Analysis of the influence of low temperature on the change of physicochemical parameters of fruit and berry raw materials during storage

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Abstract. A modern postulate of a healthy lifestyle is consuming products with a high content of natural physiologically valuable ingredients. These types of products include fruits and berries. However, the seasonality of their production makes it necessary to search for effective conservation methods that will not significantly change the physicochemical parameters. Considering that the most popular and advanced method is shock freezing, we have analyzed the influence of low temperatures on the quality characteristics of fruit and berry raw materials and the fractional composition of pectic substances. Due to the pluripotential properties, pectic substances determine the functional value of raw materials. As the research object we have chosen winter apple varieties such as Rennet Simirenko, Gloster, Granny Smith, Korey; stone fruits – cherry varieties such as Podbelskaya, Lyubskaya; cherry plum varieties such as Desertnaya and Kremen; berries - red currant varieties such as Natali and Nenaglyadnaya, black currant varieties such as Pamyat Lisavenko and Orloviya. The varieties of fruits and berries were chosen based on their regional prevalence in southern Russia. It has been established that the low-temperature storage of frozen fruit and berry raw materials decreases the weight ratio of dry solids (1.2 - 4.0%), sugars (4.0 - 9.0%) and pectic substances (4.8 - 24.9%). The titratable acid content increases. According to our findings, the fractional composition of pectic substances changed during low-temperature storage of berries, pomiferous and stone fruits. The fractional redistribution was presented in the form of reduction of protopectin and increase of soluble pectin in all studied berry samples. According to the research results, the functional properties are best preserved in berry raw materials.

1. Introduction
Considering the environmental conditions, natural biopolymers are becoming nowadays very popular. Pectin is one of such substances. Today it is well-known what influence they have on the human body [1–3]. Food products containing pectic substances enjoy well-deserved recognition.

Nowadays food industry tends to use innovative ways of preserving high quality and food safety, due to the ever-increasing desire to lead a healthy lifestyle [4]. One of such innovative methods is freezing. This method makes it possible to preserve fruit and berry raw materials with minimum alteration of biochemical composition, characterized by high content of macro- and micronutrients, minerals, vitamins, pectic substances, due to which it becomes promising for the food industry [5–7].
At the same time, the analysis of published works in the respective area shows the restrained use of low-temperature technologies for production and processing of fruits and berries in Russia due to the lack of research dedicated to the functional food factors [9–11].

For this reason, it is quite relevant to study how frozen products preserve or change their chemical composition, including pectic substances that are distinguished through their pluripotential properties [12].

2. Materials and methods
As research object we used late ripening apples, stone fruits (cherry and cherry plum) and berries (red and black currant), cultivated in southern Russia, in particular, the Krasnodar Region.

The varieties of fruits and berries were chosen with regard to their regional prevalence. For research we used winter apples – Rennet Simirenko, Gloster, Granny Smith, Korey; stone fruits – cherry varieties Podbelskaya and Lyubskaya; cherry plum varieties Desertnaya and Kremen; berries - red currant Natali and Nenaglyadnaya, black currant Pamyat Lisavenko and Orloviya.

We took at least three packaging units weighing at least 15 kg for each variety. From the selected raw materials we prepared average samples (3 kg), distributing them in three plastic bags (1 kg). We put samples in prepared containers, provided with passports with indication of the sample variety, its net weight, freezing temperature, date of placement in storage.

Then we applied shock freezing (to - 30 °C) by using special devices. Before placement in storage and after each withdrawal from storage, we analyzed the changes that occurred in the fractional composition of pectic substances. The samples were stored in ordinary refrigerators at a temperature of - 20 °C, for six months. The first samples were removed from storage after 3 months, then after 6 months. For the analysis of chemical composition of the selected samples, we used standard methods. The quantitative content of ascorbic acid and titratable acidity were determined by titration. The quantitative content of sugars was determined by capillary electrophoresis method, and quantitative content of solids – on the basis of refractometric analysis.

3. Results and discussion
The research of the influence of low temperatures on the change of biochemical composition of the chosen fruits and berries made it reasonable to analyze main quality characteristics before and after storage. The experimental findings on apple raw materials before placement in storage are presented in Table 1.

| Apple variety       | Solids content, % | Sugar content, % | Titratable acid content, % | Content of vitamin C, mg % |
|---------------------|-------------------|------------------|-----------------------------|----------------------------|
| Rennet Simirenko    | 14.1              | 9.9              | 0.76                        | 5.1                        |
| Gloster             | 17.6              | 13.9             | 0.48                        | 3.6                        |
| Granny Smith        | 11.9              | 9.9              | 0.62                        | 4.6                        |
| Korey               | 15.8              | 11.8             | 0.39                        | 3.9                        |

The experimental findings on the physical and chemical parameters of frozen apples after withdrawal from storage showed the following changes. The content of soluble solids changed. Moreover, these values were different depending on the variety. So, the solids content in Gloster and Korey apples decreased by 1.2 - 2.0%, in the other varieties – by 3.4 - 3.6%. The same was observed in the total sugar content. Comparatively high sugar content in apples such as Gloster and Korey decreased by 7–9%, as compared to other varieties.

During storage, the total acidity of all varieties increased by 5.8 - 8.3%. We observed significant changes in the quantitative content of vitamin C. The reduction of vitamin C depended largely on the apple variety and ranged from 11 to 21%.
The stone fruits placed for storage in a frozen state had the following quality characteristics (Table 2).

