Запропоновано та розроблено новий спосіб та нанотехнології оздоровчих продуктів «NatureSuperFood» – плодоовочевого морозива-сорбетів, що дозволяють отримати продукт з унікальними характеристиками. Нові види сорбетів знаходяться в нанорозмірній формі та відрізняються високим вмістом натуральних біологічно активних речовин плодів та овочів (β-каротину, хлорофілів, фенольних сполук, антоціанів, аскорбінової кислоти та ін.). Крім того, відрізняються високим вмістом розчинних пектинових речовин, що виконують в сорбетах роль натуральних загущувачів та структуроутворювачів. Це дає можливість виключити необхідність застосування синтетичних добавок.

Нанотехнології оздоровчих продуктів «NatureSuperFood» – плодоовочевого морозива засновані на виков ристанні кріогенного «шокового» заморожування та дрібнодисперсного подрібнення плодів та овочів як інноваційного методу структуроутворення та отримання сорбетів з рекордним вмістом БАР. Комплексна дія зазначених факторів призводить до активації та вилучення із плодів та овочів прихованих БАР у вільну форму, а також до трансформації пектину із неактивної форми в активну. Особливістю технологій виготовлення сорбетів є використання тільки натуральних інгредієнтів (фруктів, ягід, овочів), а також відсутність штучних харчових добавок (стабілізаторів, загусників, емульгаторів, синтетичних барвників та ін.). Технології дозволяють не тільки повністю зберегти в сорбетах вітаміни та інші БАР вихідної сировини, а також вилучити із сировини приховані неактивні зв'язані в нанокомплексах з біополімерами та мінеральними речовинами форми БАР у вільну, легкозасвоювану наноформу. Масова частка БАР в сорбетах в 2,5...3,5 рази більша ніж у свіжих плодах та овочах. Крім того, технології дозволяють більш повно (в 3,0...5,0 раз більше ніж в свіжій сировині) екстрагувати та трансформувати у розчинну форму (на 70 %) пектинові речовини, що знаходяться в плодах та овочах в неактивній прихованій формі.

Розроблено нанотехнології та рецептури оздоровчих продуктів «NatureSuperFood» – 3-х видів сорбетів із хлорофілвмісних, каротинвмісних та антоціанвмісних плодів, ягід, овочів. Натуральна сировина при виготовленні сорбетів виступає як п'ять в одному: джерело БАР, загусник, структуроутворювач, барвник і ароматизатор. Нові види сорбетів знаходяться в нанорозмірній формі та за вмістом БАР перевищують відомі аналоги. Відпрацьовані технологічні режими виробництва морозива – сорбетів на стендовому напівпромисловому устаткуванні

Ключові слова: нанотехнології, оздоровчі продукти, сорбети, кріогенне «шокове» заморожування, дрібнодисперсне подрібнення, БАР

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DEVELOPMENT OF THE NANOTECHNOLOGY FOR WELLNESS PRODUCTS "NATURESUPERFOOD" – FRUIT AND VEGETABLE ICE-CREAM SORBETS WITH A RECORD CONTENT OF BIOLOGICALLY ACTIVE SUBSTANCES

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1. Introduction

The relevance of this work relates to the fact that our planet faces the need to solve such global problems as shortages of biologically active substances (vitamins, minerals, β-carotene, chlorophyll, phenolic compounds, polyphenols) in food diet, as well as prebiotic substances [1].

