

Original Research Article

FORMATION OF FROZEN BLACKCURRANT FRUITS QUALITY

ABSTRACT

Aims: Fruits of a multivitamin culture of blackcurrant have a pronounced seasonality of consumption. The essence of the problem is in the scientific substantiation of the rational way of fruits freezing in order to preserve their quality.

Place and Duration of Study: The research was conducted during four years in the conditions of the laboratory of the Department of Technology of Storage and Processing of Plant Products at Uman National University of Horticulture and the workshop for rapid freezing of Uman canning plant.

Methodology: Prepared berries of the consumer degree of ripeness of Pilot Oleksandr Mamkin, Mynai Shmyriov, Novyna Prykarpattia, Biloruska solodka varieties in the string bags were frozen by slow (-20...-22°C) and rapid (-30...-32°C) methods, packed in paraffined boxes, polyethylene bags of 400–500 g by weight. Losses of weight, content of ascorbic acid, dry soluble substances, sugars, acids, sugar-and-acid index were determined during and for 10 months of storage (-18°C). **Results:** True chemical composition of the fruits took into account losses of their weight. It radically changed the level of indicators. Weight losses of the fruits was lower by a third during fast freezing, however, the overall indicators did not differ significantly until the end of storage: 11.9–12.1% by slow method against 10.1–11.2% by rapid way. The highest losses in the fruits were during the first 3 months, during 4–5 months – their level was stabilized and somewhat increased to the end of storage. Advantages by fruits packing in polyethylene bags were as follows: losses were 6–7 times lower than by string bags and 4–5 times – in paraffined boxes. Advantages of rapid freezing were in 1.2–1.6 times lower losses of the components of chemical composition. Usually, the frozen fruits of Biloruska solodka variety were better than other varieties under favourable weather conditions, they were not inferior.

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Keywords: *fruits, blackcurrant, freezing, storage, losses of weight, dry soluble substances, sugars, acids, ascorbic acid*

1. INTRODUCTION

There is an urgent task to organize protective nutrition, search for biologically valuable products of natural origin which can positively affect the population health under current environmental conditions in the field of nutrition [1].

The multivitamin culture of blackcurrant corresponds to this criterion, its fruits have high dietary and therapeutic properties, and there are no equal fruits and berries by the content of irreplaceable ascorbic acid and polyphenolic substances which the human body should regularly receive.

Blackcurrant contains dry soluble substances – 11–22%, including sugars – 5–14%, acids – 1.5–3%, as well as pectinates – 1.5–2.5 %, polyphenols to 1% depending on the growing area and variety. However, blackcurrant is the largest source of ascorbic acid. Its content in the fruits varies considerably [44–218 mg/100 g [2, 3], 50–350 mg/100 g [4, 5], ac

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to other data [100–200 mg/100 g [6–8], 100–300 mg/100 g [9, 10].

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The level of ascorbic acid in the blackcurrant fruits is influenced by numerous factors: peculiarities of the variety, growing area, conditions of cultivation, age of the bush, branches, their location, size and part of the fruit, degree of its ripeness, and others [11]. A characteristic feature of blackcurrant is the reduction by 1.3–2.3 times of the ascorbic acid content by the end of fruit ripening and its higher level by less favourable weather conditions during the vegetation period [9, 11, 12]. Accumulation of ascorbic acid in the blackcurrant fruits depends not only on the intensity of the synthesis, but also on the activity of enzymes. There is a reverse dependence between the content of ascorbic acid and the activity of ascorbic oxidase. The activity of the latter is non-significant or is not even displayed, while the activity of polyphenol oxidase is high which exhibits a stabilizing effect [12, 16].

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Unfortunately, natural conditions cause a strongly seasonal consumption of healthful fruits of blackcurrant. It is possible to solve the problem of providing the population with the fruits throughout the year due to their sufficient production, long-term storage and preservation. However, biological characteristics and existing ways of storing the fresh fruits of blackcurrant limit the duration of their consumption [8, 11]. The only way to improve the nutritional structure and ensure the priority way of nutrition is the use of modern canning methods. The essence of the problem is in the scientific substantiation of the rational way of fruits freezing in order to preserve biologically active substances in the fruits.

One of the most powerful and practical ways of storing the products is freezing. The high degree of preservation of the nutritional value and organoleptic properties of frozen fruits is based on the inhibition of biochemical processes and the life of the microflora. Microorganisms can develop at temperatures above -5...-8°C, and yeast -10...-12°C, mold fungi -12...-15°C [8].

Freezing is accompanied by a deep decrease in the fruits temperature and moisture transformation into ice, that is dehydration. Formation of ice crystals causes changes in the tissues structure of the product, the degree of which depends on the freezing speed [8, 11]. Ice crystals are formed primarily in the intercellular spaces by slow fruits freezing at relatively high temperatures (-4...-8°C). Ice forms more slowly inside the cells where the concentration of juice is higher. Formation of ice crystals and associated increase in the concentration of juice in the intercellular spaces leads to the increase in osmotic pressure. Water from the cells passes into the intercellular space where it freezes on the sides of the previously formed crystals. In this case, the cells are dehydrated, and large crystals are formed in the intercellular spaces and unevenly spread in the tissues. They crush on the neighbouring cells and cause damage of cell membranes and their death. Formed moisture does not have time to absorb, juice flows, the product loses its natural properties: changes the consistency, becomes watery when fruits defrosting.

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Rapid freezing (temperatures of -35...-40°C and below) does not cause significant deformation of the tissues structure. Speed of fruits cooling increases dramatically, ice crystals are formed simultaneously in the intercellular spaces and in the cells. Removal of moisture from the latter does not pass. The faster the process is performed, the more crystals are formed and their size is smaller. They are evenly spread in the cells and tissues, which does not cause significant damage to the cell membranes. More cells bind moisture and losses of cellular juice is not so significant when defrosting of these fruits.