The chemical parameters slightly changed after frozen storage. The solids content decreased by 2-3%; the sugar content decreased on average by 4-6%. The titratable acid content in all samples increased. It slightly increased by 1.2% in Podbelskaya cherry, and by up to 3.4% in Kremen cherry plum. We observed a significant decrease in the content of vitamin C. For stone fruits, these values decreased on average by 28%.

**Table 2.** Physical and chemical characteristics of cherry before placement in storage

| Name                  | Solids content, % | Sugar content, % | Titratable acid content, % | Content of vitamin C, mg % |
|-----------------------|-------------------|------------------|-----------------------------|---------------------------|
| Podbelskaya cherry    | 13.4              | 8.8              | 1.8                         | 18.4                      |
| Lyubskaya cherry      | 17.8              | 10.7             | 1.52                        | 16.8                      |
| Desertnaya cherry plum| 13.5              | 6.7              | 1.5                         | 14.7                      |
| Kremen cherry plum    | 13.1              | 8.7              | 2.0                         | 11.4                      |

The berries, namely red and black currants, had the least significant changes in chemical composition during frozen storage, as compared with other chosen fruit and berry raw materials. The experimental findings on the quality characteristics of frozen berries are presented in Table 3.

**Table 3.** Physical and chemical characteristics of berries before storage

| Berries               | Solids content, % | Sugar content, % | Titratable acid content, % | Content of vitamin C, mg % |
|-----------------------|-------------------|------------------|-----------------------------|---------------------------|
| Natali red currant    | 10.8              | 7.1              | 2.9                         | 40.5                      |
| Nenaglyadnaya red currant | 12.6           | 7.7              | 2.34                        | 50.7                      |
| Pamyat Lisavenko black currant | 14.7       | 9.6              | 2.2                         | 170.9                     |
| Orloviya black currant | 12.4              | 8.6              | 2.5                         | 155.2                     |

After frozen storage, physical and chemical characteristics of the berries changed only slightly. There was a minimum decrease of soluble solids after six months of frozen storage. In red currant varieties it decreased by 3–4%, black currant varieties - by 1.5%. The decline in sugar content was also minimal - on average by 4.5% for red currants and by 6.5% for black currants. The titratable acidity slightly increased: by 2.5% for red currants and by 3.5% for black currants. The decline of content of vitamin C was less in berries than in stone fruits. It was established that the content of vitamin C in red currant decreased on averaged by 12.6%, in black currant - by 8.6%.

In the course of research, we analyzed the changes in the content of pectic substances and their analytical characteristics.

Evaluating the preservation of functional properties due to the pectic substances in the fruit and berry raw materials, we conducted secondary analysis on the effect of sub-zero temperature on their fractional composition during storage. It is known that the fractional composition of pectic substances (PS) in plant raw materials is represented mainly by protopectin (PP) and soluble pectin (SP).

Experimental findings on the fractional composition of pectic substances before and after storage are presented in Figure 1.
According to the above findings, the pectic substances of apple raw materials underwent some changes during frozen storage. The content of pectic substances decreased during storage to a different extent. The greatest losses in winter apples were as follows: Rennet Simirenko (sample 4) and Granny Smith (sample 2) on average 15%. The losses in Gloster (sample 3) and Korey (sample 1) ranged from 4 to 6%. The low temperatures affected the soluble pectin content. It increased after storage to a greater extent in Gloster and Korey varieties. In Rennet Simirenko and Granny Smith, it increased by 10 - 12%. The original content of protopectin decreased in all varieties, to a greater extent in Renet Simirenko and Granny Smith and to a lesser extent in Gloster and Korey.

In Figure 2 you can see what changes occurred in the fractional composition of pectic substances in stone fruits during storage.

We found that during frozen storage, the total content of pectic substances in stone fruits changed less than in apples. These changes ranged from 3.3 to 5.3%. At the same time, the soluble pectin content in cherries increased by 7.7% -14.0%, in cherry plum by 10-11%.

The increase in the soluble pectin content caused the decrease of the original content of protopectins by 15-30%.

Changes in the fractional composition of pectic substances in berries during storage are presented in Figure 3.
Figure 3. Changes in the fractional composition of pectic substances in berries: (a) - before placement in storage; (b) - after withdrawal from storage: 1 - Orloviya black currant; 2 - Pamyat Lisavenko black currant; 3 - Nenaglyadnaya red currant; 4 - Natalie red currant.

The findings show that during low-temperature storage of berries, the fractional composition of pectic substances changed. These changes are similar to the changes that occurred in fruits. The changes in the fractional composition of all studied berry samples were characterized by the decrease of protopectin and the increase of soluble pectin.

4. Conclusion

During low-temperature storage of fruits and berries, which were frozen by means of shock-freezing method, we observed non-substantial changes in their physicochemical parameters. The decrease of mass fraction of solids amounted to 1.2 - 4.0%, of sugars 4.0 - 9.0% and of pectin substances 4.8 - 24.9%.

The titratable acid content increased. During defrosting of plant raw materials, redox processes shift towards oxidation reactions, which depends on the activity of oxidoreductases, including such important enzymes as polyphenol oxidase, ascorbate oxidase, catalase and peroxidase. This may be confirmed by slight decrease of the sugar-acid index, which indicates a moderate increase of acidity.

The fractional composition changed to a lesser degree in stone fruits and berries, especially in black currant. These findings should be borne in mind when conducting such a process as defrosting. The alteration of the content of pectic substances in the raw materials with hydrophilic properties will differently affect the loss of loosely bound moisture during defrosting. In addition, the findings on the alteration of pectin and vitamin C content show us the functional properties of frozen raw materials. The research revealed that functional properties are best preserved in berry raw materials.

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