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COMPARATIVE EVALUATION AND STUDING OF SOME INDIGENOUS AND INTRODUCED RED GRAPE VARIETIES

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Abstract. Azerbaijan is one of the ancient wine-growing country, and it is famous by its rich assortment of local grapes. Historically, in our country well-known brand wines have been prepared from aboriginal red grape varieties. Among them, we can mention branded Kurdamir kagoru, Shamakhi kagoru, Madasa and Khindogni natural wines, etc. wines made from such autochthonous grape varieties won the favor of consumers with their unique physical-chemical and organoleptic characteristics. In line with it, in recent years, to the country introduced a number of valuable grape varieties such as Merlot, Cabernet Sauvignon, Syrah and others. It is actually relevant comparative evaluation of such varieties cultivated in local conditions, including red ones. During the ripening of the studied grape varieties, the amount of sugars ranged between 197 and 265 g/dm³, titratable acids from 4.5 to 7.7 g/dm³, and active acidity between 3.08 and 3.61. The mass concentration of sugars in the Xindogni grape variety was 197 g/dm³ on average. The varieties were in ascending order of the mass concentration of sugars: Madrasa 222 g/dm³, Cabernet-Sauvignon 226 g/dm³, Merlot 240 g/dm³, and Shirvanshahi 265 g/dm³. One of the important indicators determining the quality of raw materials is known to be the sugar-acid potential, in other words, a glucoacidometric index (GAI). In the studied varieties, the GAI varied from 3.0 to 5.7. This index was higher in the Shirvanshahi variety (5.7), medium in Madrasa (4.9) and Cabernet Sauvignon (4.8), and lower in the Xindogni (3.0) and Merlot (3.1) grape varieties. Delphinidin, cyanidin, peonidin, and malvidin anthocyanidins were found in skin hydrolysates. The amount of resveratrol in the skin, seed, and leaf was 0.75-8.25mg/kg, 0.31-5.7mg/kg, and 0.01-0.25mg/kg, respectively, depending on varieties and years.

Local grape varieties had a noticeable level of aromatic alcohol content and were not at all inferior to the famous Cabernet Sauvignon grape variety. Aromatic alcohols such as β-phenylethanol, β-phenoxyethanol, and phenylcarbinol were among the compounds of importance for Kagor-type wines. A comparison of their quantity showed that the amount of these compounds in the Madrasa grape variety was more than in the other two grape varieties.

Keywords: grape, juice, skin, seed, sugar, acid, phenolic compounds, anthocyanins.

Introduction. Formulation of the problem

In the complex of measures to increase the productivity of vineyards and the quality of the production, the first place is given to the improvement of varietal stocks. Studies have revealed that the variety in viticulture largely determines the zone, the cultivation technology of the grape plant, the type and technology of the wine, and its economic efficiency.

The article is dedicated to the study of production technology of juice and wine, particularly to the research of the raw materials used for the preparation of quality red wines. The quality indicators of various autochthonous and introduced grape varieties that are widespread in the country, including the amount of resveratrol in the grape components (peel, seed, rind), as well as phenolic compounds and their various forms, have not been studied enough. Therefore, it is

important to determine the main quality indicators of red aboriginal and introduced grape varieties that are widespread in the country.

Analysis of recent research and publications

The influence of 3 different soil and climate zones of the Hansu region, which is the main wine-growing region of China, on the composition and antioxidant properties of grape berries was studied. Merlot was found to be more suitable for the Zhang region, Cabernet Sauvignon for Uveya, and Italian Riesling for Szyayugan. The special role of soil-climatic conditions and terroir in the quality of grapes and wine was noted [1].

The grape harvest obtained from 4 different clones of Merlot and 5 different clones of Cabernet Sauvignon was processed separately and the composition of the obtained wines was studied. Genetic material, soil and climatic conditions have been found to play a fundamental role in the selection of a new clone [2].