Changes in the qualitative indicators of the fruits caused by the activity of enzymes and chemical reactions can take place before and after freezing. The intensity of the changes is influenced by a great number of factors connected with the technology of freezing, defrosting, species and varietal characteristics of the fruits. General conclusion concerning the fact that the frozen fruits are practically the same as the fresh ones by appearance, colour, flavour, taste, nutritional and biological value is a little exaggerated. This is due not only to the physical-and-chemical changes during freezing, which cause disorder in the tissues structure, but also the preservation of enzymatic activity. As a result, commodity state and taste properties of the product become worse, its vitamin value is significantly reduced. Unwanted losses of the components of the chemical composition occur mainly at the stage of defrosting of the frozen fruits [8, 11] since biochemical processes in the fruits are inhibited, but pass slowly and continuously under low storage temperatures.

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The most labile indicator of the frozen fruits is the content of ascorbic acid. Its losses vary significantly depending on the temperature of freezing and fruit variety: 2–50% in strawberries, 4–45% in blackcurrant, 10–51% in gooseberry, 14–40% in grapes, and 48–72% until the end of storage. Increase in the content of ascorbic acid in strawberries is not excluded after freezing, but it is gradually reduced during storage. According to other data, preservation of ascorbic acid is 55–92% in frozen strawberries, depending on the method of pretreatment and 34–68% in 4–5 months [9, 17].

High preservation of ascorbic acid is in the fruits of blackcurrant: 90–102% after freezing, and 89–100% after 5–6 months of storage. Similar results were obtained after 8 months of fruits storage – 88–100% [16] and 89–93% [10]. However, preservation of vitamin C content in the frozen fruits can be reduced to 64–78% [9].

In the literature, conclusions regarding the content of individual components of the chemical composition of frozen blackcurrant fruits are ambiguous. It decreases in some cases, rises in others, remains unchanged in the third cases.

The aim of the research is to optimize the technology of blackcurrant freezing while preserving their quality. The following tasks are set to achieve the purpose – to conduct a comparative evaluation of slow and rapid freezing by changes in mass loss, chemical composition, ascorbic acid during storage in various types of packaging materials.

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2. MATERIAL AND METHODS

The research was conducted during four years in the conditions of the laboratory of the Department of Technology of Storage and Processing of Plant Products at Uman National University of Horticulture and the workshop for rapid freezing of Uman canning plant.

Blackcurrant fruits of consumer degree of ripeness were gathered in favourable weather conditions, berries were taken into boxes-trays of 4–5 kg by weight, transported to the laboratory and a rapid-freezing shop. The fruits were packed in string packages with a capacity of 400–500 g (control) after inspection, washing, removal of water from the surface, re-inspection, then they were weighed, frozen by the following variants of the experiment:

- slow freezing in "Calex" freezing chambers at a temperature of -20...-22°C;
- rapid freezing in a fast-freezing chamber with forced circulation of air at a speed of 1.5–2.5 m/sec under the temperature of -30...-32°C.

The fruits of the experimental variants were packed in paraffin boxes and polyethylene bags weighing 400–500 g with film thickness of 50–55 µm after weighing and sealed. Bags and boxes (experiment and control variant) were stored at temperatures not higher than -18°C during 10 months. Weight losses were determined in the blackcurrant fruits of Pilot O. Mamkin variety during freezing, and then after 6, 8 and 10 months of storage in string packages. Repetition of the definition was ten times. The components of the chemical composition of the frozen fruits – content of ascorbic acid, as well as dry soluble substances, sugars, acids were determined in specified terms; sugar-and-acid index was calculated. Weight losses were determined in blackcurrant fruits of Mynai Shmyriov, Biloruska solodka, Novyna Prykarpattia varieties during freezing, and then every month (after 1, 2, 3, 4, 5, 6, 8 and 10 months). Repeatability was tenfold.

Determination of the components content of the chemical composition of the fruits, taking into account weight losses, was carried out according to the formula:

$$X = \frac{A \times (100 - e)}{100}, \quad (1)$$

X – the content of substances taking into account weight losses, %; A – the content of substances at the end of storage, %; e – weight losses during storage period, %.

In the course of the research, we determined: weight losses of the fruits – by weighing, the content of ascorbic acid – by iodometric (according to B. P. Pleshkov [18]), dry soluble substances – by refractometric, acids – by titrimetric, sugars – by ferricyanidine methods [17].

Content of dry soluble substances was determined by a refractometric method. The essence of the method was to determine the mass fraction of dry substances (DSS) in the product by the refractive index of its solution. Refractometer RPL-3M was used for determining. Two drops of black current juice or jelly applied on the prism of the refractometer, holding them for 5 minutes. The eyepiece was moved to connect the visor with the boundary of dark and light fields and the percentage of dry soluble substances was determined by a scale.

Content of titrated acids of black current juice and jelly was defined by titration of water extract of weight with alkali solution of certain normality. Weight of 5 g was weighed to the nearest ±0.01 g, placed in a glass and dissolved with distilled water in a volume of 100 cm³. 3–4 drops of phenolphthalein solution were added and it was titrated with 0.1 n solution of sodium hydroxide (NaOH) until appearing of a pink colour which did not disappear within a minute.

Acidity was calculated by the formula:

$$X = 2 \times V \times K \quad (2)$$

where X – acidity, %;

V – amount of 0.1 n solution of sodium hydroxide used for titration, cm³;

K – correction factor of the solution of sodium hydroxide used for titration.

Content of sugars was determined by a ferricyanide method which was based on oxidation of reducing sugars with an alkaline solution of potassium ferricyanide (K₃[Fe(CN)₆]). Sample weight (m, g) was calculated by the formula:

$$S_n = 0.2 \times V / a \quad (3)$$

where V – volume of a volumetric flask, cm³;

a – possible sugar content in studied product, %.

Weight was weighted in a glass, put it in a measuring flask of 200 cm³, filled with distilled water to half of the capacity. The flask with weigh was kept in water bath with the temperature of 60°C for 15 minutes. Then it was cooled to the temperature of 20°C and precipitated nonsugar matters by successively adding of 10 cm³ of sulfuric acid zinc (ZnSO₄) and sodium hydroxide (NaOH) at concentrations of 1 mol/dm³. Content of the flask was brought to the mark, mixed and filtered.

