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DIVERSIFICATION USING ASSORTMENT OF LOCAL VARIETIES OF RED WINES

EMIL RUSU¹, OBADA LEONORA², GAINA BORIS³, GROSU OLGA⁴

Abstract: *The assortment of wines produced in Moldova is currently dominated by cosmopolitan varieties, mainly of the French. Global wine market study has shown that consumers are more attracted to wine-surprise, unknown. In this context many countries have resorted to valorisation of indigenous varieties and new varieties of selection. Since ancient times an assortment of vine varieties adapted to local conditions has been created in Moldova. Unfortunately, in the 40's and 50's of last century, with the collectivization was emphasized on European varieties spreading, local varieties being forgotten. Taking into account all mentioned, research of 13 local red varieties for industrial purposes have started. In terms of microvinification according to classical technology, experimental wines were produced, the organoleptic, physico-chemical composition, including content phenolic compounds and anthocyanins profile were determined. Methods for analysis recommended by the OIV were used and the profile of anthocyanins in wine samples studied using high performance liquid chromatography method (HPLC) was determined. The research results showed that the dry red wines made from indigenous varieties are distinguished by different content in phenolic substances and anthocyanins. On the research basis 4 grape varieties (Fetească neagră, Rara neagră, Negru de Căușeni and Codrinschi) for quality dry red wines production were recommended.*

Keywords: *local varieties, anthocyanins, phenolic compounds, physico-chemical composition, anthocyanin profile.*

INTRODUCTION

As a result of the policy pursued by the competent bodies of the Soviet period, Moldova inherited an assortment of grape varieties. Grapes grown mainly of classical French and from clones of these varieties such as Cabernet Sauvignon, Merlot, Pinot noir, etc. . From such varieties it is difficult to create a Moldovan national symbol of red wine.

In the current tough competition in the wine market, several countries promote wines from indigenous varieties. An example may serve Georgia with Rkatsiteli and Saperavi, Bulgaria - Mavrud, Rubin and Melnik, Romania - Fetească neagră and Tamâioasa românească, Azerbaijan - Şirvanşah and Baian Sirei [1,2,3].

In some countries, climate change of recent years have led to an increased focus on attracting local clones that are adapted to local conditions and ensure quality wines [4].

For more perspective and promising Russian Federation is considered indigenous varieties Crasnostop zolotistîi, Ţîmleanschii ciornîi, Plecistic, Sibircovîi [5]. French consultants from Krasnodar region, Russian Federation, believe that a third of the vineyards must be established with native varieties [6]. About increasing interest in local varieties mentions British oenologist Djensis Robinson [7]. Portuguese oenology aim to promote local varieties blended with international [8]. In the current climate and soil, native varieties managed to flaunt November virtues, reaching that in good years even exceed quality wines made from varieties recognized worldwide [9].

Note that in the not too distant period in Moldova assortment consisted of native varieties: Rara neagră, Plăvaie, Galbenă, Zghihara, Batuta neagră, Ţiţa capreai, Pasareasca, Cabasma, Fetească neagră and others. Many local varieties such as Rara neagră, Fetească neagră had a profound influence on the country's history and created the typical wine vineyards.

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At the moment local varieties, except for some practically no longer used in the wine industry. Currently in ampelographic collection of IȘPHTA are 41 varieties, including 10 varieties with red grapes.

Although Moldova has some native varieties tomatoes, which are invaluable, unfortunately, they have not been subject to thorough research regarding the potential phenolic substances and coloring efficient processing technology grapes study the dynamics of phenolic substances and coloring stage and maturing wine storage. The purpose of the research is highlighting the existing assortment of grape varieties indigenous black grain to produce red wines.

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MATERIAL AND METHODS

For research were used 10 varieties of grapes indigenous from the collection IȘPHTA namely: Rara neagra, Breaza, Kopceak, Batută neagră, Seina, Feteasca neagra, Ciorcuța neagra, Negru de Akkerman, Negru de Căușeni. Here was added Codrinschi, relatively young local variety, cultivated in the south. For experimental variations as a control was used Merlot, grown on plantations Institute (wine region Centre).

