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ESTABLISHMENT OF REGULARITIES OF BIOCHEMICAL TRANSFORMATIONS IN GRAPE BERRIES DURING REFRIGERATED STORAGE WITH PRELIMINARY THERMAL TREATMENT

The paper is devoted to the study of biochemical transformations in grapes during refrigeration storage with preliminary heat treatment. The object of the study was nine table grape varieties. Of these, white – Ganja Table, Karaburnu, Chasselas White, Agadai; pink – Nimrang, Marandi Shamakhi, Taifi Pink; red – Kyzyl Izyum and Muscat Hamburg. For better preservation of table grapes and reduction of nutrient losses before placing them in the refrigeration chamber, they were preliminarily subjected to heat treatment for 5 minutes at a temperature of 65–70 °C in a drying cabinet. Then the grapes were stored in refrigeration chambers for 6–8 months, at a temperature of 0–1 °C and air humidity of 85–95 %. Biochemical studies of the grapes were conducted before placing them and every 30–40 days until the end of storage, as well as before and after heat treatment. After heat treatment, all grape varieties show a gradual restoration of the activity of the studied enzymes during the storage period, but this activity does not reach the initial level. Studies have shown that after heating the products, reactivation is possible if at least a weak enzyme activity is preserved, and it is more intense during the first day of storage. During long-term refrigeration of grapes in a refrigeration chamber, a decrease in the catalytic activity of enzyme systems leads to a decrease in the rate of catalytic processes, that is, biochemical transformations of carbohydrates, phenolic substances, vitamins, organic acids, pectin substances and other components, and thereby contributes to the preservation of the nutritional value of grapes. However, storing grapes with preliminary heat treatment contributes to a greater decrease in the catalytic activity of enzymes, and thereby inhibition of biochemical transformations of grape nutrients. This, ultimately, contributes to better preservation of grapes, their aroma, taste, appearance and their chemical components. Marandi Shamakhi, Nimrang, Ganja Table and Karaburnu are distinguished by a smaller change in the content of vital components.

Keywords: *table grape varieties, heat treatment of grapes, refrigerated storage of grapes, biochemical parameters of grapes.*

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1. Introduction

In the context of addressing the food safety issue at the state level, more and more attention is being paid to programs related to the use of local raw materials for the production of safe food products that promote public health [1]. The issues of preserving fruits and vegetables, including table grapes, improving their storage conditions and reducing losses are currently of great importance [2]. In this regard, the study of the theoretical foundations and practical issues of storing grapes is a pressing issue in solving the problems of providing the population with fresh grapes throughout the year. Studies have shown that grapes are very rich in chemical components, so their waste can be used to prepare many functional products [3]. Currently, industrial centers and specialized farms of the republic have refrigerators for storing fresh grapes. The current level of development of science and technology allows, when storing grapes in special storage facilities, to significantly extend their shelf life and reduce the large losses that occur [4]. At the same time, many issues related to the storage of grapes remain poorly understood. In this regard, there is a need for extensive research in order to preserve a large number and select special varieties for this. The main attention should be paid to studying the influence of the degree of maturity on the keeping quality of grapes and storage methods to preserve the quality indicators and marketable appearance of the final product [5].

When studying these issues, it is necessary to be guided by modern concepts of the biochemical nature of the keeping quality of grapes [6]. Therefore, the development of theoretically sound, more effective methods of long-term storage with the preservation of more important biochemical parts without significant changes is of great interest: carbohydrates, vitamins, organic acids, phenolic substances and other components that determine the nutritional and biological value of the product.

The issues of storing fruits and vegetables, including grapes, have attracted the attention of researchers since ancient times [7]. For this purpose, various methods of short-term and long-term storage, new methods of storage in refrigeration chambers and controlled gas environments were used [8–11]. However, each of these methods has its drawbacks, for example, the use of manual labor, regulation of gas concentration, the use of various chemicals, etc. Therefore, the study

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of the theoretical foundations and practical issues of storing grapes is an urgent problem for the agricultural sector. *The aim of this research* is to select the optimal option for storing grapes, ensuring the extension of storage periods and preservation of the marketable appearance of table grape varieties by inhibiting the catalytic activity of enzymes. Referring to the research results, select the most suitable grape varieties for long-term refrigeration storage. Storage of grapes with preliminary heat treatment contributes to a greater decrease in the catalytic activity of enzymes, and thereby inhibition of biochemical transformations of grape nutrients. This, ultimately, contributes to better preservation of grapes, their aroma, taste, appearance and their chemical components, which will provide the population with fresh grapes not only seasonally, but also year-round.