25 cm³ of alkaline solution of potassium ferricyanide (K₃[Fe(CN)₆]), 8 cm³ of experimental solution and 2 cm³ of distilled water was put into a conical flask of 250 cm³. Solution in the flask was heated to boiling on a cooker, kept at this temperature for 1 minute, then cooled, filled the cuvette (5 mm) and colourimetric with a wavelength of 400–440 nm (blue colour filter). The number of reducing sugars in X, % was calculated by the formula:

$$X = a \times V / 10 \times C \times m \times K \quad (4)$$

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where a – number of invert sugar calculated by calibration curve, mg;

V – volume of the flask where weight was dissolved, cm^3 ;

C – volume of studied solution for colorimetric determination, cm^3 ;

m – sample weight, g;

K – correction factor took into account the oxidation of sucrose contained in the volume under study.

50 cm^3 of filtrate was transferred to the volumetric flask of 100 cm^3 , 3 cm^3 of concentrated hydrochloric acid (HCl) was added, immersed it in a thermometer flask and placed on a water bath heated to 60°C to determine the total amount of sugar. In 2–3 minutes the temperature of the solution in the flask was increased to $67\text{--}70^\circ\text{C}$ and kept at this temperature for 5 minutes. The solution was quickly cooled to the temperature of 20°C . The solution of invert sugar was neutralized with sodium hydroxide (NaOH), one drop of methyl-orange was added and it was brought to the mark.

Amount of reducing sugars after inversion was determined in the same way as before inversion. Content of total sugar, which was defined in the invert one, was calculated by the formula:

$$X_1 = \frac{a * V}{5 * m * C} \quad (5)$$

where X_1 – amount of total sugar in terms of inversion, %;

V – volume of the volumetric flask where weight was dissolved, cm^3 ;

a – number of reducing sugars found by calibration curve, mg;

m – weight, g;

C – volume of solution for calorimetry, cm^3 .

Content of sucrose S (%) was calculated by the formula:

$$S_n = 0.95 * (X_1 - X) \quad (6)$$

Repetition of chemical analyzes is threefold. Weight of the sample for analysis is 2 kg.

Statistical processing of research results was carried out using dispersion and correlation analyses using special software packages (Excel, Statistica) [16, 17, 19].

3. RESULTS AND DISCUSSION

The dynamics of the main components of the chemical composition of frozen blackcurrant fruits was studied. However, received results did not reveal the true regularity in the changes. Re-calculation of the data taking into account weight losses of the fruits during freezing and storage was done for this reason. According to data (Table 1), weight losses of the fruits were 1.2–1.6% during freezing. Specified process was logical. Partially free moisture in the fruits and water which always remains on the surface of the fruits and the walls of the package evaporates under low temperatures and low relative humidity of the air. The area of evaporation increases because of small size of blackcurrant fruits. Circulation of the air in the chamber facilitated it.

Table 1. Weight losses of frozen blackcurrant fruits of Pilot O. Mamkin variety (packaging method – string bags), %

Method of freezing	Storage time	The fruits are grown in weather conditions	
		unfavourable	favourable
Fast freezing	during freezing	1.25	1.16
	for 6 months of storage	8.63	7.65
	for 8 months of storage	9.75	8.53
	For 10 months of storage	11.2	10.11
Slow freezing	during freezing	1.57	1.41
	for 6 months of storage	8.51	7.83
	for 8 months of storage	9.92	9.44
	for 10 months of storage	12.13	11.85
$LSD_{0.05}$		0.82	

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Weight losses significantly increased under long-time storage of the frozen fruits due to the phenomenon of sublimation. They reached 10.1–12.1% depending on the method of freezing by the end of storage. However, distribution of weight losses during 10 months of storage was uneven. They were 6.5–7.4% under rapid and 6.4–6.9% under slow freezing during 6 months, which corresponded to 65 and 56% of total losses. During the next 2 months (8 months of storage), the fruits lost 0.9–1.1% under rapid and 1.4–1.6% under slow freezing, resulting in a total loss of 9.3% and 12.6% respectively. Fruit storage at the final stage from 8 to 10 months increased weight losses by 1.5–1.6% under rapid and by 2.2–2.4% under slow freezing. This increased the percentage of losses by 14.3–21.7%, respectively from the total losses. Received results indicate that the highest weight losses during frozen fruits storage were at the beginning of storage, then their size decreased (stabilized), and they again increased somewhat until the end of storage. This was confirmed by the data of monthly weight losses of the fruits. Calculations showed that losses were 1.1–1.2% monthly for 6 months of

storage irrespective of the freezing method. They were 0.5–0.6% under rapid and 0.7–0.8% under slow freezing in the period of storage from 6 to 8 months. Weight losses increased every month and were 0.7–0.8% under rapid and 1.1–1.2% under slow freezing at the storage stage from 8 to 10 months.

Weight losses of the frozen fruits during storage indicated at their monthly increase regardless of the type of packaging, variety, year of research. However, there were certain patterns in weight losses. Absolute weight losses of the fruits decreased every next month of storage, but their level increased, adding data of the previous months. The highest weight losses in the fruits were observed in the first three months of storage. They were 0.036–0.045% in string bags, 0.026–0.035% in paraffined boxes for one day. During the 4–5 month storage, there was a tendency to reducing the losses and keeping them at the level of 1 day: string bags – 0.029–0.036%, paraffin boxes – 0.020–0.025%.

The level of weight losses of the frozen fruit was almost stabilized after 5-month storage and remained unchanged until the end of storage. Namely: 0.028–0.031% in string bags, 0.019–0.021% in paraffined boxes.

The data of weight losses of the frozen fruits in polyethylene bags were different from the previous ones. They were 0.30–0.42% during the entire period of storage. And although weight losses were very low, the order of their formation remained during 10 months of storage. The products had the highest losses – 0.0014–0.0023% per day preferably to 3 months of storage. The level of losses decreased and was 0.0011–0.0014% during 4–5 months of storage. Their level was somewhat higher of 0.0016–0.0018% only in the fruits of Biloruska solodka variety. After 6 months of storage, weight losses of the fruits were stable and in the range of 0.0010–0.0011%, and 0.0014–0.0016% in the fruits of Biloruska solodka variety.

