

*Wines of the Tokay type are produced using a special technology. According to Hungarian technology, for the production of these wines, bunches of white and red grape varieties are twisted on the vine, withered for a certain time, then dropped for processing. At the same time, the percentage of sugar in grapes is artificially increased due to the evaporation of moisture. In pre-dried grapes, the percentage of sugar should be in the range of 40–45 %. For the production of Tokay-type wines, the fermentation of grape must is carried out naturally without the addition of alcohol and other ingredients. After formation in the must of 14–16 vol. % alcohol, the fermentation process is suspended naturally. As a result, natural sugar and alcohol remain in the wine material. Withered grape varieties, despite their high sugar content, are economically inefficient due to low juice yield and a quantitative decrease in extractive substances. Thus, the enrichment of wine material for the production of Tokay-type wines has not been studied. As an object of research, ripe technical grape varieties Bayan Shirey, Rkatsiteli, Cabernet Sauvignon, Madrasa cultivated in the foothills of the Geygol district and in the low-lying zone of the Samukh district were used. Grape varieties were harvested from the vineyards of the winery, located in the Goygol district and from the farm "Amin", located in the village of Gara-Yeri, Samukh district. For the production of wine, both ripe and separately withered grape varieties were used, twisting on the vine for 10–12 days. However, when twisted on the vine, about 15–20 % of the bunches of grapes break and fall to the ground. Further, in ripe and withered grape varieties, the quantitative content of dry matter, total sugar, including glucose and fructose, phenolic compounds, titratable acidity, vitamin C, and in both variants the yield of unclarified juice was determined separately. The regularities of increasing the activity of enzymes of the class oxidoreductase and a representative of hydrolase-pectinesterase were considered. The results make it possible to adjust the quality indicators of grape varieties depending on their zoning and use them for the production of high-quality Tokay-type wines*

**Keywords:** grape varieties – Bayan-shirey, Rkatsiteli, Cabernet Sauvignon, Madrasa, total sugar, titrated acidity, oxidoreductase, pectinesterase

# IMPROVEMENT OF THE PRODUCTION TECHNOLOGY OF TOKAY WINES BASED ON THE REVEALED EFFECT OF ENZYME ACTIVITY ON THE QUALITY OF GRAPE VARIETY

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Received date 16.01.2023

Accepted date 22.03.2023

Published date 28.04.2023

**How to Cite:** Baghirzade, A., Omarov, Y., Hacıyeva, A., Gurbanova, S., Gasimova, A., Ismayilov, M., Nabiyev, A. (2023). Improvement of the production technology of tokay wines on the basis of revealing the effect of enzyme activity on the quality of grape variety. *East-European Journal of Enterprise Technologies*, 2 (11 (122)), 49–62. doi: <https://doi.org/10.15587/1729-4061.2023.276251>

## 1. Introduction

Around the world, there is a decrease in the consumption of grape wines, which is associated with profound changes in this area. However, it is important to remember that wines are environmentally friendly products and in certain quantities have a beneficial effect on the human body. First, it is due to the rich chemical composition of the raw materials used in its preparation. Secondly, during the fermentation of grape must in the process of complex biochemical transformations, a huge number of components important for the human body accumulate in the finished product. The human diet should be replenished with organic and inorganic compounds. Their lack over time leads to disease of the body, es-

pecially recently common malignant tumors. Adding dessert wines to the daily diet contributes to the prevention, and even treatment of many diseases. Wine improves metabolism and compounds formed after fermentation stimulate carbohydrate, nitrogenous and mineral metabolism. Therefore, the research into this area is the most relevant. Studies on the choice of raw materials depending on the growing area for the production of Tokay-type wines are poorly understood. Recently, one of the reasons for the limited production of Tokay-type wines is the complexity of choosing a grape assortment and the process of its production. For the first time, Tokay-type wines were prepared in the city of Tokaj in the Republic of Hungary using a special technology. That is why the name of the wine was "Tokay" in honor of the city

of Tokaj. According to Hungarian laws, Tokaj wines are environmentally friendly and are produced in a natural way. It is forbidden to add alcohol and other ingredients to the wine material during its preparation. In its homeland, this wine is also called “royal” wine [1].

Bunches of grapes used to produce Tokay-type wine are withered by twisting on the vine. The main purpose of this process is to artificially increase the percentage of sugar by evaporating moisture in the berries of grapes and slowing down the fermentation process in a natural way without adding alcohol. It is known that in the process of fermentation in the juice or pulp, 14–16 vol. % of alcohol is formed, which contributes to the gradual cessation of this process. As a result, natural sugar and alcohol remain in the wine material. Withered grape varieties, despite their high sugar content, are economically inefficient due to low juice yield and a quantitative decrease in extractive substances. Therefore, the choice of local white and red grape varieties depending on the zoning, as well as the improvement of the technology for the production of Tokay-type wines is an urgent task.

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## 2. Literature review and problem statement

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In work [2] it is noted that for the production of Tokay wines, bunches of grapes are preliminarily withered by twisting bunches on the vine. In this technology, despite an increase in the amount of total sugar, including glucose and fructose, the amount of extractive substances decreases. Along with them, the amount of phenolic compounds, total or titratable acidity, vitamin C and other useful organic substances decreases due to evaporation of moisture. Therefore, this method is considered impractical since most of the bunches break after a while and the yield of raw materials decreases.

The authors in work [3] analyze the mechanical composition of grape varieties used for the production of Tokay wines. Depending on the natural and climatic conditions and agrotechnological factors, grape varieties grown in the low-lying zone and foothills differ in the indicators of mechanical composition, and, most importantly, in the yield of unclarified juice.

In work [4], the authors analyzed grape varieties for the production of wines. Particular attention was paid to local varieties, but there were unresolved issues related to the choice of grape assortment for the production of some dessert wines. This is the approach used in the work, which considers indigenous and introduced grape varieties for the production of dessert wines under local conditions. However, attention is not focused on the zoning of grapes in low-lying zones and foothills.

According to work [5], in overripe grapes, the amount of nutrients is reduced due to their expenditure on the process of respiration. It is known that the decrease in nutrients in overripe and withered grape varieties is due to the action of enzymes. Increased enzyme activity promotes the breakdown of nutrients in grapes. Therefore, in addition to reducing, the likelihood of the formation of methyl alcohol in juice and wine increases due to the active action of pectinesterase. Therefore, an important task is to produce a high-quality product from raw materials with high quality indicators.

The study of the quantitative sugar content in grapes and wine material is reported in [6]. Literature data show that dried grapes should have 38–40 % sugar, this figure can even

increase to 42–45 %. When preparing wine material, the fermentation of grape must or pulp is stopped due to naturally formed alcohol. According to the regulations, sweet dessert wines should contain 12–16 % alcohol and 16–20 % natural sugar. The prepared wine material is subjected to further technological operations and sent for storage in clean, washed, and sterile containers, as well as in oak barrels.

Work [7] notes that during the ripening, storage, and processing of food products, including fruits and berries, various complex processes occur. In grapes and in other products of plant origin, physicochemical, biochemical, biotechnological processes occur mainly with the participation of enzymes of the class oxidoreductase and hydrolases. However, changes in the activity of these enzymes are not considered.

Work [4] indicates that during the fermentation of overripe grapes, it is possible that the wine contains 15–16 % alcohol and up to 16 % residual sugar. It is known that in the process of fermentation, when 15 percent or more of alcohol is formed in an environment, the activity of the enzyme of active yeast (enzyme) stops, that is, alcohol fermentation is suspended and natural sugar remains in the wine material. However, there are no solutions to this problem.

Work [8] reports the study of anthocyanins in grapes. Anthocyanins are actively involved in many biochemical, biotechnological processes occurring in plant organisms. The composition of anthocyanins depends on the grape variety, the place of its growth. This is due to the fact that the formation of anthocyanins is associated with the general metabolism of grapes, which, in turn, affect its taste and aroma. Anthocyanins have a huge impact on the process of long-term storage of grapes and serve as an important component of the chemical composition of berries. Monoglycosides of anthocyanidins slow down the development of mold fungi. In grapes, anthocyanins slow down the vital activity of pathogens and the activity of oxidative enzymes. One of the main biological functions of anthocyanins is to reduce the cholesterol content in the human body, the expansion of cerebral vessels, which helps improve memory. In addition, anthocyanins have a positive effect on the removal of radioactive elements from the body. Some anthocyanin aglycones have antioxidant and antimicrobial properties. Ultimately, wine rich in phenolic compounds, especially anthocyanins, retains its organoleptic characteristics for quite a long time and remains stable.