2. Materials and Methods

The objects of research were nine table grape varieties. Of these, the white ones were Ganja Table, Karaburnu, Chasselas White, and Agadai; the pink ones were Nimrang, Marandi Shamakhi, and Taifi Pink; and the red ones were Kyzyl Izyum and Muscat Hamburg [12]. The grapes for storage were collected in a subsidiary farm in the Samukh district, as well as in an experimental station for viticulture and winemaking near the city of Ganja (Azerbaijan). Before storing, the grapes were sorted, packed in standard boxes, and placed in refrigerator chambers on the same day. The grapes were harvested in the afternoon. In this variant, the grapes were pre-heat treated at a temperature of 65–70 °C in a drying cabinet for 3–5 minutes, followed by storage in a refrigerator chamber. The refrigerator chambers were thoroughly disinfected with sulfur dioxide before storing the grapes. At the end of each week, fumigation with sulfur dioxide was carried out at a rate of 1–1.5 g per 1 m^3 of the refrigeration chamber. The grapes were stored in refrigeration chambers for 6–8 months, at a temperature of 0–1 °C and air humidity of 85–95 % [13]. Biochemical studies of the grapes were carried out before laying and every 30–40 days until the end of storage, as well as before and after heat treatment. The activity of some oxidative enzymes was determined in ripened grapes: ascorbate oxidase, o-diphenyl oxidase, peroxidase and catalase. The content of glucose, fructose, vitamin C, phenolic compounds, titratable acids, as well as free and total sulfite acids were determined. During the storage period of the grapes, natural and microbiological losses of the grapes were also studied [14]. The selection of an average sample of berries was carried out according to the generally accepted method. The total volume of the average sample in each variant was 2.0 kg. Biochemical parameters were determined by the following methods:

- glucose – iodometric [15];
- fructose – calorimetric [15];
- titratable acidity – direct titration method [15];
- vitamin C – dichlorophenolindophenol method [15];
- phenolic compounds by chromato-mass spectrometry;
- organic acids by chromato-mass spectrometry [16].

In addition, active acidity was determined by potentiometric method using Polish pH-meter No. 5123 [17]. Free and total sulfite acids – iodometric, and pectin substances were determined by carbazole method [18].

3. Results and Discussion

The research materials on the study of biochemical parameters of ripe table grape varieties during long-term refrigerated storage with preliminary heat treatment are given in Tables 1–8.

Table 1

Change in the activity of oxidoreductases of grape varieties after heat treatment (mg of oxidized substrate decomposed in 30 min. by enzymes of 1 g of tissue)

Grape varieties	Ascorbate oxidase				O-diphenol oxidase			
	Before laying	After storage	Difference		Before laying	After storage	Difference	
			units	%			units	%
Ganja Table	0.64	0.20	–0.44	68.7	0.70	0.27	–0.43	61.4
Karaburnu	0.55	0.18	–0.37	67.3	0.72	0.30	–0.42	58.3
Chasselas White	0.58	0.24	–0.34	58.6	0.68	0.29	–0.39	57.3
Agadai	0.55	0.24	–0.31	56.4	0.70	0.30	–0.40	57.1
Nimrang	0.64	0.18	–0.46	71.9	0.72	0.27	–0.45	62.5
Marandi Shamakhi	0.60	0.14	–0.46	76.9	0.70	0.20	–0.50	71.4
Taifi Pink	0.58	0.18	–0.40	69.0	0.66	0.26	–0.40	60.1
Kyzyl Izyum	0.55	0.22	–0.33	60.0	0.74	0.30	–0.44	59.5
Muscat Hamburg	0.68	0.26	–0.42	61.8	0.76	0.32	–0.44	57.9
Grape varieties	Peroxidase				Catalase			
	Before laying	After storage	Difference		Before laying	After storage	Difference	
			units	%			units	%
Ganja Table	2.20	0.79	–1.41	64.1	0.33	0.11	–0.22	66.7
Karaburnu	1.98	0.80	–1.18	59.6	0.39	0.16	–0.23	59.0
Chasselas White	2.42	0.98	–1.44	59.5	0.34	0.14	–0.20	58.8
Agadai	2.32	0.92	–1.40	60.3	0.36	0.15	–0.21	58.3
Nimrang	1.88	0.60	–1.28	68.1	0.34	0.10	–0.24	70.6
Marandi Shamakhi	1.86	0.52	–1.34	72.0	0.33	0.08	–0.25	75.8
Taifi Pink	1.92	0.66	–1.26	67.7	0.38	0.14	–0.24	63.2
Kyzyl Izyum	2.32	0.82	–1.50	64.5	0.36	0.26	–0.20	55.6
Muscat Hamburg	2.42	0.87	–1.55	64.4	0.40	0.17	–0.23	57.5