From a climate perspective, 2011 was characterized by the following indicators: amount of active temperatures - 3428 °C, rainfall - 349 mm. The grapes were performed following measures: carbohydrate content, tirabili acids, phenolic substances and coloring substances.

Processing and obtaining samples of wine grapes was made after the classical scheme for the production of red wines: sulphite pulp dose 70-75 mg / kg total SO₂; fermentation maceration at 25-28 °C, sulphite wine yeast pulled off dose of 20-25 mg / L SO₂ free form. The wine samples obtained were determined the main physical and chemical indicators: alcohol, sugar, titratable acidity, volatile acidity, pH, phenolic substances, antocians, non-reducing dry extract being used standard methods; total phenolic substances - with the Folin-Ciocalteu reagent; antocians by method OIV. After three months samples were subjected wine organoleptic assessment.

Profile of anthocyanins was determined by high performance liquid chromatography (HPLC) method MD-MA-AS315-11 ANCYAN. The chromatograms were recorded at Hewlett-Packard 1100 chromatograph with UV-VIS detector type using Li Chrospher separation column 100 RP 18.

RESULTS AND DISCUSSIONS

Fig. 1 shows the results of investigation of titratable acids and glucides during maturation of black grapes in local varieties. From the results it can be concluded that indigenous varieties differ in different storage capacities of glucides content and reducing organic acids. In investigations with a low potential for accumulating glucides are characterized by Batuta neagra (155g / L), Negru de Akkerman (164 g / L) and Breaza (190g / l). In other varieties glucides varies between 197-230 g / L. Thus, the technological maturation in Fetească neagra, Rara neagra, Kopceak and Codrinschii content of the glucidea was 227, 217, 213 and 230g/L, the values given in the reference to control variety or higher (218 g / L). Referring to titratable acidity, that varieties containing low in glucides have also the lowest values of titratable acid content, which varies between 5.5 and 6.4 g / L. Other

varieties have a titratable acid content, which varies between 7.0 and 8.8, with the exception of black variety Rara neagră, which has the highest value of this index - 9.2 g / L.