People can satisfy their need in them by 50 % at most [2]. There are 7.5 billion people on our planet, but every eighth person suffers from hunger [3]. Given the above, every year sees an increase in the share of products made from raw materials of poor quality with the use of synthetic components [4]. In addition, there is a growing quantity of artificially-made food additives (colorings, flavor enhancers, thickeners, stabilizers, structure-forming agents, etc.) [5]. The need to resolve the specified problems is compounded due to the deterioration in the environmental situation and the reduced immunity of people, both in Ukraine and in many countries [6]. As estimated by FAO/WHO, the Institute of Nutrition at MOZ AMN in Russia, and the scientific community worldwide, the immune system can be improved by eating foods that are high in the content of the above-enumerated BAS and prebiotics [7]. These products include fresh and frozen fruit, berries, vegetables, as well as products made from them (juices, smoothies, salads, sorbets, soup-purees, etc.) [8, 10]. In this regard, one of the prioritized and relevant trends in the food industry, which is rapidly evolving in different countries worldwide, is the development of wellness products based on fruit, berries, and vegetables. However, when processing fruit and vegetable raw materials using modern technologies, there occur difficulties that are associated with the significant loss of vitamins and other BAS (from 20 to 80 %) [9, 11]. Given the above, there is a search going on in international practice for technological methods that would make it possible to retain, while processing fruits and vegetables into wellness products, the healing BAS and to more efficiently utilize the biological potential of original raw materials. The specified field of research is explored by scientists and entrepreneurs from the world leading countries: Japan, the United States, Germany, the Netherlands, and others [2, 3, 8].

2. Literature review and problem statement

Among wellness products made from fruit, berries, vegetables, a special place belongs to sorbets, which are one of the types of ice cream that is popular around the world [12, 13]. Traditionally, sorbets are produced from fresh fruit and vegetable raw materials, as well as purees, juices without the use of milk [12, 13]. The disadvantage in the production of sorbets is the use of artificial food additives (structure-forming agents, thickeners, coloring, flavor enhancers, etc.) [14–16]. Sorbets are frozen and stored at −18 °C. This method makes it possible to obtain high-quality sorbets whose shelf life is 10 months [14, 17, 18]. However, when stored and defrosted, they lose a considerable amount of BAS (from 20 to 50 %) Thus, the shortcoming of sorbets is the low content of vitamins and other BAS, as well as the presence of synthetic components that adversely affect the human body. In this regard, the requirements to ice cream have changed in the international practice over the past 10 years, both from consumers and companies involved in the production and sale of ice cream. The main requirement to ice cream is the maximum naturalness, as well as the presence of components and substances that promote good health [19, 20].

It is known that one of the promising directions in processing fruits, berries, vegetables, and other products, is the cryogenic treatment of raw materials that employs the cryogenic "shock" freezing and cryogenic shredding. This technique provides for the highest degree of retaining vitamins and other BAS [8]. It was established that the greater the freezing speed of plant-based foods, the better the vitamins and other BAS are preserved [3, 21, 22]. In this case, a smaller loss of cellular juice at defrosting is also observed [23–25]. The texture of frozen food is preserved as well [27, 28]. There is a search for such technological methods that would make it possible to not only retain vitamins and other components of plant raw materials, but to provide for a possibility to more efficiently disclose and utilize biological potential of raw materials [2, 3, 26]. At present, the cryogenic technique is not commonly used. There are no developed cryogenic technologies; there are no detailed studies into the biochemical, physical-chemical processes occurring when freezing fruits, berries, vegetables and while manufacturing sorbets without the use of food additives, synthetic colorants, and flavor enhancers. An exception is the results of fundamental and applied research into the influence of cryogenic "shock" freezing and low-temperature finely dispersed shredding of fruit, berries, vegetables, received at the Kharkiv State University of Food and Trade (Ukraine) [2–4]. The scientific results, obtained by authors, as well as the devised technologies, were implemented at enterprises in Ukraine, Latvia, Russia [6, 8]. The developed cryogenic nanotechnologies include the frozen and cryogenically-shredded finely dispersed supplements made from fruits [2], from carotene- [3], chlorophyll-containing [4], spicy vegetables [7, 8] and Jerusalem artichoke [6]. Cryogenic technologies have made it possible to not only preserve vitamins and other BAS, but to discover their hidden, associated with biopolymers, forms (by 2...2.5 times larger than that in the original fresh plant raw materials) [2, 3, 8]. The mechanisms were elucidated that occur to low-molecular biologically active substances (which are in the nano-dimensional form) in frozen foods [4, 6, 11]. It was shown that the cryogenic shredding of frozen fruits and vegetables results in a more intensive extraction of hidden forms of BAS from raw materials (by 2.5...4.2 times larger than that in fresh original raw materials). The mechanism of such a cryogenic treatment is associated with the mechanocracking (destruction) of nano-complexes " BAS – biopolymer" and the removal of low-molecular BAS from the state, bound with biopolymers, into the free state [2, 3, 4]. The inactive hidden forms of pectin substances, proteins, were also identified, which, in fruit, vegetables, mushrooms, and other raw materials, are in the complex nano-complexes and nano-associates with other biopolymers of plant cells (specifically, cellulose, protein, etc.) [2, 9, 11].