It is evident from the data in Table 1 that after preliminary heat treatment, the catalytic activity of the studied enzymes decreases sharply in all varieties. This decrease depends on the grape variety [19]. In white varieties, after heat treatment, the enzyme activity decreases by 56.4–68.7 %, in pink varieties by 60.0–76.9 %, and in red varieties by 55.6–64.5 %. Heat treatment reduces the activity of oxidoreductases in the Marandi Shamakhi variety to a greater extent than in other grape varieties. For example, the decrease in ascorbate oxidase activity in the Marandi Shamakhi variety is 76.9 %, o-diphenol oxidase by 71.4 %, peroxidase by 72.0 %, and catalase by 75.8 %. A significant decrease in catalytic activity is observed in the Nimrang variety, then in Taifi Pink, Ganja Table and Karaburnu. The least decrease in enzyme activity is seen in Chasselas white.

The research materials show that the thermolability of the studied grape enzymes is not the same in the indicated varieties. Peroxidase and catalase are more thermolabile in all varieties, followed by ascorbate oxidase and o-diphenol oxidase (Table 2).

The data in Table 2 show that in all grape varieties (except pink) the activity of enzymes is gradually restored during long-term refrigeration storage with preliminary heat treatment, although it does not reach the initial level. These shifts occur with different intensity for individual enzymes depending on the heat treatment and duration of storage of grapes [20]. It was found that the activity of all the studied oxidoreductases during storage is restored to a greater extent in Chasselas White and Agadai, as well as in all red varieties.

Analysis of the above materials allows to conclude that enzymes, being thermolabile protein substances, reduce their activity both at low and at high temperatures. This slows down the intensity of the respiratory, i. e. metabolic process occurring in grapes during long-term storage [21].

Enzymes have a specific protein nature and are biological catalysts. They accelerate biochemical reactions and thus play an important role in the metabolism of fruits and vegetables (persimmon, pomegranate, apples), including grapes [22].

One of the most common enzymes of the grapevine is o-diphenol oxidase. The enzyme catalyzes the oxidation of phenolic compounds of atmospheric oxygen to form quinones and water [23]. In addition, the enzyme ascorbate oxidase, which catalyzes the conversion of ascorbic acid to dehydroascorbic acid, has also been found in grapes. Of great importance are the enzymes peroxidase and catalase. Peroxidase, in the presence of hydrogen peroxide, catalyzes the oxidation of various organic compounds, phenols and aromatic amines, and catalase breaks down hydrogen peroxide, which is toxic to plant cells, into water and oxygen. The results of studies of varieties for changes in the amount of glucose, fructose, invert sugar, ascorbic acid, phenolic substances, organic acids (tartaric, malic, citric, succinic, oxalic), active acidity, total and free sulfite acid, during long-term refrigeration storage with preliminary heat treatment are given in Tables 3–5.

It is evident from the data in Table 3 that the glucose and fructose content of all the studied grape varieties gradually decreases during storage, and amounts to 9.5–17.6 % for white grapes, 7.0–9.8 % for pink grapes, and 20.2–24.2 % for red grapes. With this storage option, the glucose and fructose content decreases to a lesser extent in pink varieties. This is due to the fact that after heat treatment, the activity of oxidoreductases decreases to a greater extent, which leads to a delay in the conversion of glucose and fructose, and, consequently, to their smaller losses. The ratio of glucose and fructose content during the storage period of grapes varies within the range of 0.80–1.20 %.

Table 2

Changes in the activity of oxidoreductases in grape varieties during storage with preliminary heat treatment (mg of oxidized substrate decomposed by enzymes in 30 min per 1 g of tissue)

Grape varieties	Ascorbate oxidase				O-diphenol oxidase			
	Before laying	After storage	Difference		Before laying	After torage	Difference	
			units	%			units	%
Ganja Table	0.20	0.22	0.02	10.0	0.27	0.36	0.07	25.9
Karaburnu	0.18	0.22	0.04	22.2	0.30	0.34	0.04	13.3
Chasselas White	0.24	0.30	0.06	25.0	0.29	0.38	0.09	31.1
Agadai	0.24	0.38	0.14	58.3	0.30	0.36	0.06	16.7
Nimrang	0.18	0.14	0.04	22.2	0.27	0.20	–0.07	25.9
Marandi Shamakhi	0.14	0.08	–0.06	57.1	0.20	0.14	–0.04	20.0
Taifi Pink	0.18	0.20	0.02	11.1	0.26	0.25	–0.01	3.8
Kyzyl Izyum	0.22	0.38	0.16	72.7	0.30	0.58	0.28	93.3
Muscat Hamburg	0.26	0.44	0.18	69.2	0.32	0.60	0.28	87.5
Grape varieties	Peroxidase				Catalase			
	Before laying	After storage	Difference		Before laying	After storage	Difference	
			units	%			units	%
Ganja Table	0.79	0.88	0.09	11.4	0.11	0.13	0.02	18.2
Karaburnu	0.80	0.91	0.11	13.7	0.16	0.14	–0.02	14.3
Chasselas White	0.98	1.31	0.31	31.6	0.14	0.18	0.04	28.6
Agadai	0.92	1.21	0.29	31.5	0.15	0.19	0.04	26.7
Nimrang	0.60	0.70	0.10	16.7	0.10	0.08	–0.02	20.0
Marandi Shamakhi	0.52	0.38	–0.14	26.9	0.08	0.06	–0.02	25.0
Taifi Pink	0.66	0.84	0.18	27.3	0.14	0.12	–0.02	14.3
Kyzyl Izyum	0.82	1.44	0.62	75.6	0.26	0.28	0.02	7.7
Muscat Hamburg	0.87	1.62	0.75	86.2	0.17	0.24	0.07	41.2