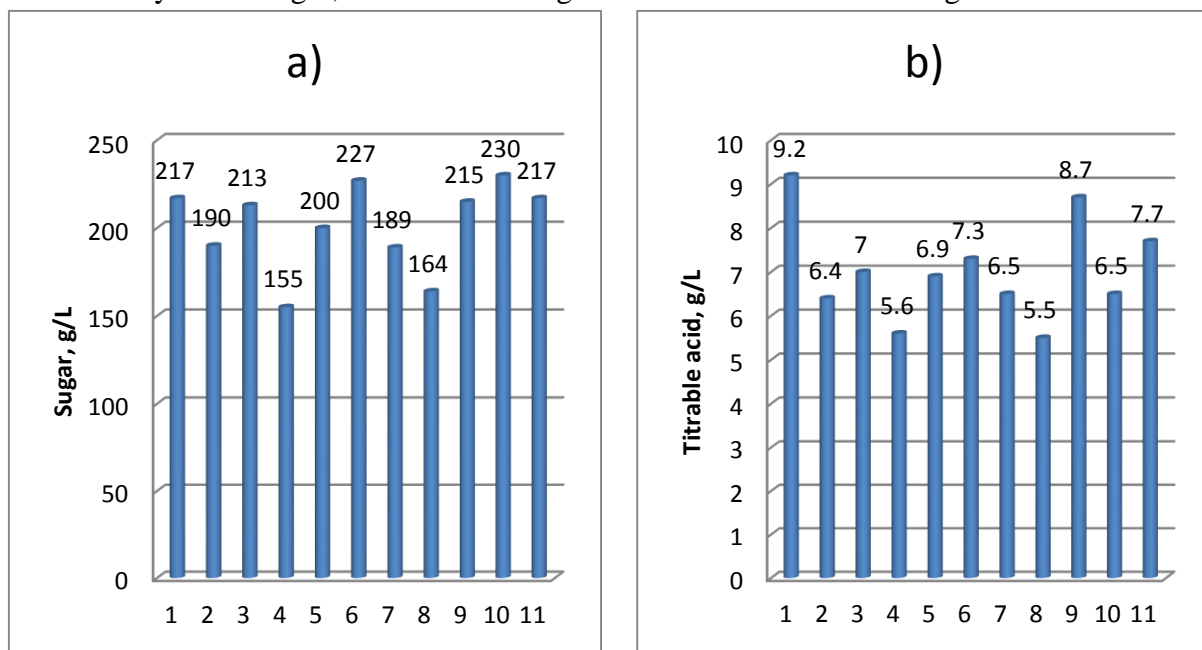


Fig. 1 The sugars (a) and titratable acids (b) local varieties at technological maturation stage.

Caption: 1-Rară neagră; 2-Breză; 3-Kopceak; 4-Bătută neagră; 5-Seina; 6-Fetească neagră; 7-Ciorcuță neagră; 8-Negru de Akkerman; 9- Negru de Căușeni; 10- Codrinschii; 11- Merlot.

Figure 2 presents data on phenolic substances and anthocyanin content in local varieties.

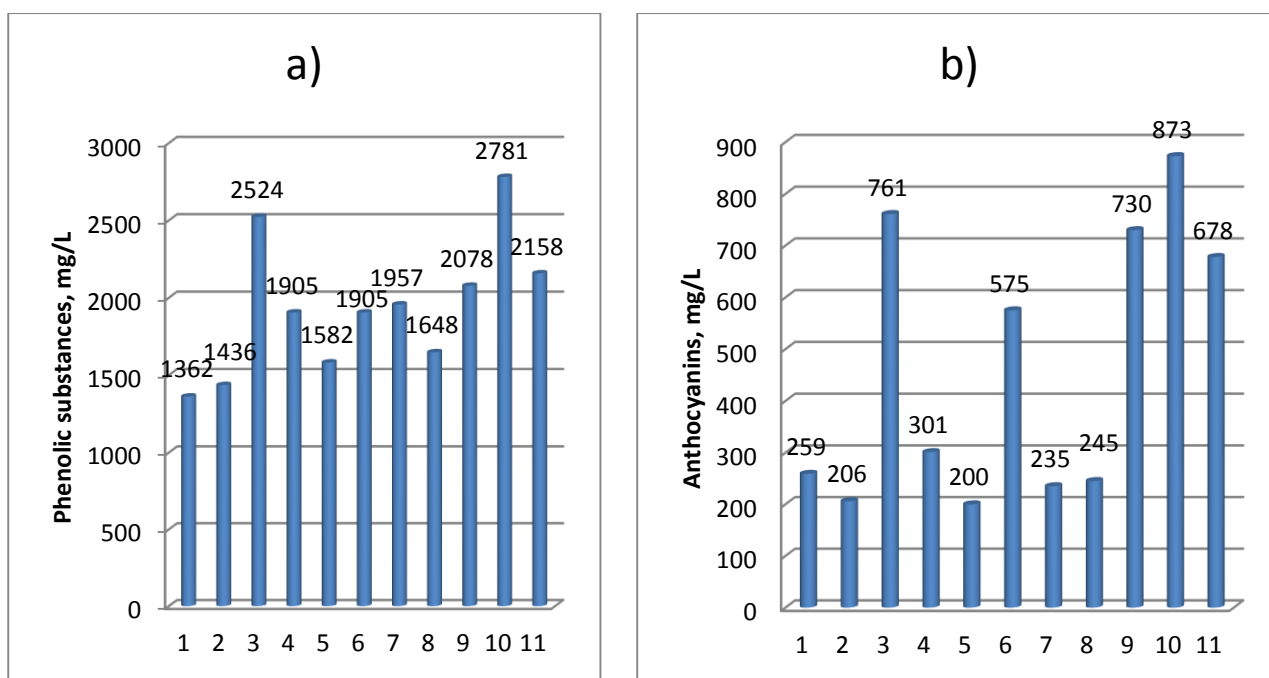


Fig.2 content in phenolic substances (a) and anthocyanins (b) local varieties at technological maturation stage.

