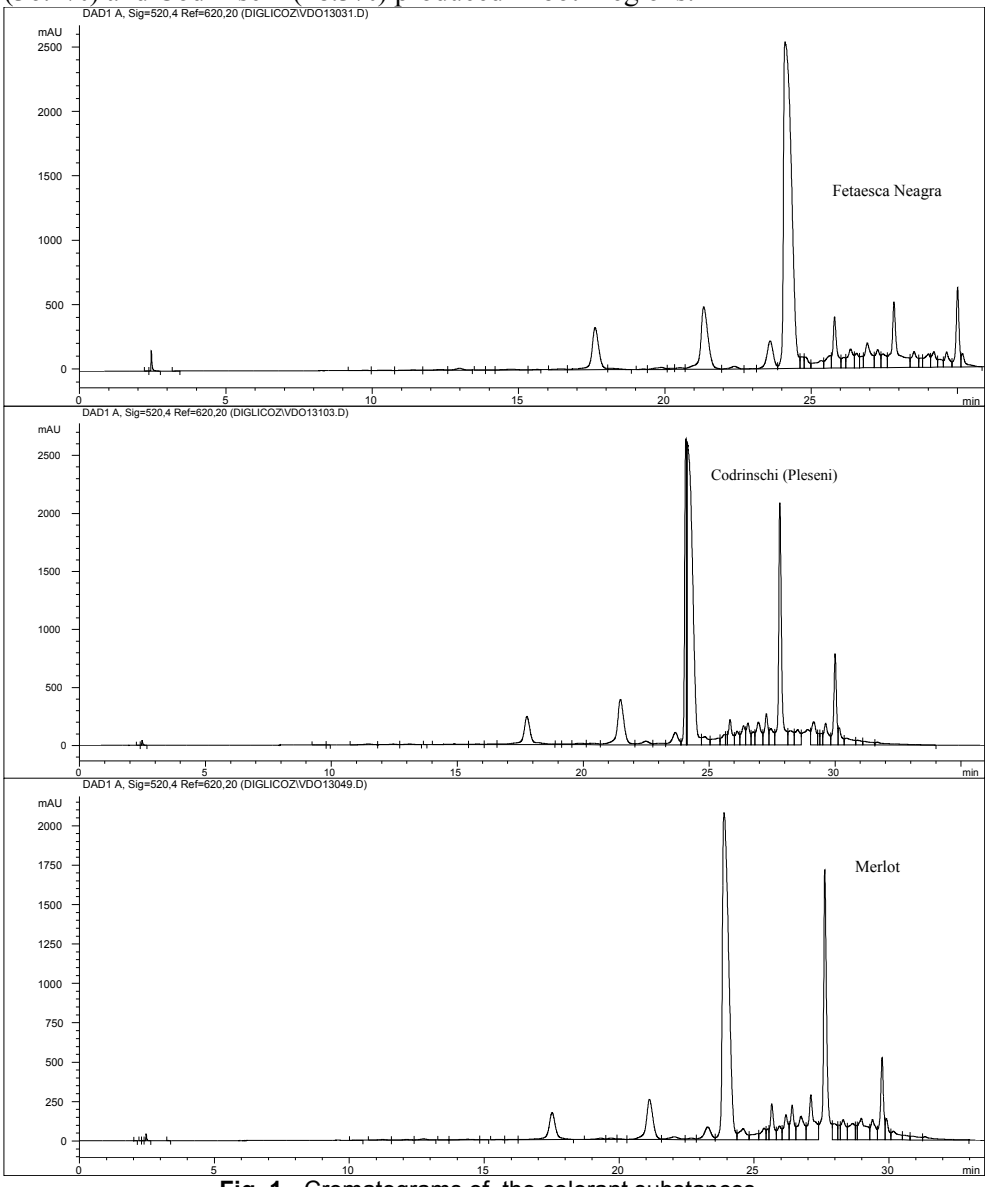

Fig. 1 - Cromatograms of the colorant substances

In the control sample Merlot this index consists 34.9%.

Besides malvidin-3-monoglycoside a significant share in creating the color of red wines has petunidin-3-monoglycoside. Higher percentage values of this compound were determined in wine Breazăă (12.7%), Feteascăă neagră (11,2%),

Kopceak (10,1%) and Negru de Căuşeni (9,9%). In wines Seină and Rară neagră the values of petunidin -3-monoglycoside consists 5.6% and in the variety Codrinschi - 6.8% and 6.4% in the Central and South region respectively. In other samples this compound varies between 1.9% and 4.8%.

In the control sample wine Merlot petunidin-3- monoglycoside value ratio is 4.8% and is lower in comparison with most experimental wines.