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Table 3

Changes in biochemical indicators of white grape varieties during storage with preliminary heat treatment

Biochemical indicators	Ganja Table				Karaburnu			
	Before laying	After storage	Difference		Before laying	After storage	Difference	
			units	%			units	%
Glucose, g/100 cm^3	9.5	8.6	–0.9	9.5	9.1	8.2	–0.9	9.9
Fructose, g/100 cm^3	9.8	8.8	–1.0	10.2	9.4	8.5	–0.9	9.6
Glucose: fructose	0.97	0.98	0.01	1.03	0.97	0.96	–0.01	1.03
Invert sugar, g/100 cm^3	19.3	17.4	–1.9	9.8	18.5	16.7	–1.8	9.7
Vitamin C, mg/100 cm^3	7.2	1.5	–5.7	79.2	7.8	1.7	–6.1	78.2
Phenolic substances, g/100 cm^3	0.08	0.054	–0.026	32.5	0.082	0.054	–0.028	34.1
Active acidity (pH)	4.1	3.9	–0.2	4.9	4.2	4.0	–0.2	4.7
Titratable acidity, g/100 cm^3	0.72	0.61	–0.11	15.3	0.74	0.62	–0.12	16.2
Organic acids:	–	–	–	–	–	–	–	–
Tartaric	0.48	0.44	–0.04	8.3	0.48	0.42	–0.06	12.5
Malic	0.19	0.15	–0.04	21.1	0.21	0.17	–0.04	19.0
Citric	0.028	0.020	–0.008	28.6	0.024	0.017	–0.007	29.2
Succinic	0.007	0.004	–0.003	42.9	0.0095	0.0045	–0.005	52.6
Oxalic	0.0065	0.0035	–0.003	46.1	0.008	0.003	–0.005	62.5
Sulfic acid:	–	–	–	–	–	–	–	–
Free	0.36	0.16	–0.20	55.5	0.38	–0.16	0.22	57.9
Total	0.78	0.30	–0.48	61.5	0.74	–0.32	0.42	56.8
Biochemical indicators	Chasselas White				Agadai			
	Before laying	After storage	Difference		Before laying	After storage	Difference	
			units	%			units	%
Glucose, g/100 cm^3	9.4	8.2	–1.2	12.8	9.5	8.2	–1.3	13.7
Fructose, g/100 cm^3	8.5	7.0	–1.5	17.6	8.8	7.6	–1.2	13.6
Glucose: fructose	1.1	1.20	0.1	9.1	1.08	1.08	0	0
Invert sugar, g/100 cm^3	17.9	15.2	–2.7	15.1	18.3	15.8	–2.5	13.7
Vitamin C, mg/100 cm^3	6.4	0.9	–5.5	85.9	6.8	1.2	–5.6	82.3
Phenolic substances, g/100 cm^3	0.075	0.043	–0.032	42.7	0.078	0.05	–0.028	36.9
Active acidity (pH)	4.2	3.8	–0.4	7.1	4.2	3.9	–0.3	7.1
Titratable acidity, g/100 cm^3	0.67	0.52	–0.15	22.4	0.65	0.52	–0.13	20.0
Organic acids:	–	–	–	–	–	–	–	–
Tartaric	0.43	0.37	–0.06	13.9	0.42	0.36	–0.06	14.3
Malic	0.18	0.11	–0.07	38.9	0.17	0.12	–0.05	29.4
Citric	0.025	0.012	–0.013	52.0	0.028	0.015	–0.013	46.4
Succinic	0.008	0.003	–0.005	62.5	0.009	0.006	–0.003	33.3
Oxalic	0.007	0.004	–0.003	42.9	0.0075	0.0045	–0.003	40.0
Sulfic acid:	–	–	–	–	–	–	–	–
Free	0.36	0.18	–0.18	50.0	0.36	–0.16	–0.20	55.5
Total	0.78	–0.30	–0.48	61.5	0.78	–0.32	–0.46	59.0