There are data from the German firm VERU on that its specialists, in the manufacture of sorbets, employed the cryogenic "shock" freezing using liquid nitrogen, which resulted in obtaining sorbets of high quality. In addition, the manufacture of sorbets did not involve any food additives (flavor enhancers, coloring, structure-forming agents, thickeners, stabilizers). The sorbets, devised without synthetic additives, are recommended as a healthy diet for VIP consumers and were priced higher than traditional products [20].

Thus, it appears appropriate to apply the cryotechnology when making health-improving sorbets from natural raw materials – fruits and vegetables without food additives.

3. The aim and objectives of the study

The aim of this work is to substantiate scientifically the activation and extraction of biologically active substances and a structure-forming agent – the pectin of fruits – from inactive form when developing nanotechnologies for wellness products "NatureSuperFood" – a fruit and vegetable ice cream – without food additives. This is achieved through the application of cryogenic treatment during freezing and finely dispersed shredding.

To accomplish the aim, the following tasks have been set:

– to substantiate scientifically and confirm experimentally, when obtaining fruit and vegetable sorbets, conditions for the activation and extraction of BAS and pectin substances of fruits and vegetables from the bound inactive form and for the transformation into a soluble form using cryogenic treatment and cryomechanolysis;

– to develop nanotechnologies for the wellness products “NatureSuperFood” – fruit and vegetable ice cream-sorbets, which are based on using the cryogenic “shock” freezing and finely dispersed shredding as an innovative technique for the structure formation of sorbets;

– to develop formulations, to explore the quality and content of BAS of 3 kinds of fruit and vegetable ice cream from chlorophyll-containing, carotene-containing and anthocyanin-containing fruits, berries, vegetables, to compare them with analogues;

– to investigate the structural and mechanical properties of the new kinds of sorbets from chlorophyll-containing, carotene-containing, and anthocyanin-containing fruits in terms of melting rate, density, in comparison with analogs, and to examine, by using infrared spectroscopy, the stabilization of the structure.

4. Materials and research methods applied in the development of nanotechnologies for wellness products

4. 1. Materials and equipment used during experimental research

We conducted our research at the Kharkiv State University of Food and Trade (KHSUFT, Ukraine) at the Scientific Research Laboratory “Innovative Cryo- and Nanotechnologies of Plant Supplements and Wellness products” at the Department of Technologies for Processing Fruits, Vegetables, and Milk. The present work involved the application, for the cryogenic freezing, of modern cryogenic original equipment, provided by the KHSUFT Department, which is the programmable cryogenic “shock” freezer that exploited liquid nitrogen as a refrigerant and inert medium. In this case, the temperature in the freezing chamber ranged from −60 °C to −100 °C. Fruits, berries, vegetables were frozen at various high rates to achieve different temperatures in a product. We used the low-temperature shredder “SIRMAN (Italy), “Robot Coupe” (France) for the finely dispersed shredding.

The study was based on fresh fruit and vegetable raw materials: apples, blackcurrant, cherries, apricots, sea buckthorn, pumpkin, spinach, olives, and lemons.

4. 2. Procedures to determine indicators for the examined samples

We determined quality of fresh fruits, berries, vegetables based on the content of basic BAS and prebiotic substances. Control was based on the content of BAS: L-ascorbic acid, low-molecular phenolic compounds, tannins, β-carotene, chlorophyll, anthocyanins. In addition, we identified such prebiotic substances as pectin (specifically, general pectin substances, soluble pectin), cellulose, protein.

The materials and research methods, as well as procedures for determining the indicators for the examined samples, are described in detail in papers [29, 30].