The anthocyanin profile of Cabernet-Sauvignon and Merlot grape varieties was studied in 5 regions and 11 locations. The results showed that the northern part of Xinjiang province has lower humidity and higher average temperature compared to its south. It has been shown that genetic factors, soil-climate conditions, altitude, and agrotechnics affect the amount of total and individual anthocyanins [3].

By determining the amount of total phenolic compounds and anthocyanins [4], the production of functional food products from grape extracts rich in polyphenols was studied [5], and the possibility of pesticides out of samples of the wine by traditional methods is determined by research [6].

Wines obtained from the Syrah grape variety grown in North-South (NS) and East-West (EW) zonation were studied. It was found that EW wine samples had higher acidity, residual sugar, alcohol, and color shades, while NS wine samples had higher color intensity, anthocyanins, total phenolic compounds, as well as total phenolic index and pH. It was noted that cultivation orientation can be used as a management tool for obtaining wine in individual styles [7].

The amount of chemical combination arising in residue is exact during the processing of various grape sorts in Brazil. The high content of ascorbic acid in grape skin and seed, also the protein in high content and pectin in seed are discovered. The same substances in various sorts of achieved residue were analyzed differently [8]. Vaporizing substance and aromatic combination have been analyzed in red wine made from grape varieties of Izabella and Ivesa. 54 combination have been researched in red wine. The differences in the main components of each wine were observed depends on the used grape contents [9]. The influence on polymerization of phenol compound were analyzed in wine by the modern research method and sensor analyzes of the rate of grape skin and seed [10].

It should be noted that introduced varieties require technological adaptation. In other words, it actualizes the research of grapes and the chemical composition of wines made from them, the selection of varieties that allow obtaining better quality products in the local soil and climate conditions, the substantiation of technological processing methods of grapes, and the implementation of works aimed at improving wine production technology. Besides, one of the important problems at present is to produce a high-quality, competitive wine product. It is also known that the quality of wine products mostly depends on the quality of raw materials. Therefore, to successfully solve the requirements facing the field, it is necessary to study extensively the characteristics of the raw material base [11].

Objectives of the research:

1. Comparative assessment of carbohydrate acid and phenol compounds content of the main aboriginal and introduced red grape varieties.
2. Comparative analysis of the amount of anthocyanins in local, introduced, including hybrid varieties.
3. Comparative assessment of resveratrol content in grape components (peel, seed, rind).
4. Research and evaluation of the amount of aroma-forming substances in grapes.

Research materials and methods

Grapes, juice, and pomace of some red grape varieties cultivated under local conditions, were taken as the objects of the research. In the research process, the indigenous Madrasa, Shirvanshahi, and Xindogni, as well as the introduced Merlot, Cabernet Sauvignon, Syrah, and Isabella grape varieties were collected and studied in the state of technical ripeness. Sugar content, titratable acidity, pH, sugar-acid potential, phenolic compounds, and aroma-forming substances were studied in grapes. For this purpose, in addition to traditional methods, gas, gas-liquid, and high-performance liquid chromatography methods were used [12,13]. Total phenolic compounds and mass concentration of polymer form were determined by colorimetric method using the Folin and Ciocalteu reagent. A Shimadzu (Kyoto, Japan) Prominence LC 20A HPLC system with a fluorescence detector (RF-30A) was used in the analysis of resveratrol.

For the determination of anthocyanins, 6 ml of the juice or wine to be analyzed was passed through an LC-18 superelecan cartridge, and the resination of anthocyanins was carried out. Then, 18 ml H₂O-HCC (99.9/0.1; v/v) was passed through the cartridge to remove sugars in the medium. At the same time, resinous anthocyanins were added to this solvent by passing 12 ml of MeOH-HCl (99.9/0.1; v/v) through the cartridge. After mixing the anthocyanins with the solvent, the resulting mixture was concentrated in an evaporator at 25°C until it dries. Then, the anthocyanins attached to the wall of the evaporator flask were dissolved in 1 ml of methyl alcohol/water/formic acid

(40/55/5:v/v/v) solvent and injected into HPLC, and the amount and profiles of anthocyanins were determined. The profiles of anthocyanins were detected by directly injecting pre-adjusted skin extractors. HPLC-MS is used in the identification of anthocyanin compounds. Delphinidin, cyanidin, petunidin, peonidin, and malvidin-3-glycoside standards were used to determine the amount of anthocyanins. For each standard, a solution of five different concentrations was prepared and injected into the HPLC, calibration curves were constructed and the amount of compounds was determined by calculation based on the obtained curves.