Data in Tables 3–5 show that during the storage period of grapes the content of invert sugar decreases and at the end of storage it is 9.8 % in Ganja Table, 9.7 % in Karaburnu, 15.1 % in Chasselas White 13.7 % in Agadai, 8.1 % in Nimrang, 7.2 % in Marandi Shamakhi, 9.6 % in Taifi Pink, 21.4 % in Kyzyl Izyum, and 23.1 % in Muscat Hamburg. Among those listed, only Marandi Shamakhi, Nirang, Taifi Pink, Ganja Table and Karaburnu grapes have lower invert sugar consumption during storage.

Long-term refrigerated storage with preliminary heat treatment leads to a decrease in total phenolic substances. This decrease fluctuates within the range of 12.0–42.7 %. The smallest decrease is characteristic of pink varieties (12.5–20.0 %) (Table 4). It is possible to found that with this storage method, the content of ascorbic acid in all grape varieties decreases by 29.4–86.5 %. By the end of storage, ascorbic acid is consumed in pink varieties significantly less (29.4–45.9 %) than in others. Under the conditions of our experiments, during the storage period of grapes, the decrease in the content of organic acids in the Ganja Table variety was 15.3 %, Karaburnu – 16.2 %, Chasselas White – 22.4 %, Agadai – 20.0 %, Nimrang – 11.8 %, Marandi Shamakhi – 9.2 %, Taifi Pink – 13.6 % in relation to the initial level.

During the storage period, the content of citric, succinic and oxalic acids in all grape varieties decreases to a greater extent (27.8–62.5 %) than the amount of tartaric and malic (6.8–38.9 %).

Table 4

Changes in biochemical parameters of pink grape varieties during storage with preliminary heat treatment

Biochemical indicators	Nimrang				Marandi Shamakhi				Taifi Pink			
	Before laying	After storage	Difference		Before laying	After storage	Difference		Before laying	After storage	Difference	
			units	%			units	%			units	%
Glucose, g/100 cm^3	9.5	8.6	–0.9	9.5	9.1	8.2	–0.9	9.9	9.2	8.3	–0.9	9.8
Fructose, g/100 cm^3	9.8	8.8	–1.0	10.2	9.4	8.5	–0.9	9.6	9.6	8.7	–0.9	9.4
Glucose: fructose	0.97	0.98	0.01	1.03	0.97	0.96	–0.01	1.03	0.96	0.95	–0.01	1.0
Invert sugar, g/100 cm^3	19.3	17.4	–1.9	9.8	18.5	16.7	–1.8	9.7	18.8	17.0	1.8	9.6
Vitamin C, mg/100 cm^3	7.2	1.5	–5.7	79.2	7.8	1.7	–6.1	78.2	8.5	4.6	–3.9	45.9
Phenolic substances, g/100 cm^3	0.08	0.054	–0.026	32.5	0.082	0.054	–0.028	34.1	0.20	0.16	–0.04	20.0
Active acidity (pH)	4.1	3.9	–0.2	4.9	4.2	4.0	–0.2	4.7	3.7	3.5	–0.2	5.4
Titratable acidity, g/100 cm^3	0.72	0.61	–0.11	15.3	0.74	0.62	–0.12	16.2	0.66	0.57	–0.09	13.6
Organic acids:	–	–	–	–	–	–	–	–	–	–	–	–
Tartaric	0.48	0.44	–0.04	8.3	0.48	0.42	–0.06	12.5	0.42	0.34	–0.08	19.0
Malic	0.19	0.15	–0.04	21.1	0.21	0.17	–0.04	19.0	0.20	0.16	–0.04	20.0
Citric	0.028	0.020	–0.008	28.6	0.024	0.017	–0.007	29.2	0.024	0.019	–0.005	20.8
Succinic	0.007	0.004	–0.003	42.9	0.0095	0.0045	–0.005	52.6	0.0064	0.0046	–0.0018	28.1
Oxalic	0.0065	0.0035	–0.003	46.1	0.008	0.003	–0.005	62.5	0.0055	0.0042	0.0013	23.6
Sulfic acid:	–	–	–	–	–	–	–	–	–	–	–	–
Free	0.36	0.16	–0.20	55.5	0.38	–0.16	0.22	57.9	0.55	0.28	–0.27	49.1
Total	0.78	0.30	–0.48	61.5	0.74	–0.32	0.42	56.8	1.16	0.60	–0.56	48.3