5. Results of research into the influence of cryogenic treatment on BAS and pectin of fruits in the development of nanotechnologies for sorbets

When designing a new technique and the nanotechnologies for the wellness products “NatureSuperFood” – fruit and vegetable ice cream – sorbets, we selected the following fruits, berries, vegetables: apples, black currants, cherries, apricots, buckthorn, pumpkin, spinach, olives, lemons with zest. The latter are known for their medicinal and curative properties. A substantiation of such properties could be the fact that the fruits, berries, and vegetables used as raw materials in developing the sorbets contain unique complexes of BAS.

The specified complexes include, in addition to L-ascorbic acid, mineral and prebiotic substances (pectin, cellulose, protein), a significant amount of phytocomponents. Thus, the mass fraction of phenolic compounds in the experimental sample ranged from 0.3 to 0.6 %, polyphenols – from 0.3 to 0.7 % (Table 1). In addition, the examined kinds of fruit and vegetable raw materials contain a significant amount of natural BAS – coloring substances: carotenoids – 9.5...11.5 mg per 100 g (carotene-containing vegetables and berries), chlorophylls *a* and *b* – 350...810 mg per 100 g (chlorophyll-containing vegetables), and anthocyanins – 2.5...4 % (anthocyanin-containing berries) (Table 1). The complexes of BAS in fruits, berries, vegetables, used in this work for the manufacture of sorbets, have healing properties. Phytocomponents of fruit promote immunity of the human body, produce detoxicating, antioxidant, antitumor effect, contribute to longevity, etc.

The proposed technique for making wellness products, fruit and vegetable ice cream-sorbets, whose distinctive feature is the application of cryogenic “shock” freezing and finely dispersed shredding is an innovative method for structure formation and enrichment it with BAS. That makes it possible to obtain products “NatureSuperFood” with unique characteristics.

The new kinds of products are in the easily-digestible, nano-dimensional form, and are characterized by the high content of natural biologically-active substances (L-ascorbic acid, β-carotene, chlorophylls *a* and *b*, phenolic compounds, anthocyanins, aromatic substances, etc.). The new technique and nanotechnologies for making sorbets differ from traditional methods by the innovative cryogenic “shock” freezing and finely dispersed shredding, whose comprehensive effect leads to the activation and extraction of hidden BAS from raw materials into a free form. In addition, the new technique and technologies result in the transformation of a thickener and the structure-forming agent pectin from inactive form into active soluble form. The obtained new kinds of sorbets are made exclusively from natural ingredients (fruits, berries, vegetables) and their composition does not contain any types of food additives (stabilizers, thickeners, emulsifiers, synthetic colorants, etc.). This technique makes it possible to not only retain vitamins and other BAS from fresh fruit and raw materials, but also makes it possible to more efficiently extract the hidden inactive forms from raw materials (bound in the nano-complexes to biopolymers and mineral substances) into free, soluble, easily-digestible form. Thus, the mass fraction of BAS in sorbets is 2.5...3.5 times larger than that in fresh fruits, berries, vegetables (Table 1). In addition, the nanotechnologies of sorbets made it possible to more efficiently, by 3.0...5.0 times, extract those pectin substances that are in the inactive hidden form in raw materials, and to transform 70 % of pectin substances into soluble form (Table 1).

The developed wellness products “NatureSuperFood”, fruit and vegetable ice cream in the form of sorbets, differ from traditional products by that they contain, as raw materials, the mixes of fruit, berries, vegetables. In addition, they do not include any synthetic food additives and milk. As an innovative technique for structure formation and obtaining sorbets with the high content of BAS, the cryogenic treatment of raw materials is employed, specifically cryogenic "shock" freezing, using liquid and gaseous nitrogen, and finely dispersed shredding, which is accompanied by non-fermenting catalysis. That makes it possible to obtain from fruit, berries, vegetables products in the nano-dimensional form, ensures the high quality of texture in sorbets and contributes to gel formation in the received polydisperse system of a nano ice-cream. The application in the production of sorbets of fruit and vegetable blends-mixes makes it possible to obtain new kinds of ice-cream with the high content of biologically-active substances, improved structural and mechanical characteristics, original natural flavor and aroma and the absence of synthetic components in their composition. These include such components as the stabilizers of structure, structure-forming agents, colorants, and flavor enhancers).