Work [9] investigated the antioxidant activity of some chemical components. Antioxidants inhibit the negative impact of the spread of radicals on the body, protecting a person from premature aging and a large number of cases of dangerous diseases. The increased content of radicals in the focus can be caused by poisoning, poor ecology, contaminated and poor-quality food, stress. It is known that phenolic compounds are inhibitors of oxidative enzymes. An option to overcome the relevant difficulties may be the regulation of enzymatic activity, which plays an important role in the production of grape wines.

Work [10] emphasizes the qualitative indicators of plant raw materials. Studies considered changes in the quality indicators during the storage of raw materials. After all, high-quality raw materials ultimately contribute to the production of environmentally friendly finished products with high commercial qualities.

The authors of [11] note that the main goal of achieving food security is a guaranteed and sustainable supply of pro-

cessing enterprises with raw materials, and the population with food, not subject to the influence of external and internal adverse effects. The most important condition for achieving food security is the potential physical availability of food for every person. Therefore, the shortage of Tokay-type wines requires new approaches to provide the population with quality products.

In work [12], the authors believe that one of the main indicators of obtaining high-quality wine is the low content of pectin substances in the composition of grapes. A high amount of pectin substances negatively affects the transparency and stability of wine, and even as a result of its enzymatic hydrolysis, the likelihood of methyl alcohol formation due to the methoxyl group increases.

The study of the influence of the dynamics of changes in the activity of certain enzymes on the qualitative indicators of grapes is considered in work [13]. In review [14], the authors consider enzymes of the class oxidoreductases. An increase in the activity of enzymes causes the breakdown of food components and their consumption for the process of respiration. One of the main reasons for the softening and wilting of grape berries, as well as the destruction of their cellular structure, is the high activity of the enzyme pectinesterase. The enzyme pectinesterase [15] catalyzes the conversion of pectin or methoxylated polygalacturonic acid to pectin (polygalacturonic) acid and methyl alcohol. However, methods for eliminating negative consequences are not indicated.

All this allows us to assert that it is advisable to conduct a study on improving the technology of production of Tokay-type wines, expanding the range of wine products and satisfying the various preferences of consumers.

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### 3. The aim and objectives of the study

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The purpose of this study is to identify the regularity of the influence of enzyme activity on the qualitative indicators of grape varieties used for the preparation of Tokay-type wines. This will make it possible to produce dessert wines of the Tokay type with high organoleptic and quality indicators.

To achieve the set aim, the following tasks have been solved:

- to determine the qualitative indicators of ripe and withered white and red grape varieties grown in the lowland zone of Samukh and in the foothills of the Goygol district;
- to study the dynamics of the activity of enzymes of the class oxidoreductase and pectinesterase on the qualitative indicators of grape varieties used for the production of Tokay-type wines during ripening and withering.

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### 4. Research materials and methods

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#### 4.1. Test materials

The object of our study is the technology of production of Tokay-type wine. As a material, ripe technical grape varieties Bayan Shirey, Rkatsiteli, Cabernet Sauvignon, cultivated in the foothills of the Geygol district and in the low-lying zone of the Samukh district, were used.

Grape varieties were harvested from the vineyards of the winery located in the Goygol district and from the Amin farm located in the village of Gara-Yeri, Samukh district [16]. The research was conducted at the Depart-

ment of Food Engineering and Expertise of the Azerbaijan Technological University, as well as in the laboratory at the Georgian Research Institute.

#### 4.2. Methods to investigate the quality indicators of ripened and withered white and red technical grape varieties

Studies were conducted in two ways:

Option I – ripened grape varieties.

Option II – by wilting bunches of grapes of each variety separately by twisting them on the vine. After aging bunches of grapes on the vine for 10–12 days, they are sent for processing. Before processing, the main indicators of the quality of grape varieties for both options were quantitatively determined:

- dry substances and total sugar by hydrometric method;
- glucose by iodometric method;
- fructose by colorimetric method;
- titrable acidity by direct titration;
- vitamin C by dichlorophenolindophenol method;
- pectin substances – by the carboxol method [17, 18];
- active acidity by potentiometric method using the Polish device pH-meter No. 5123;
- phenolic compounds by chromatography-mass spectrometry [19];
- in the course of a study in grape varieties of both variants, changes in the activity of enzymes of the oxidoreductase class were also studied – ascorbate oxidase, o-diphenol oxidase, peroxidase, catalase [20, 21];
- pectinesterase by potentiometric method [22].

In addition, the yield of unclarified juice in some of the above-mentioned ripe and withered grape varieties grown in the low-lying zones of the Samukh district and in the foothills of the Goygol district was determined. Vineyards in the low-lying zone of the Samukh district are located at an altitude of 150–180 m, and in the foothills of the Goygol district – at an altitude of 600–650 m above sea level [24].

According to assumptions, the juice yield from ripened grape varieties should be greater than from withered ones. Despite the high sugar content of dried grapes, the number of important components for wine production will decrease. The content of extractive substances, including phenolic compounds, vitamin C should be contained more in ripe berries since their consumption for metabolic processes increases in withered ones. In addition, in low-lying zones, compared to the foothills, the activity of enzymes should decrease. After all, a decrease in the activity of enzymes of the oxidoreductase class will contribute to an increase in the quantitative content of extractive substances, phenolic compounds, neutralization of hydrogen peroxide formed during metabolism in plants, including grapes. In turn, the activity of pectinesterase will increase the content of methyl alcohol in the wine material.

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### 5. Results of scientific and experimental study of the possibility of using grape varieties for the production of Tokay-type wines

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#### 5.1. Analysis of qualitative indicators of grape varieties grown in the low-lying zone of Samukh and in the foothills of the Goygol district

In the course of the study, the main qualitative indicators of ripe and withered bunches on the vine, white and red

technical grape varieties were studied. Grapes were grown in the low-lying areas of Samukh and in the foothills of the Goygol district. Qualitative indicators of ripened and withered white and red grape varieties grown in the lowland zone of the Samukh district are given in Tables 1, 2 and in Fig. 1.

Qualitative indicators of ripe and withered white grape varieties grown in the lowland zone of Samukh district

No.	Indicators	Bayan Shirey				Rkatsiteli			
		ripe	withered	difference	%	ripe	withered	difference	%
1	Dry matter, g/100 cm <sup>3</sup>	23.7	32.4	+8.7	36.7	29.8	37.9	+8.1	27.2
2	Total sugar, g/100 cm <sup>3</sup>	21.6	29.6	+8	37.3	28.5	35.2	+6.7	23.5
3	Glucose, g/100 cm <sup>3</sup>	8.7	12.2	+3.5	40.2	12.4	15.1	+2.7	21.8
4	Fructose, g/100 cm <sup>3</sup>	9.6	14.8	+5.2	54.1	13.6	17.5	+3.9	28.6
5	Titrateable acidity, g/dm <sup>3</sup>	6.2	5.1	-1.1	17.7	5.8	5.0	-0.8	13.8
6	Active acidity (pH)	3.3	3.5	+0.2	6.1	3.2	3.5	+0.3	9.4
7	Phenolic compounds, g/100 cm <sup>3</sup>	0.76	0.46	-0.30	39.5	0.70	0.42	-0.28	40.0
8	Vitamin C, mg/100 cm <sup>3</sup>	7.8	4.2	-3.6	46.1	7.4	4.1	-3.3	44.6
9	Pectin substances, g/100 cm <sup>3</sup>	0.27	0.16	-0.11	40.7	0.25	0.14	-0.11	44.0
10	Protopectin, g/100 cm <sup>3</sup>	0.14	0.06	-0.08	57.1	0.13	0.05	-0.08	61.5
11	Pectin, g/100 cm <sup>3</sup>	0.13	0.10	-0.03	23.1	0.12	0.09	-0.03	25.0
12	Unclarified juice yield, %	75.5	60.6	-14.9	19.7	77.1	62.5	-14.6	18.9

Table 1 shows that in comparison with ripened white grape varieties, in the berries of withered white varieties due to evaporation of moisture, the amount of dry substances, total sugar, including glucose and fructose, was much higher. While in ripe grape varieties the dry matter content was 23.7÷29.8 g/100 cm<sup>3</sup>, this indicator in the withered varieties changed within 32.4÷37.98 g/100 cm<sup>3</sup>. From the comparison of grape varieties, it can be concluded that the content of dry matter, total sugar, including glucose and fructose, in the Bayan Shirey variety is relatively less, and in Rkatsiteli much more. In ripe and withered grapes of the Bayan Shirey variety, the dry matter content was 23.7÷32.4 g/100 cm<sup>3</sup>, in the Rkatsiteli variety it was much more than 29.8÷37.9 g/100 cm<sup>3</sup>. The total sugar content was 21.6÷29.6 g/100 cm<sup>3</sup> and 27.5÷34.2 g/100 cm<sup>3</sup>, respectively. These indicators were identical to those of fructose and glucose. Thus, it was recorded that the amount of glucose in the ripe Bayan Shirey variety is 8.7÷12.2 g/100 cm<sup>3</sup>, and the amount of fructose is 9.6÷14.8 g/100 cm<sup>3</sup>. In the grapes of the Rkatsiteli variety, the glucose content was 11.4÷14.1 g/100 cm<sup>3</sup>, the amount of fructose – 13.6÷17.5 g/100 cm<sup>3</sup>. It is known that fructose has twice the sweeter taste than glucose. This indicator is not so important in the production of table wines since in the production of table wines, simple sugars are fermented to the end and turned into alcohol. However, in the production of dessert wines, including Tokay-type wines, the high fructose content compared to glucose has a positive effect on its taste [24, 25].