HPLC (Agilent-1100) with a double pump, double wavelength, and diode array detector was used to detect anthocyanins.

The modified method of Riu-Anmatell et al. was used for the determination of aroma compounds. Thus, 5 ml of NaCl was added and mixed for 30 seconds with IKA MS3 Basic Vortex Mixer. After holding for 40 minutes in the fiber (65 μ mPDMS/DVB) at 40°C, it was injected into a GC-MS instrument (Shimadzu GCMS-QP2010). The fiber was conditioned for 10 minutes at 200°C before each injection. Restek RTX-5 (30 m x 0.25 mm x 0.25 μ m) was used as the column and Helium was used as the carrier phase. After waiting 5 minutes at 40°C, the column temperature is programmed to increase by 4°C per minute to reach 240°C.

GAI-Glucoasimetric indicators is determined by the ratio of the vibrating acids of sugar (GAI).

Information that obtained as a result of resveratrol analysis of grape components (peel, seed, rind) of various indigenous and introduced grape varieties for the years 2017-2019 were evaluated by two-way options analysis technique (univariate ANOVA). Each grape variety was analyzed independently on the research, 3 indicators of phenol compounds - total, polymer and color substances were evaluated for different grape varieties. Repeated measurements were provided at step factor levels. Two-way option analysis technique (univariate ANOVA) was used for the purpose of statistical evaluation of the analysis results of total and other phenolic compounds (p0.05). To detect the different groups Turkey test was used (p 0.05).

The statistical analysis is carried out by using the program of SPSS18 package [14].

Results of the research and their discussion

The quality of the wine is primarily related to the raw material. Its composition is influenced by the variety of grapes, soil-climatic conditions, and growing techniques. Another factor affecting the quality is the processing technology.

Depending on the type of wine to be made, the importance of correctly determining the time of grape harvest cannot be denied. During the ripening of the grape varieties used in the study, the total amount of sugars was 182-263 g/dm³, titratable acids 4.5-7.7 g/dm³, and active acidity 3.08-3.61 (Table 1).

The mass concentration of sugars in the Xindogni grape variety was 197 g/dm³ on average.

Sugars were in ascending order of their mass concentration: Madrasa (222 g/dm³), Cabernet Sauvignon (226 g/dm³), Merlot (240 g/dm³), and Shirvanshahi (265 g/dm³).

The average mass concentration of titratable acids for the samples ranged between 4.5 and 7.7 g/dm³. In the Xindogni grape variety, this indicator was 6.6 g/dm³ on average. The mass concentration of titrated acids was 4.5 g/dm³ in the Madrasa variety, 4.7 g/dm³ in Cabernet Sauvignon, 7.7 g/dm³ in Merlot, and 4.6 g/dm³ in the Shirvanshahi variety.

Table 1 – Carbohydrate-acid content of grape varieties, n=6, p<0.05

Grape variety	Mass concentration, g/dm ³		pH	GAI
	Sugars	Titratable acids		
Xindogni	197	6.6	3.16	3.0
Madrasa	222	4.5	3.61	4.9
Cabernet Sauvignon	226	4.7	3.42	4.8
Merlot	240	7.7	3.08	3.1
Shirvanshahi	265	4.6	3.35	5.7
Syrah	231	5.3	3.36	4.3

One of the important indicators determining the quality of raw materials is known to be the sugar-acid potential, in other words, the glucoacidometric index (GAI). In the studied varieties, the GAI varied from 3.0 to 5.7. It was the highest in the Shirvanshahi variety (5.7), high in the Cabernet-Sauvignon (4.8) and Madrasa varieties (4.9), and low in the Xindogni (3.0) and Merlot (3.1) grape varieties. Shirvanshahi is known to be an indigenous grape variety that accumulates sugar in high concentrations.