We have developed fruit and vegetable ice cream of 3 kinds with a different color (green, yellow-orange, pink) from chlorophyll-containing, carotene-containing and anthocyan-containing fruits, berries, vegetables. These are such wellness products "NatureSuperFood", fruit and vegetable ice cream-sorbets, as a green product range under the title "Green pleasure", "Green power", "Green pro", an yellow-orange product range "Orange lime," "Carotene", "Caroton", and a pink product range called "Purple", " Cherry", "Berries". Natural colorants – BAS in the green product range is the chlorophyll of spinach and olives, in the yellow-orange – β-carotene and other carotenoids from apricot, sea buckthorn and pumplin, in the pink product range – anthocyanins of black currant and cherries.

Based on the results obtained in the course of experimental research, we have developed the nanotechnologies for fruit and vegetable ice cream-sorbets from fruit, berries, vegetables, which differ from the traditional kinds by employing a high freezing rate (from 1 to 20 °C/min). In this case, the temperature in a freezer is −60...100 °C, while the resulting temperature of freezing in a product must be below the generally accepted –18 °C. In addition, the nanotechnologies imply the application of finely dispersed shredding of frozen mixtures of fruits, berries, vegetables to particles whose size is ten times smaller than that in the traditional sorbets and frozen purees made from fruit and vegetable raw materials. The obtained frozen finely dispersed fruits and vegetables are frozen, packed, and sent for hardening and storing at refrigeration at a temperature of 18 °C. The new sorbets have original taste and aroma of the natural product. In addition, the sorbets differ from existing analogs by the record content of natural BAS (L-ascorbic acid, anthocyanins, phenolic compounds, tannins, β-carotene, chlorophyll), as well as by the content of prebiotic substances that are present in a product in the soluble easily-digestible nanoform (Tables 2–4). It is shown that all new kinds of ice-cream-sorbets, obtained from the fruit and vegetable carotene-, chlorophyll-, anthocyanin-containing raw materials contain a record amount of natural L-ascorbic acid.

The largest content of L-ascorbic acid is demonstrated by ice cream-sorbets from anthocyanin-containing berries (blackcurrant and cherry), whose mass fraction per 100 g of a product ranges from 143 to 202 mg. The mass fraction of L-ascorbic acid per 100 g of sorbets from chlorophyll-containing vegetables (spinach, olives) is from 136 to 145 mg, in sorbets from carotene-containing plant raw materials (apricot, sea buckthorn, pumpkin) is from 112 to 153 mg. Taking into consideration the fact that the daily need in ascorbic acid for an adult is from 70 to 100 mg, 100 g of each of the new kinds of fruit and vegetable ice cream-sorbets are capable of meeting from 1.5 to 2 daily needs of the human body in L-ascorbic acid (Tables 2–4).

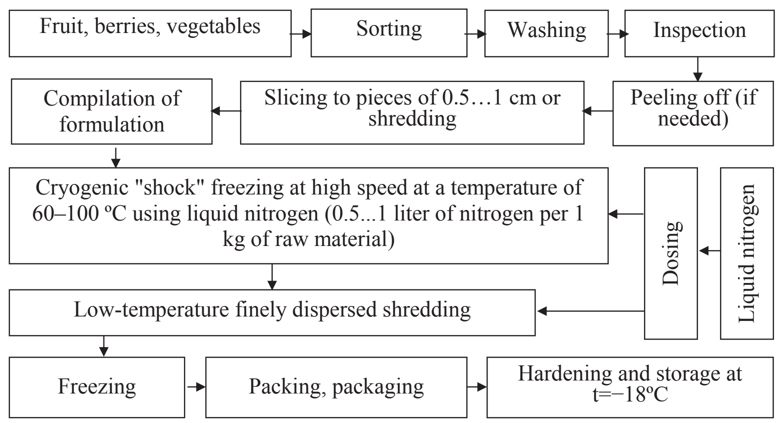


Fig. 1. Main technological diagram of production of the wellness products "NatureSuperFood", fruit and vegetable ice cream-sorbets, with a record content of BAS, obtained by using the cryogenic "shock" freezing and low-temperature finely dispersed shredding