Data in Table 1 demonstrate 1 that the quantitative content of the main indicators of grape quality such as titrated acidity, phenolic compounds, vitamin C, and pectin substances are relatively low in withered grape varieties and significantly higher in ripened ones. While the titrat-

ed acidity in ripened grape varieties was in the range of 6.2÷5.8 g/dm<sup>3</sup>, in withered grape varieties, due to twisting the bunch on the vine, this indicator changed from 5.1÷5 g/dm<sup>3</sup> and decreased to 17.7÷13.8 %.

Compared with ripe grape varieties, the content of phenolic compounds in withered grape berries is 39.5÷40.0 %, vitamin C – 46.1÷44.6 %, pectin substances – 40.7÷44.0 %, and the yield of unclarified juice decreased by 19.7÷18.9 %.

Table 1

Analysis of the studies shows that in withered grape varieties there is a quantitative decrease in titrated acidity, phenolic compounds, vitamin C, and pectin substances. The reason is a decrease in extractive substances and other qualitative indicators that play an important role in the formation and maturation of Tokay-type wines. This reduction negatively affects the taste and aroma of the finished product.

Table 2 provides a comparative analysis of the quality indicators of ripened and withered red grape varieties.

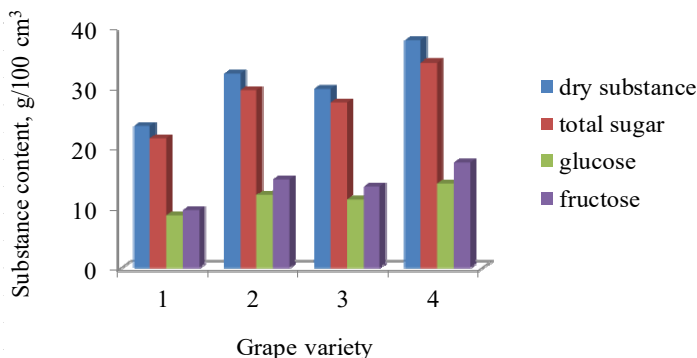


Fig. 1. Comparative analysis of qualitative indicators of ripe and withered white grape varieties: 1 – ripe; 2 – withered Bayan Shirey; 3 – mature; 4 – withered Rkatsiteli

Data in Table 2 demonstrate that compared to the ripened varieties of Cabernet Sauvignon and Madrasa grapes, the withered varieties contained much more dry matter, total sugar, glucose, and fructose. The value of such basic indicators as titrated acidity, phenolic compounds, vitamin C, even the juice yield was much less. While in ripened grape varieties Cabernet Sauvignon and Madrasa the amount of titrated acidity was recorded in the range of 6.5÷6.7 g/dm<sup>3</sup>, in withered grape varieties this figure was equal to 5.3÷5.4 g/dm<sup>3</sup> and decreased by 18.5÷19.4 %. When analyzing the variants, it was found that in comparison with ripe varieties, phenolic compounds in withered grape varieties Cabernet Sauvignon and Madrasa decreased by 40.0 % and 39.4 %, respectively. In these varieties, vitamin C decreased by 35.3÷45.6 %, pectin substances by 42.8 % ÷38.9 %. While in the ripened grape varieties Cabernet Sauvignon and Madrasa the yield of unclarified juice was 74.3÷75.2 %, this figure in the withered varieties was 59.5÷59.6 %.



Table 2

Qualitative indicators of ripe and withered red grape varieties of the lowland zone of the Samukh district

No.	Indicator	Cabernet Sauvignon				Madrasa			
		ripe	withered	difference	%	ripe	withered	difference	%
1	Dry matter, g/100 cm <sup>3</sup>	29.5	37.4	+7.9	26.8	25.5	32.9	+7.4	29.0
2	Total sugar, g/100 cm <sup>3</sup>	27.8	34.7	+6.9	24.8	22.3	29.7	+7.4	33.1
3	Glucose, g/100 cm <sup>3</sup>	11.7	14.2	+2.5	21.3	9.4	12.3	+2.9	30.8
4	Fructose, g/100 cm <sup>3</sup>	13.2	16.7	+3.5	26.5	10.5	15.1	+4.6	43.8
5	Titrateable acidity, g/dm <sup>3</sup>	6.5	5.3	-1.2	18.5	6.7	5.4	-1.3	19.4
6	Active acidity (pH)	3.4	3.5	+0.1	2.9	3.3	3.5	+0.2	6.1
7	Phenolic compounds, g/100 cm <sup>3</sup>	0.90	0.54	-0.36	40.0	0.94	0.57	-0.37	39.4
8	Vitamin C, mg/100 cm <sup>3</sup>	10.2	6.6	-3.6	35.3	12.5	6.8	-5.7	45.6
9	Pectin substances, g/100 cm <sup>3</sup>	0.42	0.24	-0.18	42.8	0.36	0.22	-0.14	38.9
10	Protopectin, g/100 cm <sup>3</sup>	0.18	0.10	-0.08	44.4	0.16	0.10	-0.06	37.5
11	Pectin, g/100 cm <sup>3</sup>	0.24	0.14	-0.10	41.7	0.20	0.12	-0.08	40.0
12	Unclarified juice yield, %	74.3	59.5	-14.8	19.9	75.2	59.6	-15.6	20.7

It is known that in the production of sweet dessert wines in the composition of used grape varieties, along with a high content of extractive substances, the percentage of sugar should be higher. This is mainly due to the fact that dessert wines, including Tokay wines, should contain from 16 to 20 % sugar [26]. From a comparative analysis of ripened grape varieties, it was established that in the Rkatsiteli and Cabernet Sauvignon grape varieties, the increased content of dry substances, especially the percentage of sugar, as well as the main quality indicators, determine their suitability for the production of sweet dessert wines (Tables 1, 2).

Tables 3, 4 give a comparative analysis of the quality indicators of ripened and withered white and red grape varieties grown in the foothills of the Goygol region.

Analysis of data in Table 3 shows that in the ripened grape varieties Bayan Shirey and Rkatsiteli, the dry matter content was 21.4÷25.6 g/100 cm<sup>3</sup>, total sugar 18.5÷22.7 g/100 cm<sup>3</sup>, glucose 8.2÷9.8 g/100 cm<sup>3</sup>, fructose 8.1÷10.1 g/100 cm<sup>3</sup>. And in the withered grape varieties Bayan Shirey and Rkatsiteli, the dry matter content was recorded in the range of 28.6÷32.8 g/100 cm<sup>3</sup>, total sugar 26.4÷30.1 g/100 cm<sup>3</sup>, glucose 11.5÷13.2 g/100 cm<sup>3</sup>, fructose 12.3÷14.7 g/100 cm<sup>3</sup>. Compared with ripe grape varieties in the berries of withered varieties due to evaporation of moisture in the Bayan Shirey variety, the glucose

and fructose content increased by 33.6÷51.8 %, and in the Rkatsiteli variety it is much more by 28.1÷45.5 %. When twisting a bunch of grapes on the vine, the content of phenolic compounds, vitamin C, titrated or non-volatile total acidity, pectin substances is spent on the process of respiration, thereby decreasing.

It is known that with prolonged non-use of foods rich in phenolic compounds and vitamin C, immunity decreases, conditions are created for the development of pathogens and viruses [27]. Phenolic compounds, like vitamin C, are organic compounds with high antioxidant, antimicrobial, and even antiviral properties. The lack of phenolic compounds and vitamin C in foods, including grapes and wine, not only negatively affects the quality of the product but also makes them predisposed to diseases [28, 29].

In addition, it is known that with a lack of phenolic compounds in the human body, vitamin C, fat metabolism is disturbed. As a result, the amount of cholesterol in the human body increases. This, without a doubt, primarily contributes to the disruption of the cardiovascular system, memory, blood circulation, and the formation of other more dangerous diseases [30]. Therefore, the presence of phenolic compounds, vitamin C, and other biologically active substances in the daily diet of people is very important from the point of view of their health [31, 32].