Unconditional advantages of polyethylene packaging were established. The total weight losses of the frozen fruits in polyethylene bags was lower compared to string bags, on average – in 5.7–7.0 times. There was a slightly smaller difference between the variants of polyethylene packaging and paraffined boxes – in 4–4.8 times.

Packing of the frozen fruits in paraffined boxes helped to reduce weight losses of the fruits by 1.4 times. However, they were considerably inferior to polyethylene bags because of the lack of sealing.

Taking into account the above-mentioned data on weight losses of the frozen fruits, the situation concerning their qualitative composition radically changed. Absolute values of the components of the chemical composition of the fruits decreased, hence the relative losses increased. In fact, losses of dry soluble substances, sugars, ascorbic acid during freezing and storage were 1.2 times higher. Increase in the acid content which was observed during the storage period of the frozen fruit was 1.2–1.3 times lower.

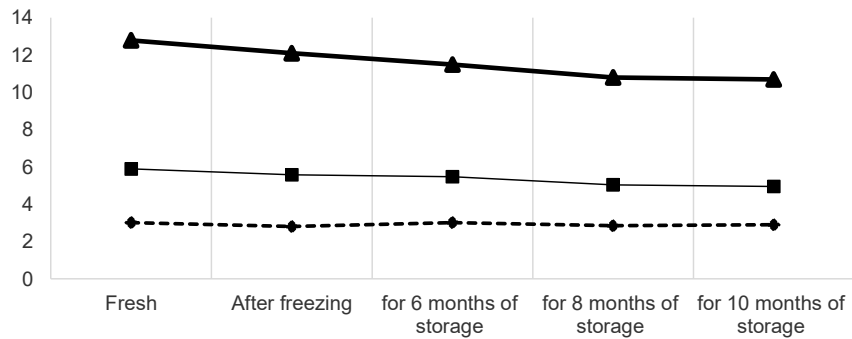
The duration of storage particularly influenced the indicators of the chemical composition. It would be a mistake to assume that the content of dry soluble substances and sugars increased by 1.0–1.7% during 6 months of storage of the frozen fruits. Recalculation showed a reverse, the latter decreased by 7–10%. There was the same during 8 and 10 months of storage. Formed appearance of increasing the content of sugars during storage was not actually true. It was obvious that the data presented in the scientific articles were so different and sometimes had opposite tendencies because not all authors took into account weight losses and studied changes in the chemical composition of the fruits in dynamics, and presented distorted data.

According to Figs. 1–2 shows that the content of components of the chemical composition of frozen fruits is lower (except for acids) than fresh ones. Significant changes in the chemical composition of the frozen fruits occurred during freezing. And freezing speed influenced greatly the level of indicators. The content of dry soluble substances decreased compared with fresh fruits by 5.2–5.9% under rapid and by 5.5–6.3% under slow freezing, the content of sugars was 4.9–5.4% and 6.0–8.6%, respectively; acid content by 7.0–9.6% and 8.6–10.4%, respectively. While, a decrease in the content of dry soluble substances was 10–11%, sugars – 2–10% regardless of the freezing method during 10 months of storage. The acidity of the fruits increased during storage and exceeded it in fresh fruits by 7.0% under rapid and 2.3–3.1% under slow freezing.

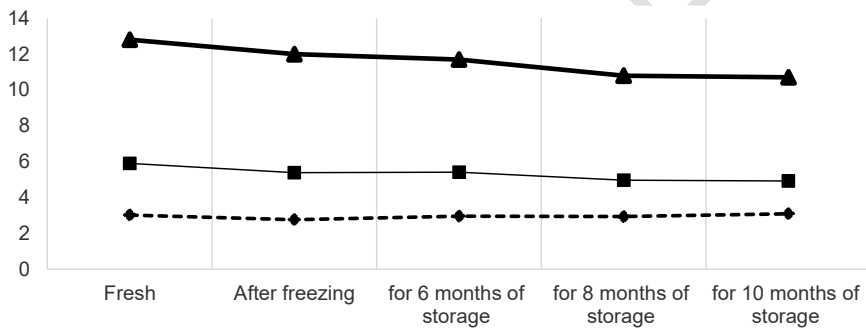
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Fast freezing



Slow freezing

-◆- Content of acids, % -■- Total content of sugars, %
 -▲- Content of dry soluble substances, %

Fig. 1. Indicators of chemical composition (taking into account weight losses) of blackcurrant fruits of Pilot O. Mamkin variety (packing method – mesh bags)

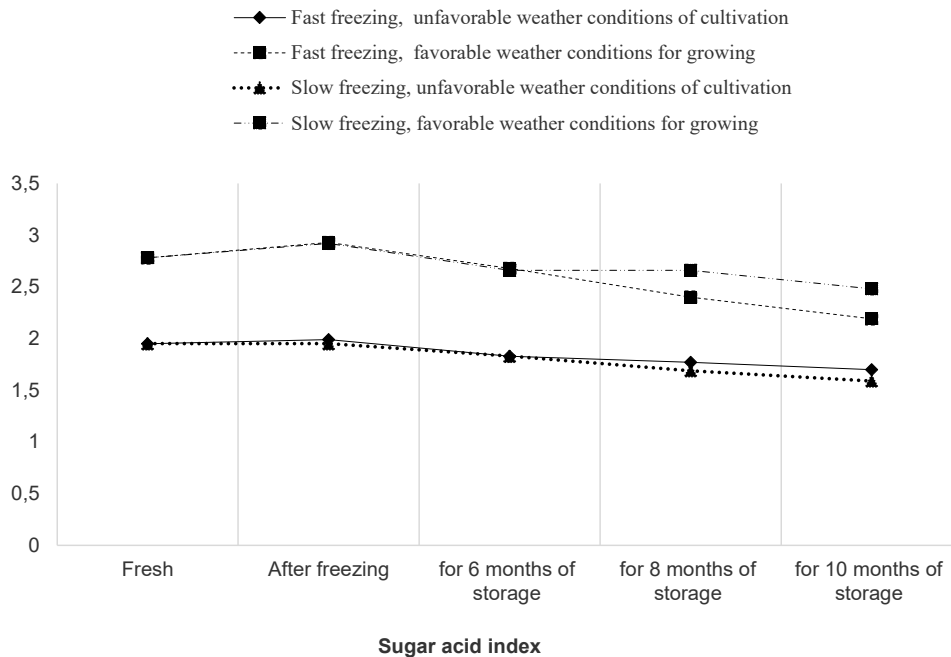


Fig. 2. Sugar acid index of blackcurrant fruits of Pilot O. Mamkin variety (packing method – mesh bags)