Table 5

Changes in biochemical indicators of red grape varieties during storage with preliminary heat treatment

Biochemical indicators	Kyzyl Izyum				Muscat Hamburg			
	Before laying	After storage	Difference		Before laying	After storage	Difference	
			units	%			units	%
Glucose, g/100 cm^3	8.9	7.1	–1.8	20.2	9.1	7.1	–2.0	22.0
Fructose, g/100 cm^3	9.3	7.2	–2.1	22.6	9.5	7.2	–2.3	24.2
Glucose: fructose	0.96	0.99	0.03	3.0	0.96	0.99	0.03	3.0
Invert sugar, g/100 cm^3	18.2	14.3	–3.9	21.4	18.6	14.3	4.3	23.1
Vitamin C, mg/100 cm^3	7.8	1.2	–6.6	84.6	7.4	1.0	–6.4	86.5
Phenolic substances, g/100 cm^3	0.48	0.32	–0.16	33.3	0.42	0.28	–0.14	33.3
Active acidity (pH)	3.7	3.4	–0.3	8.1	3.7	3.4	–0.3	8.1
Titratable acidity, g/100 cm^3	0.65	0.48	–0.17	21.1	0.63	0.47	–0.16	25.4
Organic acids:	–	–	–	–	–	–	–	–
Tartaric	0.44	0.35	–0.09	20.4	0.42	0.34	–0.08	19.0
Malic	0.18	0.12	–0.06	33.3	0.19	0.12	–0.07	37.0
Citric	0.024	0.014	–0.010	41.7	0.026	0.011	0.0015	57.7
Succinic	0.006	0.003	–0.003	50.0	0.0065	0.0025	0.004	61.5
Oxalic	0.0055	0.0025	–0.003	54.5	0.005	0.002	0.003	60.0
Sulfic acid:	–	–	–	–	–	–	–	–
Free	0.26	0.14	–0.22	61.1	0.38	0.16	–0.22	57.9
Total	0.70	0.30	–0.40	57.1	0.74	0.32	–0.42	56.8

Long-term refrigeration storage with preliminary heat treatment helps to reduce active acidity. Thus, in the studied varieties during the storage period, active acidity decreases within 2.7–8.1 %. Its smallest change was found in the varieties Ganja Table, Nimrang, Karaburnu and Marandi Shamakhi.

During long-term refrigeration storage with preliminary heat treatment, the content of free and total sulfurous acid in all studied grape varieties decreases, which is a favorable indicator for the taste qualities of the product.

It is evident from the data in Table 5 that the content of pectin substances decreases by the end of storage in all varieties. A noticeable decrease in the amount of pectin substances (water-soluble pectin and protopectin) during storage was found in red grape varieties. After heat treatment, pectinesterase activity decreases significantly [24]. Then, during storage, this activity gradually increases in all grape varieties (Table 5). Pectinesterase activity increases especially after two to three months of refrigeration storage [25–28]. Among the studied grape varieties, red varieties have the highest pectinesterase activity, which leads to their significant softening. As can be seen from Table 7, the activity of ascorbate oxidase, o-diphenyl oxidase, peroxidase, and catalase gradually increases during the sale of grapes. This is more typical of red varieties. It was found that the studied oxidoreductases slightly change their activity in pink varieties. Therefore, during their realization, darkening and softening of berries is not observed (Table 8).

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Table 6

Change in the content of pectin substances of grape varieties during storage with preliminary heat treatment (% of raw weight)

Grape varieties	Sum of pectin substances				Water-soluble pectin				Protopectin			
	Before laying	After storage	Difference		Before laying	After storage	Difference		Before laying	After storage	Difference	
			units	%			units	%			units	%
Ganja Table	0.25	0.12	–0.13	52.0	0.12	0.06	–0.06	50.0	0.13	0.05	–0.08	61.5
Karaburnu	0.26	0.13	–0.13	50.0	0.11	0.05	–0.06	54.5	0.15	0.08	–0.07	46.7
Chasselas White	0.27	0.11	–0.16	59.2	0.13	0.05	–0.08	61.5	0.14	0.05	–0.09	64.3
Agadai	0.27	0.12	–0.15	55.6	0.12	0.05	–0.07	58.3	0.15	0.06	–0.09	60.0
Nimrang	0.30	0.20	–0.10	33.3	0.13	0.08	–0.05	38.4	0.17	0.14	–0.03	17.6
Marandi Shamakhi	0.28	0.24	–0.04	14.3	0.10	0.08	–0.02	20.0	0.18	0.16	–0.02	11.1
Taifi Pink	0.32	0.18	–0.14	43.7	0.13	0.07	–0.06	46.1	0.19	0.11	–0.08	42.1
Kyzyl Izyum	0.35	0.13	–0.22	62.9	0.15	0.07	–0.08	53.3	0.20	0.04	–0.16	80.0
Muscat Hamburg	0.36	0.13	–0.23	63.9	0.16	0.07	–0.09	56.2	0.20	0.04	–0.16	80.0