Table 3

Study of qualitative indicators of white grape varieties grown in the foothills of the Goygol district

No.	Indicator	Bayan Shirey				Rkatsiteli			
		ripe	withered	difference	%	ripe	withered	difference	%
1	Dry matter, g/100 cm <sup>3</sup>	21.4	28.6	+7.2	33.6	25.6	32.8	+7.2	28.1
2	Total sugar, g/100 cm <sup>3</sup>	18.5	26.4	+7.9	42.7	22.7	30.1	+7.4	32.6
3	Glucose, g/100 cm <sup>3</sup>	8.2	11.5	+3.3	40.2	9.8	13.2	+3.4	34.7
4	Fructose, g/100 cm <sup>3</sup>	8.1	12.3	+4.2	51.8	10.1	14.7	+4.6	45.5
5	Titrateable acidity, g/dm <sup>3</sup>	8.3	6.1	-2.2	26.5	6.7	4.8	-1.9	28.3
6	Active acidity (pH)	3.4	3.5	+0.1	2.9	3.3	3.5	+0.2	6.1
7	Phenolic compounds, g/100 cm <sup>3</sup>	0.84	0.41	-0.43	51.2	0.78	0.38	-0.40	51.3
8	Vitamin C, mg/100 cm <sup>3</sup>	8.5	4.4	-4.1	48.2	8.1	4.0	-4.1	50.6
9	Pectin substances, g/100 cm <sup>3</sup>	0.34	0.25	-0.09	26.5	0.31	0.20	-0.11	35.5
10	Protopectin, g/100 cm <sup>3</sup>	0.20	0.13	-0.07	35.0	0.18	0.12	-0.06	33.3
11	Pectin, g/100 cm <sup>3</sup>	0.14	0.12	-0.02	14.3	0.13	0.08	-0.05	38.5
12	Unclarified juice yield, %	74.6	56.4	-18.2	24.4	75.6	59.5	-16.1	21.3

It should be noted that while in ripe grape varieties the content of phenolic compounds was 0.84 g/100 cm<sup>3</sup>, in the dried varieties aimed at processing, this figure decreased by 51.2÷51.3 % and amounted to 0.41 g/100 cm<sup>3</sup>.

This indicator is almost identical to vitamin C. While in the ripened grape varieties Bayan Shirey and Rkatsiteli the content of vitamin C fluctuated between 8.5÷8.1 mg/100 cm<sup>3</sup>, in the withered grape varieties this indicator was, respectively, 4.1÷4.0 mg/100 cm<sup>3</sup> and decreased by 48.2÷50.6 %.

From the study of literature data and research results, it became known that a decrease in the content of pectin substances in overripe and withered grapes negatively affects the production process [33]. This is mainly explained by the fact that under the action of the enzyme pectinesterase, as a result of the breakdown or hydrolysis of pectin substances in grape berries, methyl alcohol is formed, which destroys its cellular structure. As a result, the berries soften, and certain defects appear in the taste and aroma.

While the yield of unclarified juice in ripe grape varieties Bayan Shirey and Rkatsiteli was in the range of 74.6÷75.6 %, this figure in withered grape varieties was significantly less and amounted to 56.4÷59.5 %. This, of course, is not economically feasible.

In the course of the study for the production of Tokay wines, the qualitative indicators of red technical grape varieties Cabernet Sauvignon and Madrasa grown in the foothills of the Goygol region were also studied. Qualitative indicators of grape varieties are given in Table 4.

As in white grape varieties, in red varieties there were also similarities in the change in quality indicators. When studying red grape varieties, it was found that, in comparison with ripened grape varieties, in withered varieties the content of the analyzed substances, as well as the juice yield, was significantly less (Table 4).

Comparison of grape varieties revealed that the quantitative content of dry matter, total sugar, including glucose and fructose, differs. While in the Bayan Shirey grape variety, growing in the foothills of the Goygol district, the total sugar was 18.5 g/100 cm<sup>3</sup>, in the Rkatsiteli variety this figure was 22.7 g/100 cm<sup>3</sup>. In the red grape variety Cabernet Sauvignon, this figure was 22.6 g/100 cm<sup>3</sup>, and in the Madrasa variety it was 19.7 g/100 cm<sup>3</sup>. While in the withered variety of Bayan grapes the quantitative content of total sugar is 26.4 g/100 cm<sup>3</sup>, in the withered grape variety Rkatsiteli this indicator is 30.1 g/100 cm<sup>3</sup>, in Cabernet Sauvignon – 29.1 g/100 cm<sup>3</sup>, in Madrasa – 27.5 g/100 cm<sup>3</sup>.

Data in Tables 3, 4 clearly demonstrate that for the production of Tokay-type wines in ripe and withered grape varieties, the total sugar content is different. The highest total sugar content is recorded in the Rkatsiteli and Cabernet Sauvignon grape variety, then in the Madrasa variety, and the lowest in the Bayan Shirey variety. The differences recorded in the content of dry matter, total sugar, glucose, and fructose depend on the specific characteristics of the grape variety, natural and climatic conditions, the complexity of the process of photosynthesis, and other factors.

In addition, a comparative analysis of the qualitative indicators of ripe and withered white and red grape varieties grown in the lowland areas of the Samukh district and in the foothills of the Goygol district was also conducted.

The quantitative change in the dry matter of grape varieties by region is given in Table 5 and Fig. 2.

Table 5 and Fig. 2 show that in the mature variety Bayan Shirey, grown in the low-lying zones of the Samukh district, the dry matter content is 23.7 g/100 cm<sup>3</sup>. In the withered varieties, the amount of dry matter is 32.4 g/100 cm<sup>3</sup>, and in varieties grown in the foothills of the Goygol district, this figure is 21.4 and 28.9 g/100 cm<sup>3</sup>, respectively.

Table 4

Study of qualitative indicators of red grape varieties grown in the foothills of the Goygol district

No.	Indicator	Cabernet Sauvignon				Madrasa			
		ripe	withered	difference	%	ripe	withered	difference	%
1	Dry matter, g/100 cm <sup>3</sup>	25.8	32.2	+6.4	24.8	22.6	30.8	+8.2	36.3
2	Total sugar, g/100 cm <sup>3</sup>	22.6	29.1	+6.5	28.8	20.7	27.5	+6.8	32.8
3	Glucose, g/100 cm <sup>3</sup>	9.5	13.6	+4.1	43.2	8.6	12.4	+3.8	44.2
4	Fructose, g/100 cm <sup>3</sup>	10.1	13.8	+3.7	36.6	8.5	12.5	+4.0	47.1
5	Titrateable acidity, g/dm <sup>3</sup>	7.4	5.1	-2.3	31.1	8.7	6.2	-2.5	28.7
6	Active acidity (pH)	3.4	3.6	+0.2	5.9	3.5	3.6	+0.1	2.9
7	Phenolic compounds, g/100 cm <sup>3</sup>	1.10	0.76	-0.34	30.9	1.20	0.75	-0.45	37.5
8	Vitamin C, mg/100 cm <sup>3</sup>	12.1	7.6	-4.5	37.2	12.8	7.7	-5.1	39.8
9	Pectin substances, g/100 cm <sup>3</sup>	0.48	0.34	-0.14	29.7	0.46	0.32	-0.14	30.4
10	Protopectin, g/100 cm <sup>3</sup>	0.26	0.20	-0.06	23.1	0.29	0.18	-0.11	37.9
11	Pectin, g/100 cm <sup>3</sup>	0.22	0.14	-0.08	36.4	0.22	0.14	-0.08	36.4
12	Unclarified juice yield, %	75.1	57.2	-17.9	23.8	74.2	56.2	-18.0	24.3

Table 5

Quantitative change of dry matter in white and red grape varieties by region, g/100 cm<sup>3</sup>

Indicator	Bayan Shirey		Rkatsiteli		Cabernet Sauvignon		Madrasa	
	Samukh district	Goygol district	Samukh district	Goygol district	Samukh district	Goygol district	Samukh district	Goygol district
Ripe	23.7	21.4	29.8	25.6	29.5	25.8	26.5	22.6
Withered	32.4	28.6	37.9	32.8	37.4	32.2	32.9	30.8

The amount of dry matter in the grape variety Rkatsiteli, grown in the Samukh district, is 29.8 g/100 cm<sup>3</sup>, in the dried grape variety 37.9 g/100 cm<sup>3</sup>, in the foothills of the Goygol district this figure is respectively 25.6÷32.8 g/100 cm<sup>3</sup>. The amount of dry matter in the ripened grape variety Cabernet Sauvignon, grown under the conditions of the Samukh district is 29.5 g/100 cm<sup>3</sup>. In a dried grape variety, the amount of dry matter is 37.4 g/100 cm<sup>3</sup>, and in the Goygol district, respectively, it is 25.8 g/100 cm<sup>3</sup> and 32.2 g/100 cm<sup>3</sup>.