Consequently, a significant decrease in the content of dry soluble substances and sugars occurred at the freezing stage and was 53–63% and 47–52%, respectively, of the total reduction in substance content for 10 months of storage. This indicated that the frozen fruits did not remain stable in the content of dry soluble substances, including sugars during storage. Reducing of the content of dry soluble substances was 7.8–10.1% for 6 months of storage, 12.3–15.5% for 8 months and 15.1–16.7% for 10 months of storage of the content in the fruits after freezing. Losses of sugars in the frozen fruits during storage were smaller but significant. Reduction was 6.0–8.3% for 6 months, 7.2–15.9% for 8 months and 7.9–16.9% for 10 months.

The dynamics of acids in the frozen fruits represented interest. As already noted, the acidity of the fruits decreased at the stage of freezing. But a progressive increase in the number of acids in the fruits was observed during 10 months of storage. This was especially evident when comparing data with the content of acids in the freshly frozen fruits. Their number increased by 6.0–7.8% for 6 months of storage, by 5.8–11% for 8 months, by 5.8–15.9% for 10 months of storage. On average, the frozen fruits for 10 months of storage had an acid content in 1.2 times higher than in the fruits immediately after freezing. However, the acidity of the frozen fruits was within the range of fresh ones or grew by 0.07–0.19%, and it was 2.3–7.0%.

The objective indicator of the fruits state was sugar-and-acid index. The level of sugar-and-acid index significantly depended on the weather conditions of the vegetative period. A tangible increase in the index level – for fruits of Pilot O. Mamkin variety in 1.4 times was under favourable conditions for the synthesis of sugars. It remained unchanged or slightly increased during freezing. A tendency towards a gradual decrease in the level of the indicator was observed when storing of the frozen fruits, but only by 0.1–0.3 units, which was 3–10% of the fresh fruits. But the level of the indicator dropped in 1.2 times for 10 months of storage – the fruits became even sourer.

Fruit freshness, taste and appearance are confirmed by the correlation (Fig. 3–5) between quality indicators. A direct strong relationship was established between the content of dry soluble substances and sugars ($r = 0.94$) and the inverse average between the content of dry soluble substances and acids and the content of sugars and acids ($r = 0.70$). The sugar-acid index directly and strongly correlated with the content of dry soluble substances ($r = 0.88$), sugars ($r = 0.95$), and cautiously with the content of acids ($r = 0.91$).

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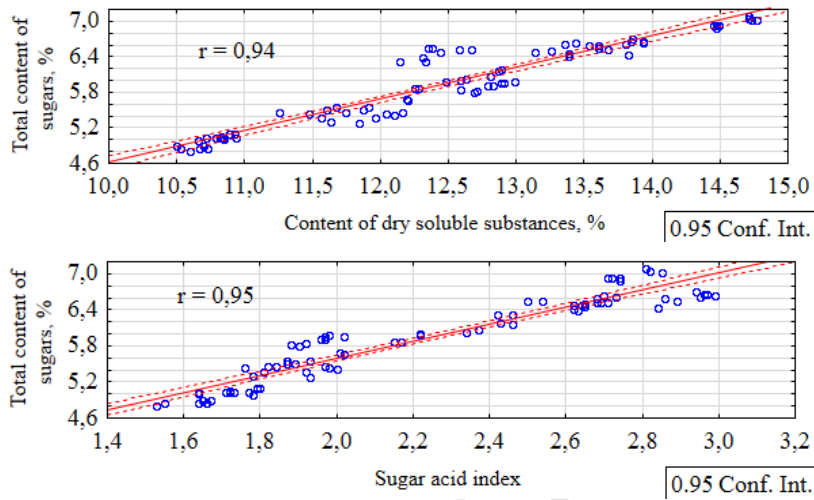
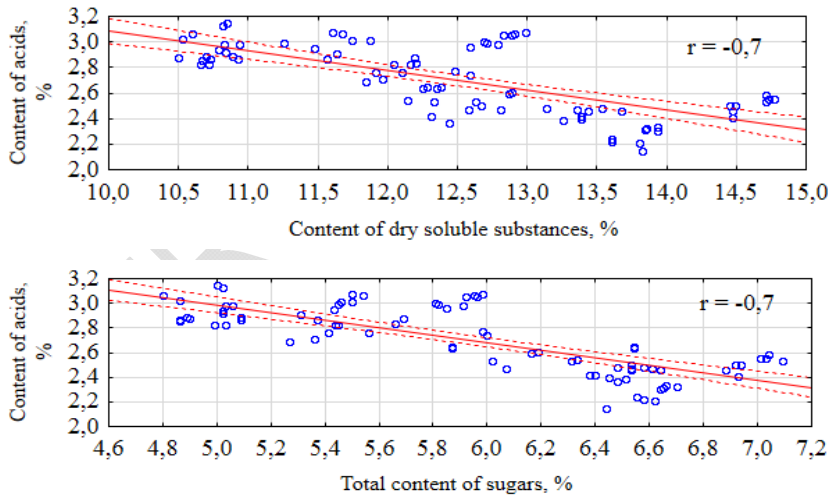


Fig. 3. Correlation between total sugar content and dry soluble substances content and sugar-acid index