Caption: 1-Rară neagră; 2-Breză; 3-Kopceak; 4-Bătută neagră; 5-Seina; 6-Fetească neagră; 7-Ciorcuță neagră; 8-Negru de Akkerman; 9- Negru de Căușeni; 10- Codrinschii; 11- Merlot.

The research results show that local varieties are characterized with very different potential of phenolic complex.

After the content in phenolic substances and coloring substances are placed as follows:

- coloring content below 300 mg/L and phenolic substances below 1600 mg/L: Ciorcuță neagra - 235/1957 mg/L; Negru de Akkerman - 245/1648 mg/L; Rara neagra - 259/1362 mg/L; Breaza - 206/1436 mg/L; Seina - 200/1582 mg/L.
- Average content (colored substances 300-500 mg/L and phenolic substances - 1600 to 1900 mg / L: Batuta neagra - 301/1905 mg/L.
- Containing more (coloring more than 500 mg/L and phenolic substances more than 1,900mg/L): Codrinschii - 873/2781 mg/L; Negru de Căușeni - 730/2078 mg/L; Fetească neagra - 575/1905 mg/L; Kopceak - 761 / 2524 mg/L.

After complex phenolic only varieties Kopceak, Negru de Căușeni, Feteasca neagra and Rara neagra (wine region South) indicated close to the control - in 2158 and 678 mg/L, and the variety Codrinschii is characterized by the highest values - 2780 mg/L phenolic substances and 870 mg/L anthocyanins.

Table 1 presents physico-chemical indexes of red wines made from indigenous varieties, harvest of 2011. The data presented in Table 1 may be mentioned that red wines from indigenous varieties have a high alcohol between 12.0 and 14.9% vol., except those produced from varieties Batuta neagra (9.5% vol.) and Negru de Akkerman (9,7 % vol.). Titratable acids in the wine investigated ranges between 6.1 and 9.4 g/L, the lowest value recorded in Seina wine, and the highest in Negru de Căușeni wine. The pH values vary from 3.2 up to 3.62. Residual sugar content, although high alcohol level not exceeding 2.1 g/L and is below the maximum allowed for red wines.

Tabelul 1 Physico-chemical indices in red wines made from indigenous varieties and classic variety – control, the harvest of 2011

Nr. d/o	Name of the variety and variant	Alcohol, % vol.	Sugar, g/L	Titrate acid, g/L	Volatile acid, g/L	pH	Phenolic substance, mg/L	Anthocyanins, mg/L	Dry nonreducing extract, g/L	Note organoleptic, points
1	Rara Neagră	13,5	1,8	7,7	0,33	3,45	1053	211	25,0	7,80
2	Brează	12,0	1,0	6,4	0,26	3,20	995	95	20,1	7,80
3	Kopceak	13,8	1,6	9,2	0,26	3,37	2340	634	25,8	7,92
4	Bătuță Neagră	9,5	0,8	7,4	0,26	3,54	1170	85	17,2	7,71
5	Seină	12,7	1,4	6,1	0,40	3,59	1346	127	21,3	7,84
6	Fetească Neagră	14,4	1,7	7,6	0,26	3,62	1814	391	24,6	7,94
7	Ciorcuță Neagră	13,0	1,4	7,0	0,26	3,45	1463	180	22,1	7,88
8	Negru de Căușeni	13,7	1,3	9,4	0,26	3,14	2048	793	27,4	7,96
9	Negru de Akkerman	9,7	0,8	7,3	0,20	3,23	1463	116	19,5	7,81
10	Codrinschi	14,9	2,1	7,5	0,26	3,43	3159	634	27,1	8,02
11	Merlot (martor)	12,8	1,0	6,5	0,26	3,47	1697	296	23,2	7,98