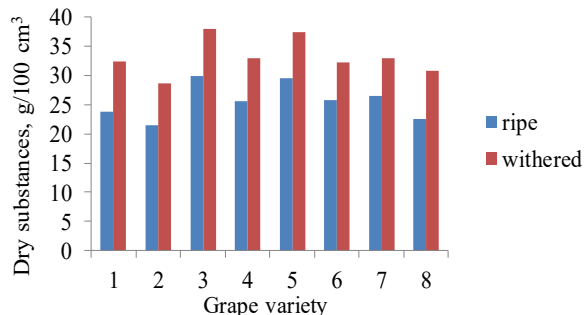


Fig. 2. Quantitative change of dry matter in white and red grape varieties grown in the low-lying zone of the Samukh district and in the foothills of the Goygol district: 1, 2 – Bayan Shirey; 3, 4 – Rkatsiteli; 5, 6 – Cabernet Sauvignon; 7, 8 – Madrasa; 1, 3, 5, 7 – Samukh district; 2, 4, 6, 8 – Goygol district

The amount of dry matter in the ripened red grape variety Madrasa, grown in the Samukh district, was 26.5 g/100 cm<sup>3</sup>, in the withered – 32.9 g/100 cm<sup>3</sup>. In the conditions of the Goygol district, this figure in the ripened variety was 22.6 g/100 cm<sup>3</sup> and 30.8 g/100 cm<sup>3</sup> in withered.

Table 6 and Fig. 3 show the comparative change in total sugar in ripe and withered white and red grape varieties grown in low-lying areas of Samukh district and in the foothills of Goygol district.

Quantitative change in total sugar in white and red grape varieties by region, g/100 cm<sup>3</sup>

Indicator	Samukh district		Goygol district		Samukh district		Goygol district	
	Bayan Shirey	Rkatsiteli	Bayan Shirey	Rkatsiteli	Cabernet Sauvignon	Madrasa	Cabernet Sauvignon	Madrasa
Ripe	21.6	27.5	18.5	22.7	26.8	22.3	22.6	19.7
Withered	29.6	34.2	26.4	30.1	33.7	29.7	29.1	27.5

Data in Table 6 and Fig. 3 demonstrate that the amount of total sugar in the ripened white grape variety Bayan Shirey grown in the low-lying zone of the Samukh district is 21.6 g/100 cm<sup>3</sup>, in the withered – 29.6 g/100 cm<sup>3</sup>, in the Rkatsiteli variety this figure is, respectively, equal to 27.5÷34.2 g/100 cm<sup>3</sup>. This figure under the conditions of the Geygol district, respectively, was 18.6÷28.6 g/100 cm<sup>3</sup> in the Bayan Shirey variety and 22.7÷30.1 g/100 cm<sup>3</sup> in the Rkatsiteli variety.

In ripe red grape varieties grown in the Samukh district, the total sugar content was 26.8, in withered grape varieties – 33.7 g/100 cm<sup>3</sup>, and in the Madrasa variety this figure ranged from 22.3÷29.7 g/100 cm<sup>3</sup>. The amount of total sugar in the grapes of the Cabernet Sauvignon variety grown in the foothills of the Goygol district was 22.6 g/100 cm<sup>3</sup>, in withered –

29.1 g/100 cm<sup>3</sup>, and in the Madrasa variety there was a change in the range of 19.7÷27.5 g/100 cm<sup>3</sup> (Fig. 3).

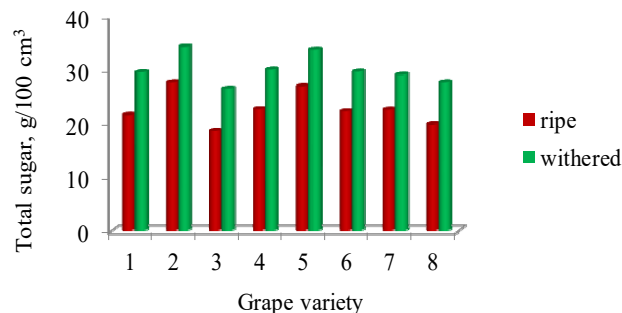


Fig. 3. Quantitative change in total sugar in white and red grape varieties grown in low-lying areas of Samukh district and in the foothills of Goygol district: 1, 3 – Bayan Shirey; 2, 4 – Rkatsiteli; 5, 7 a Cabernet Sauvignon; 6, 8 – Madrasa; 1, 2, 5, 6 – Samukh district; 3, 4, 7, 8 – Goygol district

Despite the high content of dry matter, total sugar, as well as glucose and fructose in withered grape varieties, their main quality indicators compared to ripe grape varieties are significantly reduced. This negatively affects the quality of wine, its enrichment with extractive substances, and its long-term stability.

### 5. 2. Investigating enzyme activity in grape varieties grown in low-lying areas of Samukh and foothills of Goygol districts

From the study of literature data, it is known that the main reason for the withering of grapes by twisting bunches on the vine, softening of berries is an increase in the activity of enzymes of the class oxidoreductases and some enzymes of the hydrolase class [34]. An increase in the activity of enzymes also contributes to a decrease in the quality of grapes [35, 36]. Softening of grape berries occurs due to an increase in the

Table 6

activity of a representative of pectin enzymes – the enzyme pectinesterase. At this time, under the action of the enzyme pectinesterase, pectin in grape berries is hydrolyzed to pectinic acid and methyl alcohol. The formed methyl alcohol destroys the cellular structure of grape berries and reduces its quality [37]. This, of course, negatively affects the quality of the Tokay-type wines produced.

From this point of view, it is necessary to investigate the change in the activity of enzymes of the oxidoreductase class. This class includes ascorbate oxidase, o-diphenol oxidase, peroxidase, and catalase. Along with them, in ripe and withered grape varieties, the activity of the enzyme pectinesterase, which belongs to the class of hydrolases, was studied.

Enzymes belonging to the class of oxyreductases catalyze redox reactions. Most representatives of oxidoreductases are widely studied in the food industry, in fruits and berries, including grapes and wine. Ascorbate oxidase (FT.1.10.3.3.), being a representative of aerobic dehydrogenases, is one of the most important enzymes that play an important role in the ripening and processing of grapes. Aerob dehydrogenases are also called oxidases. Aerob dehydrogenases take

hydrogen from oxidized substances and transfer it to oxygen. Anaerobic dehydrogenases take hydrogen from oxidized substances and transfer instead of oxygen to another acceptor, other enzymes. Oxygen is not involved in the reactions they catalyze. The enzyme ascorbate oxidase refers to aerobic dehydrogenases and catalyzes the conversion of ascorbic acid (vitamin C) to dehydro-L-ascorbic acid [38].

The enzyme o-diphenol oxidase (FT.1.14.18.2.) refers to aerobic dehydrogenases and catalyzes the conversion of a wide range of phenolic compounds, including ortho- and para-diphenols, into o-quinone. Peroxidase (FT.1.11.1.7.) refers to anaerobic dehydrogenases and catalyzes the oxidation of polyphenols and a number of aromatic amines in the presence of hydrogen peroxide. Its action takes place in an oxygen-free environment. The enzyme catalase neutralizes hydrogen peroxide formed during metabolism in plants, including grapes, by splitting it into water and molecular oxygen [39].

During the ripening, withering, and processing of grapes, complex biochemical and biotechnological processes occur. The role of enzymes in the regulation of these processes is indispensable. Increasing the activity of enzymes accelerates the consumption of nutrients of food products, including grapes and wine, on the process of respiration.

For this purpose, the dynamics of changes in the activity of the above enzymes in ripe and withered grape varieties studied in the lowland zone of the Samukh district and in the foothills of the Goygol district were studied. First, the dynamics of changes in the activity of the above enzymes in mature and pre-withered white and red grape varieties grown in the lowland zone of the Samukh district were studied. These indicators are given in Table 7.

Data in Table 7 demonstrate that the activity of the studied enzymes in withered grapes is significantly higher than in ripened grapes. When wilting a ripe variety of Bayan Shirey grapes by twisting on the vine, the activity of the enzyme ascorbate oxidase increased by 86.1 %, and in Rkatsiteli by 74.3 %.