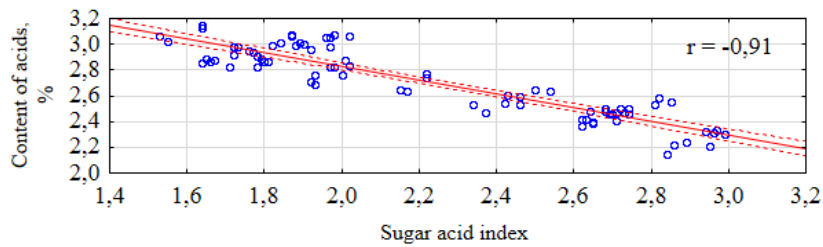


Fig.4. Correlation dependence between the content of acids and the content of dry soluble substances, sugar and sugar-acid index

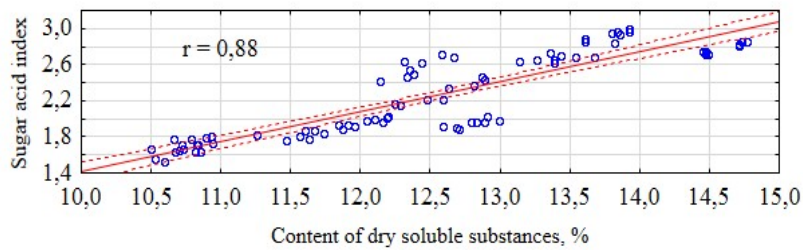


Fig. 5. Correlation dependence between sugar-acid index and the content of dry soluble substances

A tendency to decrease its level in the frozen fruits was established in the dynamics of ascorbic acid (Fig. 6). Moreover, a sharp decline of vitamin C content was found at the stage of fruits freezing. Its quantity decreased by 15–21% in rapidly frozen and 22–24% in slow frozen fruits.

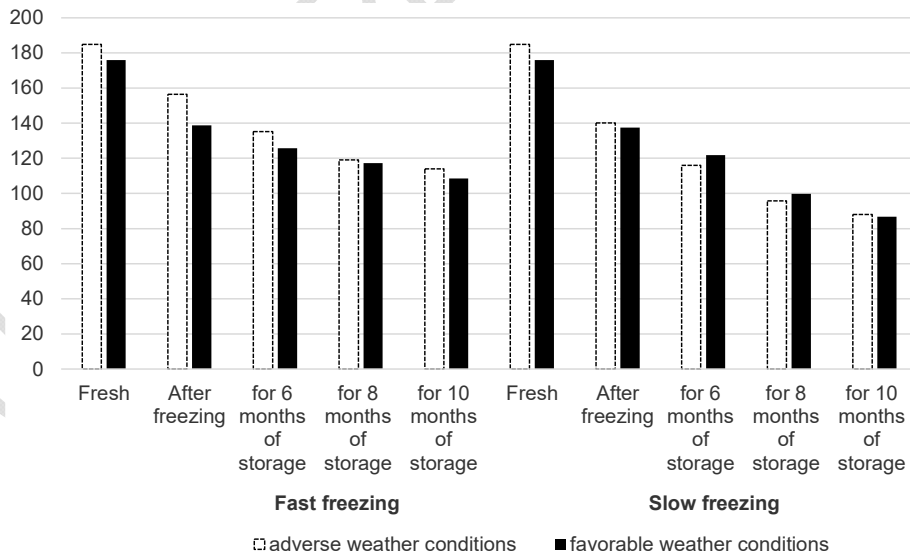


Fig. 6. The dynamics of the content of ascorbic acid (taking into account weight losses) of blackcurrant fruits of Pilot O. Mamkin variety depending on the duration of storage (packing method – mesh bags), mg/100 g

Losses of ascorbic acid in the fruits increased significantly when increasing the duration of storage. Its number in fruits decreased by 27–29% under rapid and by 30–37% under slow freezing for 6 months; by 33–36 and 43–48%, respectively, for 8 months; by 38% and 51–52%, respectively, for 10 months. That is, 39–55% of all losses of ascorbic acid in the fruits occurred during freezing.

Conducted analysis confirmed the benefits of rapid freezing for preserving the chemical composition of the fruits. Losses of these components were lower in 1.2–1.6 times during freezing by this time. The benefits were not always significant when stored, but the tendency remained well expressed, especially by the content of ascorbic acid. The level of the latter in the rapidly frozen fruits was 1.3 times higher.

Monthly decrease or increase in the level of indicators under research compared with fresh fruits and after freezing were calculated to determine the tendencies in the changes of the chemical composition of the frozen blackcurrant fruits.

Data in the Tabl. 2 show: monthly decrease in the content of dry soluble substances in the frozen fruits during storage was most pronounced up to 8 months. Monthly losses decreased or remained at the previous level, both in comparison with the fresh and frozen fruits under subsequent storage up to 10 months.

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Table 2. Monthly decrease (+ increase) in the content of the components of the chemical composition of the frozen blackcurrant fruits of Pilot O. Mamkin variety (taking into account weight losses)