Table 7

Change in the activity of pectinesterase in grape varieties during storage with preliminary heat treatment (in relative units per mg of acetone preparation)

Grape varieties	Incubation time of the reaction mixture, 30 minutes		
	Before laying	After heat treatment	After storage
Ganja Table	22.4	10.1	28.4
Karaburnu	21.6	9.8	26.3
Chasselas White	23.8	12.2	33.2
Agadai	23.2	11.4	31.4
Nimrang	14.6	7.2	16.4
Marandi Shamakhi	12.3	5.1	13.6
Taifi Pink	15.6	8.4	18.1
Kyzyl Izyum	26.4	14.2	38.2
Muscat Hamburg	27.6	14.5	39.8

Table 8

Changes in the activity of oxidoreductases of grape varieties after storage with preliminary heat treatment during their realization

Grape varieties	Ascorbate oxidase				O-diphenol oxidase			
	After storage	During realization	Difference		After storage	During realization	Difference	
			units	%			units	%
Ganja Table	0.22	0.27	0.05	22.7	0.36	0.45	0.09	25.0
Karaburnu	0.22	0.26	0.04	18.2	0.34	0.42	0.08	23.5
Chasselas White	0.30	0.38	0.08	26.7	0.38	0.50	0.12	31.6
Agadai	0.38	0.48	0.10	26.3	0.36	0.47	0.11	30.5
Nimrang	0.14	0.16	0.02	14.3	0.20	0.23	0.03	15.0
Marandi Shamakhi	0.08	0.09	0.01	12.5	0.14	0.16	0.02	14.3
Taifi Pink	0.20	0.25	0.05	20.0	0.25	0.30	0.05	20.0
Kyzyl Izyum	0.38	0.52	0.14	36.8	0.58	0.78	0.20	34.5
Muscat Hamburg	0.44	0.59	0.15	34.1	0.60	0.82	0.22	36.7
Grape varieties	Peroxidase				Catalase			
	After storage	During realization	Difference		After storage	During realization	Difference	
			units	%			units	%
Ganja Table	0.88	1.10	0.22	25.0	0.13	0.16	0.03	23.1
Karaburnu	0.91	1.14	0.23	25.3	0.14	0.18	0.04	28.6
Chasselas White	1.31	1.69	0.38	29.0	0.18	0.24	0.06	33.3
Agadai	1.20	1.57	0.36	29.7	0.19	0.26	0.07	36.8
Nimrang	0.70	0.78	0.08	11.4	0.08	0.10	0.02	25.0
Marandi Shamakhi	0.38	0.41	0.03	7.9	0.06	0.07	0.01	16.7
Taifi Pink	0.84	0.96	0.12	14.3	0.12	0.15	0.3	25.0
Kyzyl Izyum	1.44	1.88	0.44	30.5	0.28	0.41	0.13	46.4
Muscat Hamburg	1.62	1.14	0.48	29.6	0.24	0.37	0.13	54.2

Thus, pink varieties (especially Marandi Shamakhi) better retain their marketable appearance and quality after long-term refrigerated storage with preliminary heat treatment.

Viticulture as a branch of agriculture is rapidly developing, so specialists are faced with the task of expanding areas, increasing gross harvests and providing the population with fresh grapes not only in the fall, but also in the winter-spring period.

Much attention is paid to the problem of extending storage periods, improving storage conditions, and ultimately increasing the consumption period, ensuring high-quality preservation and reducing natural and microbiological losses. It is known from literary data that there are many different options for storing grapes, for example, in greenhouses, with fumigation with sulfur dioxide, in a controlled gas environment, etc. However, due to the high cost of construction, low yields, use of labor, and therefore the high cost of final products, these methods have proven ineffective. The current level of development of science and technology allows to significantly extend the shelf life of grapes and reduce the large losses that occur when storing them in special storage facilities. However, modern technologies for storing grapes remain poorly understood. In this regard, there is a need for extensive research in order to preserve a large number and select special varieties for this purpose. The main attention should be paid to studying the effect of the degree of maturity on the shelf life of grapes.

A decrease in the catalytic activity of the studied oxidoreductases and other grape enzymes during heat treatment is associated with a violation of their native concentration, secondary and tertiary structure, and partially inhibited active centers of enzyme molecules. In subsequent periods, their long-term storage in refrigerated chambers promotes the restoration of enzyme activity, but their original level is not achieved. The process of restoring the activity of grape enzymes is the result of the presence of residual activity.