Table 7

Comparative analysis of the activity of some enzymes of the oxidoreductase class in grape varieties grown in low-lying areas of the Samukh region

Grape varieties	Indicators	Enzymes			
		Ascorbate oxidase	O-diphenol oxidase	Peroxidase	Catalase
Bayan Shirey	ripe	0.72	0.88	2.40	0.46
	withered	1.34	1.45	3.88	0.78
	difference	+0.62	+0.57	+1.48	+0.32
	%	86.1	64.5	61.7	69.6
Rkatsiteli	ripe	0.78	1.01	2.50	0.48
	withered	1.36	1.64	4.06	0.82
	difference	+0.58	+0.63	+1.56	+0.34
	%	74.3	62.3	62.4	70.8
Cabernet Sauvignon	ripe	0.66	0.72	2.10	0.44
	withered	0.14	1.16	3.40	0.70
	difference	+0.46	+0.44	+1.30	+0.26
	%	67.6	61.1	61.9	59.41
Madrasa	ripe	0.72	0.88	2.20	0.48
	withered	1.17	1.41	3.48	0.78
	difference	+0.45	+0.33	+1.28	+0.30
	%	62.5	60.2	58.2	62.5

Note: the activity of the enzyme is determined in mg of oxidized substrate, decomposed in 30 minutes by enzymes of 1 g of tissue

Increasing the activity of the enzyme accelerates the consumption of ascorbic acid (vitamin C) contained in dried grapes for the process of respiration. At this time, as a result of the redox process, the natural color of grape juice changes and becomes much darker. The activity of all the studied enzymes in withered white grape varieties in comparison with the ripened varieties was constantly increasing.

Data in Table 7 show that the enzymes o-diphenol oxidase and peroxidase were reduced to the enzymes ascorbate oxidase and catalase less activated. While in withered white grape varieties, the activity of the enzymes ascorbate oxidase and catalase was equal to 86.1÷70.8 %, this figure for the enzymes o-diphenol oxidase and peroxidase was 61.7÷64.5 %. The relatively low activation of the enzymes o-diphenol oxidase and peroxidase in withered grapes is due to the anti-oxidant property of the phenolic compounds contained in the withered varieties.

The activity of enzymes was also studied in ripe and withered red grape varieties Cabernet Sauvignon and Madrasa, grown in low-lying areas of the Samukh region. When comparing grape varieties, it became clear that in the Cabernet Sauvignon grape variety, the activity of all the studied enzymes increased by 67.6÷59.4 %, and in the Madrasa variety – by 62.5÷58.2 %.

Compared with the white grape variety, in red varieties the relative low activity of enzymes is explained by a slowdown in the oxidation process due to the action of anthocyanins, which are representatives of phenolic compounds.

The change in the activity of the enzyme pectinesterase in ripe and withered grape varieties in the lowland zone of the Samukh district was also studied. These indicators are given in Table 8.

Table 8

Comparative analysis of the activity of the enzyme pectinesterase in grape varieties grown in the lowland zones of the Samukh district

No.	Grape variety	Ripe	Withered	Difference	%
1	Bayan Shirey	22.8	38.6	+15.8	69.3
2	Rkatsiteli	24.5	40.8	+16.3	66.5
3	Cabernet Sauvignon	27.4	42.4	+15.0	54.7
4	Madrasa	28.2	44.3	+16.1	57.1

Note: in relative units per mg of acetone preparation

The enzyme pectinesterase, related to pectin enzymes, catalyzes the conversion of pectin or methoxylated polygalacturonic acid into methyl alcohol and polygalacturonic acid (pectinic acid). In the next step, polygalacturonic acid is hydrolyzed (in the presence of water) to a large amount of galacturonic acids and other monosaccharides (hexose, pentose, etc.) under the action of the enzyme polygalacturonase or pectinase.

Data in Table 8 demonstrate that the activity of the enzyme pectinesterase compared to ripened grape varieties is significantly higher in withered varieties. This figure in the Bayan Shirey variety was 69.3 %, in Rkatsiteli – 66.5 %, in Cabernet Sauvignon – 54.7 %, in Madrasa – 57.1 %. Compared with white grape varieties, the activity of the enzyme pectinesterase was significantly lower than that of red grape varieties. The main reason for this is that red grape varieties contain more phenolic compounds, including anthocyanins, than



white ones. Therefore, phenolic compounds are considered as antioxidants of the enzyme pectinesterase.

Table 9 shows the change in the activity of some enzymes of the class oxidoreductase in ripe and withered grape varieties grown in the foothills of the Goygol region.

Table 9

Comparative analysis of the activity of some enzymes of the class oxidoreductase in ripe and withered grape varieties grown in the foothills of the Goygol district

Grape varieties	Indicators	Enzymes			
		Ascorbate oxidase	O-diphenol oxidase	Peroxidase	Catalase
Bayan Shirey	ripe	0.68	0.70	1.98	0.33
	withered	1.01	0.98	2.83	0.45
	difference	+0.33	+0.28	+0.85	+2.12
	%	48.5	40.0	42.9	36.4
Rkatsiteli	ripe	0.72	0.77	2.20	0.39
	withered	1.08	1.09	3.0	0.53
	difference	+0.36	+0.32	+0.08	+0.14
	%	50.0	41.5	36.4	35.9
Cabernet Sauvignon	ripe	0.64	0.66	1.86	0.38
	withered	0.89	0.87	2.41	0.51
	difference	+0.25	+0.21	+0.55	+0.13
	%	39.1	31.8	29.6	34.2
Madrasa	ripe	0.55	0.74	1.88	0.40
	withered	0.73	0.95	2.37	0.54
	difference	+0.18	+0.21	+0.49	+0.14
	%	32.7	28.4	26.1	35.0

Note: the activity of the enzyme is determined in mg of oxidized substrate, decomposed in 30 minutes by enzymes of 1 g of tissue

Data in Table 9 demonstrate that the activity of the studied oxidoreductases compared to ripened grape varieties is higher in withered varieties. For example, compared with ripened grape varieties Bayan Shirey and Rkatsiteli, the activity of the enzyme o-diphenol oxidase in withered grapes varied between 40.0÷41.5 %. These rates increased by 48.5÷50.0 % for the enzyme ascorbate oxidase, 42.9÷36.4 % for peroxidase and 36.4÷35.9 % for catalase. The activity of enzymes in ripe varieties of Cabernet Sauvignon and Madrasa grapes grown in the foothills of the Goygol region changed in different ways.

Compared with the ripened grape variety Cabernet Sauvignon and Madrasa in the withered varieties, the activity of enzymes increased by 29.6÷39.1 %, this figure in the Madrasa variety increased by 35.0÷26.1 %. Compared with ripe and withered red grape varieties, white varieties grown in the foothill zone of the Goygol region had much higher enzymatic activity (Table 9).

Table 10 gives a comparative analysis of the activity of the enzyme pectinesterase in ripe and withered grape varieties grown in the foothills of the Goygol district.

Data in Table 10 demonstrate that in comparison with ripened grape varieties, the activity of the enzyme pectinesterase is higher in withered varieties. In addition, it was found that the activity of the enzyme pectinesterase is higher in white grape varieties than in red ones. For example, while in the withered white grape varieties Bayan Shirey and Rkatsiteli in comparison with the ripened ones, the activity of the enzyme pectinesterase increased by 71.8÷65.5 %, this indicator in the grape varieties Cabernet Sauvignon and Madrasa increased by 50.6÷51.0 %.

Table 10

Comparative analysis of the activity of some pectinesterase enzyme in ripe and withered grape varieties grown in the foothills of the Goygol region

No.	Grape variety	Ripe	Withered	Difference	%
1	Bayan Shirey	20.6	35.4	11.8	71.8
2	Rkatsiteli	22.4	37.1	14.7	65.6
3	Cabernet Sauvignon	24.1	36.3	12.2	50.6
4	Madrasa	25.3	38.2	12.9	51.0

Note: in relative units per mg of acetone preparation

The main reason for this is the higher content of phenolic compounds with antioxidant and antimicrobial properties and vitamin C in red grape varieties compared to white grapes. Increased enzyme activity in withered grape varieties leads to the fact that more nutrients, including pectin, are spent on the process of respiration.

Fig. 4 shows the indicators of comparative analysis of the activity of enzymes belonging to the class of oxidoreductases in ripe and withered varieties of white grapes grown in the foothills of the Goygol and lowland zone of the Samukh districts.

Data in Tables 7, 9, and Fig. 4 show that the activity of enzymes in white grape varieties was high in the Samukh district and relatively low in the Goygol district. Compared with the Bayan Shirey variety, grown in the low-lying zone of the Samukh district, enzymes were activated by 86.1÷61.7 %, this figure for the Bayan Shirey variety grown in the foothills of the Goygol district increased by 48.5÷36.4 %. The results obtained were identical for the grape varieties Rkatsiteli, Cabernet Sauvignon, and Madrasa. A comparative analysis of the change in enzyme activity on the example of white grape varieties by region is shown in Fig. 4.

Fig. 4 shows that the activity of enzymes in the grape varieties Bayan Shirey and Rkatsiteli (3, 4) grown in the Samukh region is significantly higher than in the same grape varieties grown in the Goygol district.

We also performed a comparative analysis of the activity of the enzyme pectinesterase by region. This indicator is shown in Fig. 5.