The volatile acidity in wines is investigated within 0.2-0.4 g/L, denoting compliance with production technology experimental samples. Nonreducing dry extract reaches between 22.1 and 27.1g/L, except for varietal wines Batuta neagra, Negru de Akkerman, Breaza and Seina, where this index is only 17.2; 19.5; Respectively 20.1 and 21.3 g/L, which is not enough for a young red wine.

Investigated wines are distinguished more by the content of phenolic compounds. Obviously, phenolic substances and coloring substances are in smaller quantities in wines made from low varieties in these compounds.

It is known that the content of the coloring matter of red wines must be not less than 200 mg / L, and the phenolic substances - not less than 2000 mg / L.

Considering the above, we can say that wine samples obtained from experimental varieties Seina Breaza, Negru de Akkerman, Batuta neagra and Ciorcuță neagra not meet requirements for this category of wines.

It should be noted that from all investigated wines, Codrinschii has the highest content of phenolic substances - 3159 mg / L and anthocyanin - 634 mg / L. The wine is characterized with deep red color, rich aroma with notes of fruit, harmonious taste, noble tannins and organoleptic was rated at 8.02 points. With high values of the content in phenolic compounds are distinguished wines from the variety Kopceak - 2340 and respectively 634 mg/L, followed by the variety Negru de Căușeni - 2048 and 793 mg/L.

Kopceak wine has dark red color, pure flavor, made with fruit nuances, organoleptic grade being 7.92 points. The sample obtained from the variety Negru de Căușeni has a red, pure flavor, rich; The taste is full, extractive, harmoniously (7.96 points). The last three wines can be placed in category extractive wines with rich content of phenolic substances and antocians.

Fetească neagra wine obtained by the content in phenolic compounds and organoleptic peculiarities is located closer to the control. Thus, the content of phenolic substances that are 1814 and 1697 mg/L, while the coloring matter - respectively 391 and 296 mg/L. This wine has a deep red color, rich aroma with notes of red fruit, moderate flavor mining, soft, harmonious. Organoleptic assessment notes were high and constituted 7.94 and 7.98 points respectively. After complex phenolic Fetească neagra wine is part of extractive medium red wines. Regarding the Rara neagra wine variety may be mentioned that it is characterized by a lower content in phenolic substances - 1053 mg/L and anthocyanin - 211 mg/L. It has red, pure varietal aroma, with notes of red berries light, clean taste, slightly astringent. After phenolic constituents of this wine is part of lighter red wines.

The data presented in the literature (Cotea V.D. 2009) we notice that the color formation grapes and red wines participating various forms of anthocyanins - anthocyanidins, antocianosides and acylated anthocyanins. So particular interest is the research profile of anthocyanins of red wines made from indigenous varieties in relation to classic Merlot variety, the results presented in Table 2.

Data Table 2 shows that wines made from indigenous varieties are distinguished and compared to the control wine of Merlot, with a distinct anthocyanin profile. The main component of anthocyanins in wine determined experimental and control the harvest of 2011 is malvidina 3-monoglycoside, but its percentage ratio of the amount of anthocyanins differ greatly.

Thus, Rara neagra wine value of this index is 70%. This index has higher values in varieties: Seina - 64.5%, Ciorcuță neagra - 59.4%, Kopceak - 55.7%, Batuta neagra - 52.9% and Negru de Căușeni - 50.6%. Malvidin-3-glucoside and sample wine predominant Fetească Neagra - 53.6%. Codrinschii wine is distinguished with the lowest share of malvidine 3-monoglycoside - 48.1% and in the control sample Merlot index is 34.9%. Besides malvidina 3-monoglycoside a significant share in creating color has petunidin-3-monoglycoside. The varietal wines Breaza, this compound has higher percentage values (12.7%), Fetească neagra (11.2%) and the variety Kopceak (10.1%). In other wine samples petunidin- 3-monoglycoside share is below 10% and the lowest values were determined in Negru de Akkerman wines (1.9%) and Batuta neagra (3.4%). The sample Merlot value ratio petunidin-3-glucoside is 4.8% and is lower against most experimental wines.