As it is known, phenolic compounds play a fundamental role in the formation of the taste, color, and bouquet of Kagor wines. Therefore, it was determined in grape varieties. The amount of phenolic compounds in the studied grape varieties is given below (Figure 1).

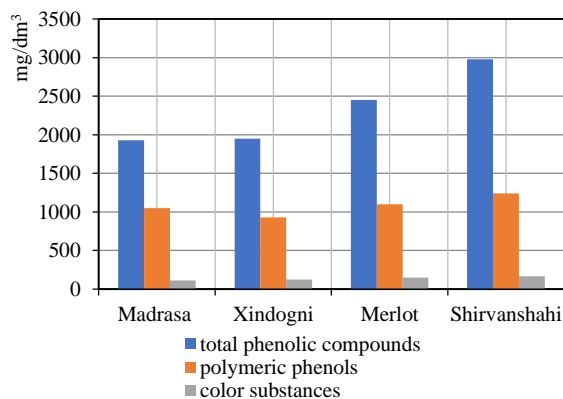


Fig. 1. Amounts of phenolic compounds in different grape varieties n=6, p<0.05

Quantification of phenolic compounds showed that the total phenolic compounds were high in the

Shirvanshahi and Merlot varieties, and the polymeric phenolic compounds were high in the Shirvanshahi, Merlot, and Madrasa grape varieties. The superiority of the Shirvanshahi grape variety was noticeable in terms of color substances.

It is interesting to study the amount of aglycons of anthocyanins in grape varieties and the changes they undergo during further processing.

The anthocyanin content of red grape varieties belonging to different species (*Vitis Vinifera* and *Vitis Labruska* x *Vitis Vinifera*) and varieties was studied by the high-performance liquid chromatography method (Table 2).

Significant differences in the anthocyanin content of Madrasa, Xindogni, and Cabernet Sauvignon varieties belonging to the *Vitis Vinifera* species were noticed compared to the Isabella variety belonging to the *Vitis Vinifera* X *Vitis Labruska* hybrid. Thus, delphinidin, petunidin- and peonidin-3,5-di-0-glycosides were found among di-glycosides in the Isabella grape variety, while these compounds were not found in other grape varieties. One of the more marked parameters was the amount of Malvidin-3-0-glycoside. This indicator varied between 57.0 and 58.0% in other varieties, except the Isabella variety. In the Isabella variety, this parameter amounted to 4.5%.

Malvidin-3-0-(6-0-acetyl-glycoside) have the leading position among acetyl-glycosides. Its amount varied between 8.5 and 19.6% in varieties. The highest value (19.6%) of the parameter was detected in the Isabella variety. Acetylated forms, such as peonidin-3-0-(6-0-acetyl-glycoside) and peonidin-3-0-(6-0-coumaroyl-glycoside) were completely absent in the Isabella variety. The most notable compounds for this

variety were cyanidin-3-0-glycoside (18.7%), delphinidin-3-0-glycoside (31.1%), and malvidin-3-0-(6-0-acetyl-glycoside) (19.6%). In the Isabella variety, these three compounds accounted for 69.4% of all anthocyanins. Other varieties were distinguished by the smaller amounts of these compounds.

The study of the ratio of di- and mono-glycoside derivatives of anthocyanins did not reveal the di-glycoside forms of anthocyanins in local red grape varieties (Table 3).

As seen, the amount of mono-glycosides in the Madrasa and Xindogni grape varieties, unlike Isabella, was 100%. It can be concluded that the anthocyanin complex in local grape varieties was represented only by mono-glycosides.

There is no second compound with antioxidant properties as strong as resveratrol among the polyphenols in grapes. Resveratrol (trans-3,5,4'-trihydroxystilbene) is a phenolic compound belonging to the stilbene group that strengthens the mechanism of resistance to environmental stress and threats in the evolutionary process of plants. Although it is found in a number of products, higher quantities of this compound are in red grapes and wines [15,16].