Analyzing the experimental data, it should be noted that after heat treatment, all grape varieties show a gradual restoration of the activity of the studied enzymes during the storage period, but this activity does not reach the original level. Studies have shown that after heating, reactivation of products is possible if at least weak enzyme activity is preserved, and it is more intense during the first day of storage.

These studies confirm the information about the chemical composition of grapes, depending on the activity of oxidoreductases under the influence of heat and cold. This may be important information for understanding how storage and processing methods affect the physiological processes of grapes and their quality. A study of the effect of heat treatment on the activity of other classes of enzymes could complement the previous data, providing a more complete picture of the processes occurring during storage of grapes and affecting their quality and nutritional properties.

4. Conclusions

The study shows that during storage of grapes with preliminary heat treatment, the activity of all enzymes in all varieties sharply decreases. A decrease in the catalytic activity of the studied oxidoreductases and other grape enzymes during heat treatment is associated with a violation of their native concentration, secondary and tertiary structure, partially inhibited active centers of enzyme molecules, and the absence of their connection with the substrate. In subsequent periods, their long-term storage in refrigerated chambers contributes to the restoration of enzyme activity, but their initial level is not achieved. The process of restoring the activity of grape enzymes is the result of the presence of residual activity, as well as the result of reversible changes in the conformation of their molecules and the functioning of most inactivated centers. Analyzing the experimental data, it should be noted that after heat treatment, all grape varieties show a gradual restoration of the activity of the studied enzymes during the storage period, but this activity does not reach the original level. Studies have shown that after heating the products, reactivation is possible in the case of maintaining at least a weak activity of enzymes and it is more intense during the first day of storage. In all the studied grape varieties, the content of glucose and fructose gradually decreases during storage. Marandi Shamakhi is characterized by a smaller change in the content of glucose and fructose. The greatest decrease in the content of glucose and fructose is manifested in all red varieties, and among the white varieties – Chasselas White and Agadai. In this storage option, the ratio of glucose to fructose is less than one, which is characteristic of the varieties Marandi Shamakhi, Nimrang, Ganja Table and Karaburnu, i. e. during storage, they have a lower consumption of fructose for respiration than glucose. Therefore, for storage, it is necessary to use those grape varieties in which the fructose content exceeds glucose. Since fructose is twice as sweet as glucose, these grape varieties have a sweeter taste during storage. During storage, vitamin C in pink grape varieties is less spent on metabolic processes, which is associated with the activity of the enzyme ascorbate oxidase. Organic acids are also spent comparatively less on respiration during preliminary processing of grapes before storage. The acidity of grapes plays an important role and affects taste qualities, and also influences enzymatic processes. Studies have shown that low values and minor changes in pH inhibit the action of oxidative enzymes. Thus, with this storage option, the pH value of pink grape varieties does not change.

It has been established that the content of phenolic substances is spent on oxidation in pink grape varieties to a much lesser extent. It has been revealed that the activity of pectinesterase in white and red varieties increases more than in pink varieties (5.1–14.5 %). The consequence of this is that the decrease in the content of pectin substances in grapes in white and red varieties is greater than in pink varieties. It is known that an increase in the activity of pectinesterase, and, consequently, the consumption of pectin substances, leads to softening of berries. It has also been established that during the implementation, the activity of enzymes in them is gradually restored (13.6–33.2 %). The activity of the studied oxidoreductases during the implementation of grape varieties is slightly restored in pink (Nimrang, Taifi Pink), and from white – in Karaburnu and Ganja Table. In the Marandi Shamakhi variety, the activity does not change at all. Therefore, for a long time in these grape varieties, especially in the Marandi Shamakhi variety, darkening and softening of the berries are not observed during their implementation. Thus, grape varieties containing more pectin substances are not suitable for long-term storage. The analysis of the study confirmed that during long-term refrigerated storage of grapes in a refrigeration chamber, a decrease in the catalytic activity of enzyme systems leads to a decrease in the rate of catalytic processes, i. e. biochemical transformations of carbohydrates, phenolic substances, vitamins, organic acids, pectin substances and other components. This favors the preservation of the nutritional value of grapes. However, storing grapes with preliminary heat treatment contributes to a greater decrease in the catalytic activity of enzymes. This leads to inhibition of biochemical transformations of grape nutrients, which ultimately contributes to better preservation of grapes, their aroma, taste, appearance and their chemical components.

Conflict of interest

The authors declare that they have no conflict of interest regarding this study, including financial, personal, authorship or other, which could influence the research and its results presented in this article.

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The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies in creating the presented work.

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