Fruits	Content of dry soluble substances, %		Total content of sugars, %		Content of acids, %		Content of ascorbic acid, mg/100 g	
	Fruits grown under weather conditions ³							
	-	+	-	+	-	+	-	+
Rapid freezing								
Fresh	12.8	14.6	5.90	6.98	3.02	2.51	184.8	176.0
After freezing	0.75	0.76	0.32	0.34	0.21	0.24	28.4	37.3
for 6 months of storage	<u>0.22</u> ²⁾	<u>0.22</u>	<u>0.07</u>	<u>0.07</u>	<u>0.01</u>	<u>0.01</u>	<u>8.3</u>	<u>8.4</u>
	0.09	0.09	0.02	0.01	+0.03	+0.03	3.6	2.2
for 8 months of storage	<u>0.25</u>	<u>0.22</u>	<u>0.11</u>	<u>0.11</u>	<u>0.02</u>	<u>+0.01</u>	<u>8.2</u>	<u>7.3</u>
	0.15	0.13	0.07	0.07	+0.01	+0.04	4.7	2.7
for 10 months of storage	<u>0.21</u>	<u>0.22</u>	<u>0.09</u>	<u>0.11</u>	<u>0.01</u>	<u>+0.02</u>	<u>7.1</u>	<u>6.8</u>
	0.14	0.14	0.06	0.07	+0.01	+0.04	4.2	3.0
Slow freezing								
Fresh	12.8	14.6	5.90	6.98	3.02	2.51	184.8	176.0
After freezing	0.80	0.80	0.51	0.42	0.23	0.26	44.7	38.5
for 6 months of storage	<u>0.18</u>	<u>0.19</u>	<u>0.08</u>	<u>0.06</u>	<u>0.01</u>	<u>0.01</u>	<u>11.5</u>	<u>9.0</u>
	0.05	0.06	+0.03	0.01	+0.03	+0.03	4.1	2.6
for 8 months of storage	<u>0.25</u>	<u>0.26</u>	<u>0.12</u>	<u>0.06</u>	<u>0.01</u>	<u>0.01</u>	<u>11.1</u>	<u>9.5</u>
	0.15	0.16	0.05	0.01	+0.02	+0.03	5.5	4.7
for 10 months of storage	<u>0.21</u>	<u>0.23</u>	<u>0.10</u>	<u>0.06</u>	<u>+0.01</u>	<u>+0.01</u>	<u>9.7</u>	<u>8.9</u>
	0.13	0.15	0.05	0.01	+0.03	+0.03	5.2	5.1
<i>Pe (Partial eta-squared)</i>	0.96		0.84		0.63		0.96	

Notes: ¹ acid content in terms of citric acid; ² above the line – comparison with the fresh fruits, under the line – comparison with the fruits after freezing; ³ + favourable; – unfavourable

A similar tendency was observed with the content of sugars. Monthly content of sugars decreased compared with the fresh fruits; and what is more, losses of sugars were smaller with each subsequent period of storage. Comparing the content of sugars in the frozen fruits during storage with such fruits during freezing indicated: losses of sugars could increase every month, be approximately the same or decrease.

Changes in the content of sugars in the frozen fruits, of course, had their nature. Decrease in sugars content during freezing is explained by losses of monosaccharides for respiration, which was particularly intense in the process of freezing (as a corresponding reaction of a plant cell to lowering the temperature) and after defrosting, especially in the presence of damaged cells. Partial reduction of sugars content during storage occurred as a result of their spending for residual respiration and other processes. In addition, there was information that the amount of pectin substances especially protopectin could increase during the freezing process as a result of formation of uronic acids because of the activation of enzymatic oxidation of monosaccharides in the damaged fruit tissues [11]. This correlated with a sharp decrease in the reduced sugars in the process of freezing.

Increasing in the content of sugars in the frozen fruits during storage should be found in the changes not only mobile, but also slow-moving and stationary carbohydrates. It was established [8] that there was destruction of structural

carbohydrates in the frozen fruits: losses of pectin substances, hemicellulose and α -cellulose were increased. Moreover, the degree and nature of these changes depended on the variety, freezing temperature and duration of storage. At the same time, as indicated, increase in insoluble polysaccharides and soluble pectin associated with the reaction of a fruit tissue to damage, as well as the formation of mucus and gums synthesized by a damaged plant tissue was detected. It was known that 60% of mucus was pentosan (a group of hemicellulose) [17]. The number of polysaccharides by the end of the storage decreased [8]. It was possible that the hydrolysis of polysaccharides and release of sugars from complex compounds was a source of their insignificant increase in the frozen fruits of blackcurrant during storage.

Changes in the acidity of the fruits were quite characteristic and stable. Increase in the content of acids in the frozen fruits occurred in the 8th–10th months of storage and increased monthly by 0.01–0.02% when comparing the frozen fruits with fresh ones. There was a tendency towards a monthly progressive increase in the acid content in 1.3–1.5 times if we compared the acidity of the frozen fruits during storage with the acidity of the freshly frozen fruits.

Causes of a characteristic increase in the acids content of the fruits were apparently contained in destructive changes. Acid fell for oxidizing-and-reducing processes the most in the process of freezing and storage. Decrease of the acids content during freezing was due to their inclusion as a substrate to the process of respiratory gas exchange. Increasing of the acids content in the storage of the frozen fruits was probably the result of enzymatic hydrolysis which occurred at the expense of easily-hydrolyzed polymer molecules which amount in the damaged tissues increased.

The dynamics of a significant decrease in ascorbic acid in the frozen fruits was observed. Comparing the content of ascorbic acid in the frozen fruits during storage with such in the fresh fruits was characterized by the following: its monthly losses decreased from 8 to 7 mg/100 g or from 12 to 9 mg/100 g. But this tendency reflected only relative indicators. In fact, the amount of ascorbic acid was reduced by 3–5 mg/100 g almost equally every month in the frozen fruits.

Causes of undesirable reduction of ascorbic acid in the fruits appeared while freezing. The activity of enzymes was sharply reduced by 25–30%, but not lost [8]. This was due to the low temperature which inhibited all biochemical processes, including enzymatic. But catalytic ability of enzymes was restored when defrosting. Restoration of the activity of enzymes was different and it was experimentally proved by a change in the oxidizing-and-reducing potential and by direct determination of the activity of enzymes [11]. Oxidizing enzymes restored their activity faster than restorative ones. As a result, ascorbic acid was irreversibly oxidized. The way of reducing the C-vitamin activity of the frozen fruits was established. Transformation of ascorbic acid came to its oxidation to dehydroascorbic acid, and then to the physiologically inert form of 2,3-diketogulonic acid [9, 10].

Significant influence of the weather conditions of the vegetation period on components saving of the chemical composition of the fruits. If the content of dry soluble substances and sugars was higher in the fresh fruits then after fruits freezing the tendency to their smaller losses during storage was maintained.

The opposite tendency in relation to the content of acids and ascorbic acid was expressed: the content of acids including ascorbic acid was lower in the fresh fruits, but there were the greater losses of them during freezing. In addition, acids in the frozen fruits accumulated more intensively during storage.