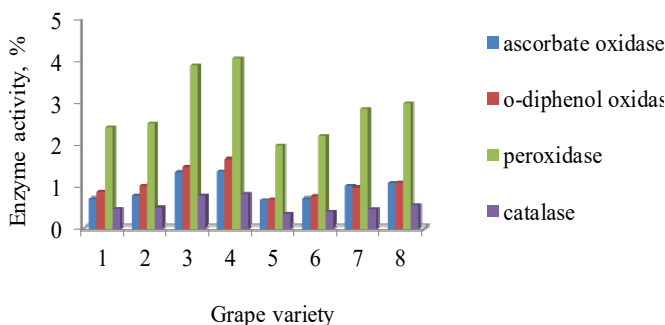


Fig. 4. Dynamics of changes in the activity of enzymes of the oxidoreductase class in white grape varieties by districts: Samukh district: 1 – Bayan Shirey (ripe); 2 – Rkatsiteli (mature); 3 – Bayan Shirey (withered); 4 – Rkatsiteli (withered); Goygol district: 5 – Bayan Shirey (ripe); 6 – Rkatsiteli (mature); 7 – Bayan Shirey (withered); 8 – Rkatsiteli (withered)

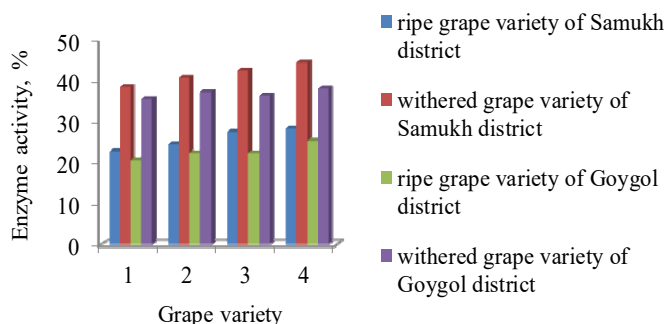


Fig. 5. Dynamics of changes in the activity of the enzyme pectinesterase in white and red grape varieties by districts: 1 – Bayan Shirey; 2 – Rkatsiteli; 3 – Cabernet Sauvignon; 4 – Madrasa

Compared with ripened grape varieties, in the withered grapes grown in the lowland zone of the Samukh district, the activity of the enzyme pectinesterase increased within 69.3÷57.4 %, while in the GayGöl district this figure increased by 71.8÷50.6 %. The analysis of Fig. 4, 5 revealed that in mature and withered grape varieties, there is no noticeable difference in the activity of the enzyme pectinesterase, in contrast to enzymes belonging to the class of oxidoreductases.

## 6. Discussion of experimental results of investigating the possibility of using grape varieties for the production of Tokay-type wines

Improving the organoleptic properties of wines requires the right choice of grape assortment. This is possible only if the mechanical and chemical compositions of the raw materials used to produce high-quality wines with the best organoleptic characteristics are known.

Analysis of studies of qualitative indicators of grape varieties shows that in withered varieties there is a quantitative decrease in titrated acidity, phenolic compounds, vitamin C, and pectin substances. The reason is a decrease in extractive substances and other qualitative indicators. They play an important role in the formation and maturation of Tokay-type wines. This reduction negatively affects the taste and aroma of the finished product.

As a result of the analysis, it was found that when withering the studied grape varieties, by twisting bunches on the vine grown in the low-lying areas of the Samukh and in the foothills of the Goygol districts, the number of basic qualitative indicators of grapes increases. The main qualitative indicators include total sugar, including glucose and fructose. In addition, favorable conditions are created to reduce the amount of extractive substances, including phenolic compounds, total or titratable acidity, vitamin C, and other useful organic substances due to evaporation of moisture.

From the results of the study of the qualitative indicators of grapes, it is clear that the total sugar content in ripened grape varieties grown in the Samukh district ranged from 21.6÷27.5 %. Total sugar in the withered varieties changed within 29.6÷34.2 % (Tables 1, 2). This indicator for the Goygol district was 18.5÷22.7 and 26.4÷30.1 %, respectively (Tables 3, 4). A comparison of grape varieties showed that among the ripened and withered varieties, sugar accumulates the most in the Rkatsiteli and Cabernet Sauvignon varieties grown under the conditions of the Samukh district (Fig. 1).

From a comparative analysis of ripened grape varieties, it has been established that the Rkatsiteli and Cabernet Sauvignon grape varieties are superior in dry matter content (Table 5 and Fig. 2). It is the increased percentage of sugar, as well as the main quality indicators, that determine their suitability for the production of sweet dessert wines.

From the results of the studies given in Table 6, it is clear that for the production of Tokay-type wines, the total sugar content differs in ripe and withered grape varieties. The highest content of total sugar was recorded in the Rkatsiteli and Cabernet Sauvignon grape varieties, then in the Madrasa variety, and the lowest in the Bayan Shirey variety (Fig. 3). Differences recorded in the content of dry matter, total sugar, glucose, and fructose depend on the specific features of the grape variety, natural and climatic conditions, the complexity of the photosynthesis process, and other factors.

Despite the high content of dry matter, total sugar, as well as glucose and fructose in withered grape varieties, their main quality indicators compared to ripe grape varieties are significantly reduced. This negatively affects the quality of wine, its enrichment with extractive substances, and its long-term stability.

It is known that one of the main indicators of obtaining high-quality wine is the low content of pectin substances in the composition of grape varieties. With a large number of pectin substances, they adversely affect the transparency and stability of wine, and even as a result of its enzymatic hydrolysis, the likelihood of methyl alcohol formation increases due to the methoxyl group (CH<sub>3</sub>O-). When studying grape varieties, it was found that a high content of pectin was found in grape varieties grown under the conditions of the Goygol district, and less in the Samukh district.

From the results of the analysis of Table 8, it was found that the activity of the enzyme pectinesterase compared to ripened grape varieties is significantly higher in withered varieties. This figure in the Bayan Shirey variety was 69.3 %, in Rkatsiteli – 66.5 %, in Cabernet Sauvignon – 54.7 %, in Madrasa – 57.1 %. Compared with white grape varieties, the activity of the enzyme pectinesterase was significantly lower than that of red grape varieties (Table 10). The main reason for this is that red grape varieties contain more phenolic compounds, including anthocyanins, than white ones. Therefore, phenolic compounds are considered as antioxidants of the enzyme pectinesterase. The activity of enzymes in Bayan Shirey and Rkatsiteli grape varieties grown in the Samukh region is much higher than in the same grape varieties grown in the Goygol district.

From the results of studies of the activity of enzymes, it became clear that when withering bunches on the vine, the amount of nutrients in the berries decreases due to their expenditure on the process of breathing. It is known that the decrease in nutrients in overripe and withered grape varieties is due to the action of enzymes. Therefore, in studies in both areas in ripe and withered grape berries, the dynamics of changes in the activity of certain enzymes of the oxidoreductase class and a representative of pectin enzymes – pectinesterase – were studied.

Compared with ripened grape varieties, withered grapes grown in the lowland zone of the Samukh district, the activity of the enzyme pectinesterase increased within 69.3÷57.4 %, while in the Goygol district this figure increased by 71.8÷50.6 % (Fig. 5). From the analysis of the activity of the enzyme of the hydrolase class, it was revealed

that in mature and withered grape varieties, there is no noticeable difference in the activity of the enzyme pectinesterase, in contrast to enzymes belonging to the class of oxidoreductases.

The results of the study of enzyme activity showed that the activity of all the studied enzymes increased in withered white and red grape varieties (Tables 7, 9). Increased enzyme activity contributed to the breakdown of nutrients in grapes. Therefore, in addition to reducing, the likelihood of methyl alcohol formation in juice and wine increases due to the action of pectinesterase. It goes without saying that it is impossible to make a quality product if the quality indicators of raw materials, used for the production of wine, are low.

It is known that when preparing sweet dessert wines of the Tokay type, in contrast to table wines, it is more expedient to use ripe technical grape varieties with a high sugar content and rich nutritional components. The development of new technological methods for the use of local grape varieties rich in nutrients, especially glucose and fructose, vitamin C, phenolic compounds, etc. will improve existing technologies for the production of Tokay-type wines and provide the population with environmentally friendly products.

According to Hungarian technology, for the production of Tokay-type wines, bunches of white and red grape varieties are twisted on the vine. A certain time is withered, then served for processing. At the same time, the percentage of sugar in grapes is artificially increased due to the evaporation of moisture. The percentage of sugar in pre-dried grape berries should be in the range of 40–45 %. For the production of Tokay-type wines, the fermentation of grape must is carried out naturally without the addition of alcohol and other ingredients. After formation in the must 14–16 vol. % alcohol, the fermentation process is suspended naturally. According to the existing technology, approximately 15–20 % of bunches of grapes by twisting on the vine for 10–12 days are washed and fall to the ground. And this reduces the yield of raw materials and juice. The authors in their studies did not address the issues of zoning varieties and the effect of enzyme activity on changes in the quality indicators of grapes [37]. Whereas in this work, changes in qualitative indicators are analyzed in grape varieties depending on the place of cultivation and the dynamics of enzyme activity.