It is interesting that the content of the anthocyanin peonidina -3-monoglycoside in wines from local varieties varies less than the petunidin -3-monoglycoside. The percentage values of this compound in studied wine is between 2.0 and 4.7%, excluding wines Kopceac, Fetească neagră and Busuioacă de Bohotin, which has higher levels of peonidin- 3-monoglycoside - 5.2%, 5.3% and 10.5%, respectively. In the cosmopolitan wine Merlot the percentage of peonidin-3-monoglycoside is 2.8%, ranking close to the lower limit of the content of this compound in experimental wine samples.

Higher values of delphinidin-3-monoglycoside were identified in wine variety Brează (9,3%), Negru de Căuşeni (8,9%), Kopceak (7,8%), Codrinschi in both regions (6.6 % -6.9%) and Fetească neagră (6.7%). The lowest values of this compound (2.3-2.7%) were detected in wines Negru de Akkerman, Busuioacă de Bohotin, Ciorcuţă neagră and Seină. In the cosmopolitan wine Merlot the percentage of delphinidin-3-monoglycoside is small, just like the last named varieties, and it is 2.8%.

The percentage of malvidol-3 ,5- diglycoside in investigated wines is below 0.5%, except for wine Codrinschi in which this index has higher values (2.8%). The quantitative determination of the compound was found up to 1.4 mg / L, which is much less than the maximum allowable value.

According to the data presented in table 1 can be concluded that the amount of glycosylated anthocyanins is very different and depends on the used grape variety. The highest percentage of glycosylated anthocyanins amount is recorded in wine Rară neagră -81.5% and varieties Brează and Kopceak - about 80%. The higher values of the sum of glycosylated anthocyanins are inregistrated in wine Fetească neagră -78.6%, Seină - 78.4% , Busuioacă de Bohotin - 75.7%, Negru de Căuşeni - 73.1% and Ciorcuţă neagră - 70.1%

As regards to the samples of wine Codrinschi, content in anthocyanins glycosylated is 68.9% and 68.5% for both regions. Of all the studied wines lowest value of glycosylated anthocyanins has wine Negru de Akkerman -45.1% and this value is closer to wine sample Merlot from cosmopolitan variety - 48.1%.

Based on the presented data it can be concluded that the formation of color of wine made from variety Merlot participate less glycosylated anthocyanins. It is predominantly acylated forms, as well as free anthocyanins. However, it is known that acylated anthocyanins are beneficial for color quality of red wines (Cotea D. V. et al., 2009). Process of acylation with glucosydic residues, particularly hydroxycinnamic acids increases the stability of anthocyanins and its ability dye molecule, a phenomenon known as copigmentation. In this context, the analysis showed that the amount of the percentage ratio of the sum of free and acylated

anthocyanins in Merlot wine sample is 48.1% and is higher than in all experimental wines. Among investigated black varieties, wine produced from Negru de Akkerman variety is highlighted by a value closer to witness 46.8%, followed by Codrinschi from South -29.8%. The lowest values of this index were detected in wines Kopceak - 15.9%, Rară neagră -17.4% and Fetească neagră - 17.6%. We assume that this is explained by the greater intensity of the color of the wine from Merlot variety, and and consequently its stability. Indigenous varieties of wine from the mentioned variety Codrischi (Pleseni), which differs from the others by a rich and intense color.

CONCLUSIONS

1. Comparative analysis has shown that the anthocyanin fingerprint of red wines produced from local varieties of the crop of 2011 are distinguished between them, just as they witnessed over wine made from Merlot.

2. It was found that most wines from indigenous varieties are distinguished by the highest percentage values of malvidine, peonidine and delphinidin monoglycosides than Merlot.

3. In the color formation of wine of local grape varieties are involved mainly glycosylated anthocyanins, while the Merlot wine color formation - forms of free and acylated anthocyanins.

REFERENCES

1. **Coşofreț S., Niculaua M., Odăgeriu Gh., Cotea V.V., Zamfir C**., **2005 -** *Cercetări asupra modificării profilului antocianilor la vinul Fetească neagră în urma unor tratamente de limpezire* . Lucrări ştiinţifice USAMV Iasi, seria Horticultura, vol. I (48).
2. **Cotea D.V., Zănoagă V.C., Cotea V.V., 2009 -** *Tratat de oenochimie* . Editura Academiei Romane, Bucureşti.
3. **Pomohaci N., Cotea V. V., Stoian V., Năml**o**şanu I., Popa A., Sîrghi C., Antoce Arina, 2001 -** *Oenologie. Vol.II. Îngrijirea, stabilizarea şi îmbutelierea vinurilor. Construcţii şi echipamente vinicol.* Editura Ceres, Bucureşti. 399 p.
4 *** - Reglementarea tehnică "*Metode de analiză în domeniul fabricării vinurilor*", aprobată prin Hotărîrea Guvernului Republicii Moldova nr.708 din 20 septembrie 2011, Monitorul Oficial al Republicii Moldova nr.164-165 din 04.10.2011