The results of our research on the amount of resveratrol in the berry components are given. Results are based on fresh weight (Figure 2).

As can be seen in the figure, the amount of resveratrol in the skin of the studied red varieties was different for the years 2017–2019. A better result was observed in the variety Shirvanshahi in 2017. In general, the amount of resveratrol in the skin changed in a wide range (0.75–8.25 mg/kg) depending on years and varieties.

Table 2 – Anthocyanin content of different grape varieties

n=6, p<0.05

№	Compounds	Grape varieties			
		Madrasa	Isabella	Cabernet Sauvignon	Xindogni
		amounts, %			
1	Delphinidin-3,5-di-0- glycoside	0.0	1.4	0.0	0.0
2	Petunidin-3,5-di-0- glycoside	0.0	1.3	0.0	0.0
3	Delphinidin -3-0- glycoside	11.5	31.1	11.0	10.5
4	Peonidin-3,5-di-0- glycoside	0.0	0.2	0.0	0.0
5	Cyanidin 3-0-glycoside	2.2	18.7	2.1	2.5
6	Malvidin-3,5-di-0- glycoside	0.0	1.3	0.0	2.0
7	Petunidin-3-0- glycoside	6.2	6.6	6.8	6.7
8	Peonidin-3-0- glycoside	10.0	1.3	9.8	9.5
9	Malvidin-3-0- glycoside	57.0	4.5	57.1	58.0
10	Delphinidin-3-O-(6-O- acetyl)glycoside)	0.4	4.7	0.5	0.3
11	Malvidin-3,5-di-0-(6-0- acetyl)glycoside)	0.0	3.8	0.0	0.1
12	Petunidin-3-0-(6-0- acetyl)glycoside)	0.5	1.5	0.7	0.6
13	Peonidin-3-0-(6-0- acetyl)glycoside)	1.2	0	1.2	1.3
14	Malvidin-3-0-(6-0- acetyl)glycoside)	8.7	19.6	9.1	8.5
15	Delphinidin-3-0-(6-0-n-coumaroyl- glycoside)	0.2	1.3	0.3	0.2
16	Petunidin-3-0-(6-0-n-coumaroyl- glycoside)	0.3	0.4	0.3	0.4
17	Peonidin-3-0-(6-0-n-coumaroyl - glycoside)	0.3	0.0	0.2	0.2
18	Malvidin-3-0-(6-0-n- coumaroyl -glycoside)	1.0	2.3	0.9	1.2
Total		100	100	100	100

Table 3 – Amount of anthocyanins in local and hybrid varieties

n=6, p<0.05

No	Grape varieties	Mass concentration of anthocyanins, mg/dm ³			Ratio between mono-glycosides and di-glycosides
		Total amount	Di- glycosides	Mono-glycosides	
1	Madrasa	1561	0.0	1561	0.00
2	Xindogni	1496	0.0	1496	0.00
3	Izabella	1251	15	1236	0.01

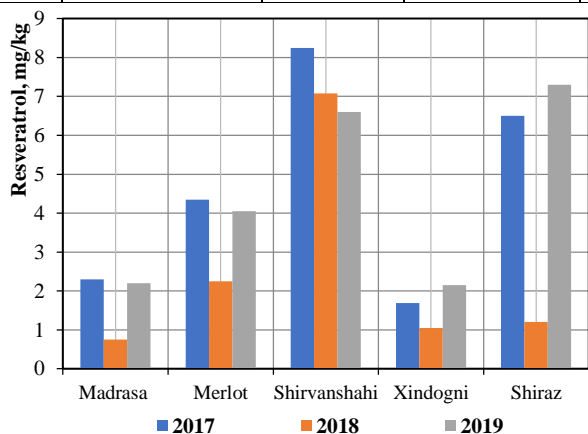


Fig. 2. Amount of resveratrol in grape skins n=6, p<0.05

The berry component with the second highest resveratrol content was the seed (Figure 3). As seen, the amount of resveratrol in the seed was much lower than in the skin, and it ranged between 0.31 and 5.7 mg/kg depending on years and varieties.