The effect of freezing method on the content of dry soluble substances in fruits – 90%, ascorbic acid – 44%, sugars – 21%, acids – 14%.

The study of the suitability of blackcurrant fruits to freezing showed (Table 3) that the chemical composition of the frozen fruits changed. However, decrease or increase in the content of the individual components in the tested fruits was not always reliable. Acid suffered the greatest changes. Their content in the frozen fruits in comparison with the fresh ones increased by 2.1–4.5%, which was reflected at the level of dry soluble substances. Since the content of sugars in the fruits did not change significantly, and the content of acids increased, the sugar-and-acid index decreased – by 2.7–5.6%. It remained the highest in the frozen fruits of Biloruska solodka variety – 3.3–3.4. The peculiarities of the variety had greatest influence at the level of dry soluble substances, sugars, acids in the frozen fruits – 66, 66, 46%, respectively.

Table 3. Chemical composition of the blackcurrant fruits (slow freezing, storage in polyethylene bags)

Indicator	Mynai Shmyrov variety		Biloruska solodka variety				Novyna Prykarpattia variety				LSD ₀₅		
	Fruits grown under weather conditions ³												
	+		-		+		-		+				
	fresh	freezing	fresh	freezing	fresh	freezing	fresh	freezing	fresh	freezing	fresh	freezing	
Dry soluble substances, %	14.8	<u>15</u> 14.77 ²	16.0	<u>16.2</u> 15.97	16.0	<u>16.4</u> 16.07	16.0	<u>16.2</u> 15.93	15.0	<u>15</u> 14.8	14.6	<u>14.8</u> 14.61	<u>0.10</u> –
Sugars, %	7.45	<u>7.5</u> 7.38	7.26	<u>7.32</u> 7.21	9.25	<u>9.28</u> 9.09	8.82	<u>8.89</u> 8.74	6.89	<u>6.93</u> 6.84	7.91	<u>8.01</u> 7.91	<u>0.84</u> –
Acids ¹ , %	2.78	<u>2.96</u> 2.91	3.32	<u>3.44</u> 3.39	2.59	<u>2.75</u> 2.7	2.55	<u>2.68</u> 2.64	3.05	<u>3.18</u> 3.14	2.61	<u>2.74</u> 2.71	<u>0.09</u> –
Sugar acid index	2.68	<u>2.53</u> 2.53	2.19	<u>2.13</u> 2.12	3.57	<u>3.37</u> 3.37	3.46	<u>3.32</u> 3.31	2.26	<u>2.18</u> 2.18	3.03	<u>2.92</u> 2.92	<u>0.10</u> –
Ascorbic acid, 109.1	<u>88.2</u>	182.1	<u>148.6</u>	167.2	<u>128.7</u>	273.5	<u>207.4</u>	118.8	<u>97.8</u>	229.3	<u>185.1</u>	<u>9.68</u>	

mg/100 g	86.8	146.1	126.1	204	96.5	182.7	–
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Notes: ¹ acidity in terms of malic acid; ² under the line – the content during storage taking into account weight losses; ³ + favourable; - unfavourable

The content of ascorbic acid in the frozen fruits depending on the variety has decreased by 19–24%. Preservation of ascorbic acid in the frozen fruits of Novyna Prykarpattia and Mynai Shmyriov varieties was 80-81%, while it was slightly lower – 75% in Biloruska solodka variety. Power of influence of the variety on the content of ascorbic acid was 28% in the frozen fruits, the process of freezing – 12%, and weather conditions of growing – 60%.

The regularity remained unchangeable – the variety of blackcurrant and conditions that influenced the formation of the biochemical composition were the main objective indicators for establishing of their suitability for freezing.

The fruits of Biloruska solodka variety were distinguished by the qualitative composition, taste properties, content of ascorbic acid. Noted less preservation of ascorbic acid in the frozen fruits of this variety correlated with a significant tendency of the fruits towards cracking – 42%.

The chemical composition of the frozen fruits of Novyna Prykarpattia, Mynai Shmyriov and Pilot O. Mamkin varieties depended largely on the weather conditions of yield formation. They were not inferior to the fruits of Biloruska solodka variety under favourable weather conditions during the period of blackcurrant vegetation.

4. CONCLUSION

Qualitative indicators of the frozen blackcurrant fruits depended on the method of freezing, packaging, duration of storage, pomological variety and weather conditions of the vegetation period.

It was necessary to take into account weight losses of the fruits during freezing and storage in order to determine their true chemical composition. It radically changed the level of indicators.

On average, weight losses were 1.3 times lower under rapid method of freezing. Total weight losses were not significantly different at the end of storage: 11.9–12.1% under slow method versus 10.1-12.2% under rapid one. However, the fruits had the greatest losses during the first 3 months of storage, the level of losses stabilized during 4-5 months and somewhat increased until the end of storage. The advantages of packing of the frozen fruits in polyethylene packages were established. Total weight losses of the fruits for 10 months of storage was 6–7 times lower than in string bags and 4-5 times than in paraffined boxes.

The most significant changes in the chemical composition of the fruits occurred during freezing. Reduction in the content of dry soluble substances in the fruits was 53–63%, sugars – 47–52% of the total decrease for the entire period of storage. By the end of fruits storage, the amount of dry soluble substances and sugars in them decreased by 8–17% of the content in the fresh ones, and the acidity rose by 6–16% leading to a decrease of sugar-and-acid index in 1.2 times. The content of ascorbic acid in the fruits during freezing was reduced by 15–24%, which was 39–55% of all losses. Monthly storage resulted in a reduction in its amount in the fruits by 3–5 mg/100 g. Advantages of rapid freezing were justified by 1.2–1.6 times lower losses of the content of dry soluble substances, sugars, acids, ascorbic acid and preservation of the appearance of the fruits.

The frozen fruits of Biloruska solodka variety had benefits by the chemical composition, taste and content of ascorbic acid. The chemical composition of the frozen fruits of Novyna Prykarpattia, Mynai Shmyriov and Pilot O. Mamkin varieties largely depended on the weather conditions. Their quality was not inferior to Biloruska solodka variety under favourable weather conditions.

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