Table 2 Reports values of anthocyanins in red wines made from indigenous varieties and classic variety - witness the harvest of 2011,% of total

Nr. d/o	Name of the variety and variant	Delfinidina-3-glicozid	Cianidina-3-glicozid	Diglicozid-malvidol	Petunidina-3-glicozid	Peonidina-3-glicozid	Malvidina-3-glicozid	Σ antocian free and acylates	Σ antocianin glycosides
1	Rara Neagră	2,4	<0,5	<0,5	5,6	2,5	70,0	17,4	81,5
2	Brează	9,3	1,2	<0,5	12,7	4,7	51,7	18,4	80,1
3	Kopceak	7,8	0,8	0,9	10,1	5,2	55,7	15,9	80,5

4	Bătuță Neagră	1,9	<0,5	<0,5	3,4	3,6	52,9	37,1	62,8
5	Seină	2,7	<0,5	<0,5	5,6	4,6	64,5	21,4	78,4
6	Fetească Neagră	6,7	1,3	<0,5	11,2	5,3	53,6	17,6	78,6
7	Ciorcuță Neagră	2,3	1,4	<0,5	4,6	2,0	59,4	28,9	70,2
8	Negru de Căușeni	8,9	<0,5	<0,5	9,9	2,7	50,6	22,6	73,1
9	Negru de Akkerman	2,2	0,5	0,6	1,9	3,5	36,4	46,8	45,1
10	Codrinschi	6,6	1,5	2,7	6,4	3,2	48,1	29,8	68,5
11	Merlot (martor)	4,6	<0,5	<0,5	4,8	2,8	34,9	48,1	48,1

Higher values of delphinidin-3-monoglycoside identified in varietal wines Condrișchii (6.6%), Breaza (9.3%), Negru de Căușeni (8.9%) and Fetească neagră (6.7%). The lowest values of this compound were found in wines Negru de Akkerman - 2.2%, Seina - 2.7% and Rara Neagră - 2.4%. The control sample weight of delphinidin-3-monoglycoside is the level of 4.6%. Monoglycoside-3-peonidina content in wine samples investigated in this varies are between 2.0 and 5.3%. The value of control wine Merlot peonidinei-3-monoglycoside is low and is 2.8%. In most samples malvidol-diglicozid content in the wine is less than 0.5%, with allowance for Condrișchii and Kopceak varieties that have higher values of the index. The data in Table 2 it can be concluded that the amount of anthocyanin glycoside is very different depending on the grape variety used. The largest share of the amount recorded in the wine glycosides anthocyanins Rare Black - 81.5% and in the variety of Kopceak - 80.5%. The higher values of the amount of anthocyanins glycosides are distinguished wines made from varieties: Seina - 78.4% Breaza - 80.1%, Ciorcuță neagră - 70.1% and Fetească neagră - 78.6%. In Condrișchii wine - 68.5%. The samples investigated with lower values of the amount of anthocyanin glycosides wine variety is accentuate Negru de Akkerman - 45.1% and the value is closer to the control Merlot wine samples - 48.1%.

In conclusion we can say that the color formation Merlot wine made from less participating glycosides anthocyanins. It is predominantly acylated forms, and to free the anthocyanins. However, it is known that the acylated anthocyanins are beneficial for color quality red wines (Cotea V.D., 2009). Acylation glucoside residues, particularly the hydroxy acids, anthocyanins increases stability and ability to dye molecule, a phenomenon known as copigmentation. In this context, the analyzes demonstrated that the acylated anthocyanins ratio proportionate amount and free in Merlot wine sample is 48.1% and is higher than the experimental wines. The red varieties investigated, wine produced from the variety Negru de Akkerman value is highlighted by closer control - (46.8%).