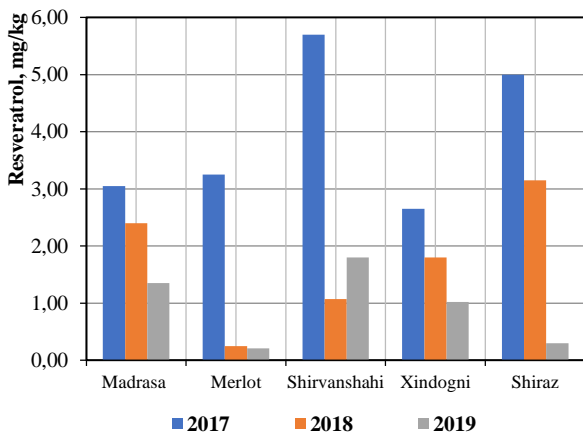


Fig. 3. Amount of resveratrol in grape seeds n=6, p<0.05

Resveratrol was absent or very low in berry skin depending on varieties and years (Figure 4).

Thus, the maximum amount was 0.25mg/kg.

In the 90s of the last century, interest in resveratrol increased after the research conducted by US scientists was made public. At present, resveratrol is successfully used in the prevention and treatment of severe diseases such as cardiovascular disease, cancer, and Alzheimer's disease. Therefore, knowing the distribution of resveratrol in the individual components of the grape (skin, seed, pulp) for each variety and condition, it is

possible to adjust the corresponding wine technology. This issue is especially important for Kagor-type wines, which are rich in polyphenols. Based on the above, we consider it important to apply technologies that involve long-term contact with the solid parts of the berry for Kagor-type wines.

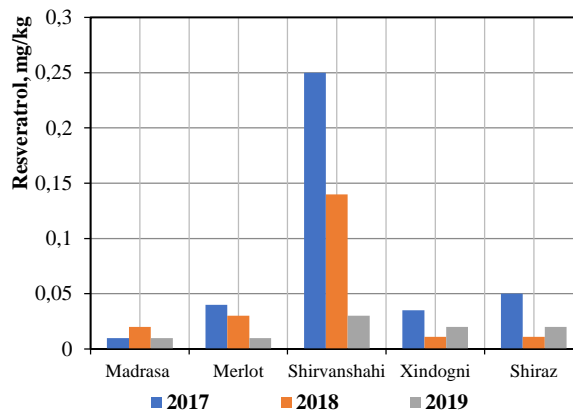


Fig. 4. Resveratrol in grape pulp n=6, p<0.05

Aroma substances have a unique role in the formation of the typicality and bouquet of Kagor wine. Studies show that there are various sources of its formation in wine. The role of the raw material, i.e. grape, as the first source is not a subject of debate. However, this indicator is known to be different even in the same variety depending on the cultivation conditions and harvest year [17].

Aroma-forming compounds in the studied grape varieties were found to have a noticeable quality in the local grape varieties and some indicators even surpassed those in the Cabernet-Sauvignon grape variety (Table 4). Aromatic alcohols such as β -phenylethanol, β -phenoxyethanol, and phenyl carbinol are among the compounds of importance for Kagor-type wines. The amount of these compounds in the Madrasa grape variety was more than in the other two grape varieties.

The amount of lactones changed between 121.6 and 131.4 $\mu\text{g}/\text{dm}^3$ in different grape varieties. Higher amounts of them in local varieties compared to the Cabernet-Sauvignon grape variety can be attributed to better adaptation of indigenous grape varieties to local conditions. γ -butyrolactone, followed by γ -hexalactone were the lactones with the highest amount in all varieties. Lactones are known to create mainly the basis for the formation of fruit aroma type in grapes.