The results of the study of the activity of enzymes and their influence on the change in the qualitative indicators of grapes make it possible to adjust the qualitative indicators of grape varieties depending on their zoning and use for the production of high-quality wines of the Tokay type (Fig. 4).

The study revealed limitations associated with the fact that in the production of Tokay-type wines in raw materials, the percentage of sugar should increase naturally. When fermenting, no additional ingredients (granulated sugar, concentrated juice or *bekmez*) are added to the must. In addition, in withered grape varieties, due to an increase in the activity of enzymes, the nutritional value of the finished product decreases. An increase in the activity of ascorbatoxidase contributes to a decrease in vitamin C. The activity of peroxidase leads to the breakdown of aromatic amines. O-diphenol oxidase by activating breaks down phenolic compounds. In withered berries, the activity of pectinesterase promotes the breakdown of pectin into methyl alcohol and polygalacturonic acid. In the production of wines to create a bouquet and aroma, as well as saturate the finished product with aromatic substances, it is important to regulate the activity of enzymes.

Our studies have made it possible to determine the suitability of grape varieties and their zoning for the preparation of Tokay-type wines.

Tokay wines are sweet dessert wines, and therefore, in comparison with other indicators, the quantitative content of total sugar, including glucose and fructose, should be higher. In addition, analyzes indicate that ripened grape varieties are rich in extractive substances, vitamin C, phenolic compounds, while in withered berries their number decreases.

Analysis of the studies shows that in withered grape varieties there is a quantitative decrease in titrated acidity, phenolic compounds, vitamin C, and pectin substances (Fig. 1). The reason is a decrease in extractive substances and other qualitative indicators that play an important role in the formation and maturation of Tokay-type wines. This reduction negatively affects the taste and aroma of the finished product.

It is known that in the production of sweet dessert wines in the composition of used grape varieties, along with a high content of extractive substances, the percentage of sugar should be higher. This is mainly due to the fact that dessert wines, including Tokay wines, should contain from 16 to 20 % sugar.

For the production of Tokay-type wines in ripe and withered grape varieties, the total sugar content is different. The highest content of total sugar is recorded in the grape variety *Rkatsiteli* and *Cabernet Sauvignon*, then in the *Madrasa* variety, and the lowest in the *Bayan Shirey* variety. Differences recorded in the content of dry matter, total sugar, glucose, and fructose depend on the specific features of the grape variety, natural and climatic conditions, the complexity of the photosynthesis process, and other factors. From a comparative analysis of ripened grape varieties, it was established that in the *Rkatsiteli* and *Cabernet Sauvignon* grape varieties, the increased content of dry substances, especially the percentage of sugar, as well as the main quality indicators, determine their suitability for the production of sweet dessert wines.

An important indicator is also the yield of unclarified juice, which in ripened varieties of *Rkatsiteli* grapes was 75.6 %, and in withered grape varieties it was much less and amounted to 59.5 %. This, of course, is not economically feasible.

Despite the high content of dry matter, total sugar, as well as glucose and fructose in withered grape varieties, their main quality indicators compared to ripe grape varieties are significantly reduced. This negatively affects the quality of wine, its enrichment with extractive substances, and its long-term stability. Analysis of the qualitative indicators of grape varieties showed that among the white varieties of *Rkatsiteli*, and among the red varieties of *Cabernet Sauvignon*, grown in the *Samukh* region, the most suitable for the production of Tokay-type wines.

It should be noted that the technological process of wine production is more influenced by the chemical composition of the raw materials. The correct choice and successful practical application of raw materials in the future will be an incentive to improve the relevant technological parameters of wine production in order to achieve greater preservation of nutrients.

A high-quality, environmentally friendly product is the most excellent indicator. The parameters of the process should be improved taking into account the use of raw

materials of high nutritional value to limit the biologically non-active components. This diversity will further expand the range of sweet dessert wines.

The development of new technological techniques using local grape varieties rich in nutrients, especially easily digestible sugars, vitamin C, phenolic compounds, etc. will modernize existing technologies for providing the population with environmentally friendly products.

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## 7. Conclusions

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1. It has been established that for the production of Tokay-type wines it is more expedient to use ripe grape varieties grown in low-lying areas. Wines produced from withered grape varieties, despite the increased amount of sugars, are poor in extractive substances, vitamin C, phenolic compounds, etc. The full taste, aroma, and other organoleptic characteristics of wine consist precisely of the sum of the above compounds. The amount of dry matter of the Bayan Shirey grape variety in the Samukh region was 23.7 g/100 cm<sup>3</sup> in ripened berries, 32.4 g/100 cm<sup>3</sup> in withered berries. Total sugar was recorded in the range of 21.6 and 29.6 g/100 cm<sup>3</sup>, and the amount of glucose compared to ripened in withered increased by 40.2 %. The fructose content in dried grapes was equal to 14.8 g/100 cm<sup>3</sup>, which exceeded by 54.1 % the ripened variety. The titrated acidity in the ripened grape variety was in the range of 6.2 g/100 dm<sup>3</sup>, decreased in the withered variety by 17.7 %. The content of phenolic compounds in mature Rkatsiteli grapes was 0.70 g/100 cm<sup>3</sup>, in dried 0.42 g/100 cm<sup>3</sup>. The active acidity in this variety in withered increased by 9.4 %. The content of vitamin C in the ripened Rkatsiteli variety compared to the withered increase by 44.6 %. Pectin substances, including pectin and protopectin in both grape varieties decreased compared to ripe in withered grapes. This decrease is due to the activity of the enzyme pectinesterase. An important indicator of the wine industry, the yield of unclarified juice was much greater in ripe grape varieties. These indicators in the red grape varieties Cabernet Sauvignon and Madrasa grown in the Samukh region were distinguished by the fact that in the ripened varieties the total sugar content fluctuated between 22.3–34.7 g/100 cm<sup>3</sup>. The amount of dry matter increased, and the titrated acidity, phenolic compounds, vitamin C decreased. It was established that these indicators in white and red grape varieties grown in the foothills of the Goygol district were identical. However, the analysis of white and red grape varieties showed that the ripened white variety Rkatsiteli and the red variety Cabernet Sauvignon are superior in their quality indicators to other varieties, and therefore are recommended for the production of Tokay-type wines.

2. It was found that the decrease in nutrients in withered white and red grape varieties is associated with an increase in the activity of enzymes of the oxidoreductase class, especially under the conditions of the Samukh region. The activity of ascorbate oxidase in the mature variety Bayan Shirey increased by 86.1 % compared to the withered one, by 74.3 %

in Rkatsiteli, 67.6 % in Cabernet Sauvignon, and 62.5 % in Madrasa. O-diphenol oxidase, respectively, increased by 64.5, 62.3, 61.1, and 60.2 %. The remaining enzymes were identical. Due to the climatic conditions of the foothill zones of the Goygol region, the activity of enzymes of the oxidoreductase class decreases and less nutrients are consumed for metabolic processes.

Increased activity of the enzyme pectinesterase promotes the breakdown of pectin substances, especially pectin. As a result of decay, the resulting methyl alcohol destroys the cellular structure of grape berries, and as a result, softening and wilting of berries occurs. It was found that the activity of pectinesterase is higher in white grape varieties than in red ones. It was found that in comparison with ripened grape varieties, in withered grapes grown in the lowland zone of the Samukh district, the activity of the enzyme pectinesterase increased (69.3÷57.4 %). In the conditions of the Goygol district, this indicator increased by 71.8÷50.6 %. It was revealed that in mature and withered grape varieties there was no noticeable difference in the activity of the enzyme pectinesterase, in contrast to enzymes belonging to the class of oxidoreductases.

It was established that in comparison with the low-lying zone of the Samukh district, the amount of total sugar in the studied varieties was lower than in grape varieties grown in the foothills of the Goygol district. Therefore, for the production of sweet dessert wines of the Tokay type, it is more expedient to use the white technically ripened grape variety Rkatsiteli and the red grape variety Cabernet Sauvignon, grown in the low-lying areas of the Samukh region. Grape varieties Bayan Shirey and Madrasa, grown in low-lying areas, are recommended for the preparation of strong and table wines, as well as champagne wine materials.

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## Conflicts of interest

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The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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## Funding

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The study was conducted without financial support.

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## Data availability

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All data are available in the main text of the manuscript.

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## Acknowledgements

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We express our gratitude to the Department of Food Engineering and Expertise at Azerbaijan Technological University.

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