The lowest values of this index were detected in wines Kopceak - 15.9%, Fetească Neagră - Rara neagră 17.6% and - 17.4%. We assume that this is explained by more advanced color intensity in wine produced from Merlot and its higher stability this wine. From the local varieties of wine, Condrișchii differs by a richer color and intensity. Given that dyes are subject to frequent changes, it was examined their behavior in the storage of the wine made from indigenous varieties and witness for 12 months.

Table 3 presents the results of research on the dynamics of acylated anthocyanins and the amount glycosides at the initial stage and after 12 months of storage. From the data of Table 3 we can see that during 12 months of storage there is a percentage increase of the share acylated anthocyanins and that a reduction in all forms glycosides wine samples subject to investigation. Acylated anthocyanins increase the amount varies quite high in value from wine Condrișchi constituting 6.8% and Rara neagră up to 23.6%. The Feteasca neagră wines index is 18.9% and in Negru de Căușeni - 21.8%.

Table 3 The dynamic acylated anthocyanins and glycosides in red wines made from local varieties after 1 year of storage, the harvest of 2012,% of total

Nr d/r	Name of wine	Initial		1 year		The increase free anthocyanins and acylated% of the total
		Σ anthocyanins acylated	Σ anthocyanins glycosides	Σ anthocyanins acylated	Σ anthocyanins glycosides	

1	Rara neagra	13,2	84,1	36,8	61,8	23,6
2	Feteasca neagră	17,8	78,5	36,7	58,9	18,9
3	Kopceak	17,9	78,0	28,5	70,5	10,6
4	Negru de Căușeni	18,6	76,8	40,4	58,2	21,8
5	Codrinschii	24,8	73,5	31,6	66,1	6,8
6	Merlot	36,8	57,0	61,0	33,7	24,2

After a year of storage of the Kopceak wine, acylated anthocyanins increase amount is 10.6%. In acylated anthocyanins control wine Merlot is increased by 24.2%.

Based on investigations it appears that during a year of storage of red wines from indigenous varieties, both in experimental wine samples and in control wine, there is an increase of acylated anthocyanins percentage party.

CONCLUSIONS

1. After complex phenolic potential, producing red wines from indigenous varieties Codrinschii, Fetească neagra, Kopceak, Negru de Căușeni and Rara neagra perspective is considered.
2. Wines investigated indigenous varieties are distinguished by the content in phenolic compounds. Codrinschii wine variety has the highest content of phenolic substances - 3195 mg/L and anthocyanin - 634 mg/L. Kopceak variety wines - 2340 mg/L and 634 mg/L are distinguished by high values of the content in phenolic compounds, followed by the variety Negru de Căușeni - 2048 mg/L and 793 mg/L. These three wines can be placed in category extractive wines with rich content of phenolic substances and antocians. After the content in phenolic compounds and organoleptic peculiarities, the wine Fetească neagra is located closer to the control and is part of the mining environment. The variety Rara neagra characterized by a potential phenolic more modest, yield a wine with a lower content of phenolic substances - 1053 mg/L and antocians - 211 mg/L, which can be placed in the category of red wines light.
3. Wines made from indigenous varieties of anthocyanins have a different profile, both among themselves and against the control. The wines produced from local varieties predominate glycosides anthocyanins, the amount of which varies from 68.5 to 80.5%, excluding wine Negru de Akkerman, the value of this indicator is 45.1% and is closer to sample wine control-48.1%. The color of Merlot wine is made mostly of acylated anthocyanins forms, actually explaining color intensity most advanced and stable.
4. During 12 months of storage of red wines from indigenous varieties, both in experimental samples and in control wine occurs acylated anthocyanins increase the percentage party, leading to the stabilization of color.

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