Table 4 – Amount of aroma-forming substances in grape (n=6, p<0.05)

Compounds	Mass concentration, $\mu\text{g}/\text{dm}^3$		
	Madrasa	Cabernet-Sauvignon	Xindogni
Aliphatic alcohols			
2-(2-butoxy)-ethanol	37.0	50.0	38.0
2,4-dimethylpentanol-3	180	142	165
2-methyl-pentanol	13.0	12.0	12.2
Cis-2-pentanol	56.0	66.0	78.0
Trans-3-hexen-1-ol	18.3	14.9	18.7
Cis-3-hexen-1-ol	24.0	31.0	16.0
Trans-2-hexen-1-ol	96.0	103	134
Cis-2-hexen-1-ol	605	679	830
2-Hexanol	19.7	34.5	10.1
2-ethylhexanol	798	230	231
Octanol			
Terpene compounds			
Geraniol	28.0	27.0	31.0
α -pinene	6.2	4.5	0
Linalyl acetate	13.5	15.6	12.5
3-oxy- β -damascus	36.1	27.5	56.8
Aromatic alcohols			
β -phenylethanol	983	765	655
β -phenoxyethanol	318	151	136
Phenylcarbinol	865	922	1136
Lactones			
Dihydroactinidiolide	16.5	14.2	17.4
λ -butyrolactone	41.6	56.1	45.5
λ -hexalactone	45.7	34.9	38.5
λ -heptalactone	21.7	16.4	30.0
Ethers, ketones, aldehydes			
Ethyl caprine	104	10.0	84.0
2-octanone	47.0	0	19.1
2-nonanone	10.2	11.1	16.6
4-methoxy-4-methyl-2-pentanone	17.3	16.5	12.3
6-methyl-5-hepten-2-one	11.7	11.3	13.5
Nonanol	16.5	13.1	9.7
Hexanal	261	322	467
Phenylacetaldehyde	36.4	48.2	38.5
Decanal	25.0	16.0	27.0
Benzaldehyde	32.0	33.0	36.0
Vanillin	148	259	141
Furfurol	16.4	13.6	16.9

Conclusions

1. During the ripening of the studied grape varieties, the amount of sugars varied in the range 197–265 g/dm^3 , titratable acids 4.5–7.7 g/dm^3 , and active acidity 3.08–3.61. The mass concentration of sugars in the Xindogni grape variety was 197 g/dm^3 on average. The varieties are in ascending order of mass concentration of sugars: Madrasa 222 g/dm^3 , Cabernet-Sauvignon 226 g/dm^3 , Merlot 240 g/dm^3 , and Shirvanshahi 265 g/dm^3 .

2. One of the important indicators determining the quality of raw materials is known to be the sugar-acid potential, in other words, a glucoacidometric index (GAI). In the studied varieties, the GAI varied from 3.0 to 5.7. This index was higher in the Shirvanshahi variety (5.7), medium in Madrasa (4.9) and Cabernet

Sauvignon (4.8), and lower in the Xindogni (3.0) and Merlot (3.1) grape varieties.

3. Although delphinidin, petunidin- and peonidin-3,5-di-0-glycosides were found among the diglycosides in the Isabella hybrid grape variety, these compounds were absent in other grape varieties. One of the more marked parameters was the amount of Malvidin-3-0-glycoside. This indicator varied between 57.0 and 58.0% in other varieties, except the Isabella variety. In Isabella variety, this parameter amounted to 4.5%. Of the acetylated forms, peonidin-3-0-(6-0-acetyl-glycoside) and peonidin-3-0-(6-0-coumaroyl-glycoside) were completely absent in the Isabella variety.

4. Delphinidin, cyanidin, peonidin, and malvidin anthocyanidins were found in skin hydrolysates, the amount of resveratrol in the skin was 0.75-8.25mg/kg,

seed 0.31–5.7 mg/kg and pulp 0.01–0.25 mg/kg depending on years and varieties.

5. The amount of aromatic alcohols in the local grape varieties was at a marked level and they were not inferior to the famous grape variety like Cabernet Sauvignon. Aromatic alcohols such as

β -phenylethanol, β -phenoxyethanol, and phenyl carbinol are among the compounds of importance for Kagor-type wines. Besides, the amount of these compounds in the Madrasa grape variety was more than in the other two grape varieties.

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