100 g of new kinds of ice cream-sorbets, derived from chlorophyll-containing vegetables (spinach, olives) contain a significant amount of chlorophylls (from 200 to 248 mg per 100 g). The sorbets obtained using the carotene-containing fruit, berries, vegetables are distinguished by the record amount of β-carotene (from 20.4 mg to 25.8 mg per 100 g), which is 4–5 daily needs in β-carotene. The anthocyanin product range of sorbets derived using the berries of black currant and cherry are characterized by the high content of anthocyanins – the unsaturated BAS with a highly reactivity; their mass fraction ranges from 0.8 to 1.3 % (Tables 2–4). In addition, all new kinds of fruit and vegetable ice cream-sorbets contain a significant amount of phytocomponents, in particular, the mass fraction of low-molecular phenolic compounds (by chlorogenic acid) is from 0.55...0.78 % (in the carotenoid sorbets) to 0.9...1.0 % (in sorbets from anthocyanin-containing berries). All new kinds of natural ice cream-sorbets contain a significant amount of phenolic compounds (by rutine) – from 158 to 340 mg per 100 g, as well as tannins – from 425 to 712 mg per 100 g (Tables 2–4). The established record amount of BAS contained in the new kinds of fruit and vegetable ice cream-sorbets relates to the application of cryogenic treatment of raw materials while obtaining them. The cryogenic treatment of fruit and vegetable raw materials results in the extraction of hidden bound inactive forms of BAS, whose mass fraction, compared with fresh (original) raw materials, increases by 2...5 times, which is defined by conventional chemical methods.

It was established that the mass fraction of BAS in the new sorbets exceeds the amount of BAS in fresh fruits, berries and vegetables by 2.5...3.5 times, as well as the amount of BAS in the Ukrainian and foreign analogs (Tables 1–4).

Table 1

Influence of cryogenic "shock" freezing and mechanolysis on BAS and pectin when obtaining one-component nanosorbets from fruits, berries, vegetables (n=3, $P \geq 0.95$)

Product	Mass fraction, mg per 100 g						Mass fraction, %	
	L-ascorbic acid	phenolic compounds (by chlorogenic acid)	phenolic compounds (by rutine)	tannins	β-carotene	chlorophylls *a* and *b*	anthocyanins	soluble pectin
Fresh apple	55.0	580.1	160.3	380.2	0.1	0	0.2	1.5
Apple sorbet	135.1	980.2	390.1	720.4	0.2	0	0.5	7.2
Fresh black currant	280.5	720.5	175.2	602.1	4.8	0	4.0	1.6
Black current sorbet	840.0	1,330.0	280.1	1,000.1	13.8	0	8.0	7.4
Fresh cherry	68.1	670.1	142.1	420.1	0.2	0	2.5	1.4
Cherry sorbet	150.2	1,102.0	280.1	740.2	0.3	0	5.0	6.5
Fresh apricot	49.2	320.5	70.2	250.2	9.5	0	0	1.4
Apricot sorbet	140.1	560.4	120.6	480.4	32.5	0	0	7.2
Fresh sea buckthorn	95.2	570.2	95.1	420.0	11.5	0	0	1.2
Sea buckthorn sorbet	250.1	940.6	170.2	780.1	40.2	0	0	6.8
Fresh pumpkin	40.2	260.2	60.2	215.1	9.8	0	0	1.0
Pumpkin sorbet	108.1	480.6	105.2	401.2	41.2	0	0	4.5
Fresh spinach	60.2	320.6	105.0	380.5	6.8	810.1	0	0.7
Spinach sorbet	178.6	560.0	175.2	720.1	21.0	1,650.2	0	5.2
Frozen olives	38.5	280.1	50.4	250.1	3.5	350.1	0	0.5
Olive sorbet	75.2	460.2	75.6	400.1	7.5	700.2	0	3.8
Fresh lemon	80.2	101.1	75.0	300.4	0.2	0	0	1.8
Lemon and zest sorbet	200.1	180.2	135.1	560.2	0.4	0	0	7.8

Table 2

Content of BAS in the new kinds of fruit and vegetable ice cream-sorbets (pink product range) based on mixtures-mixes of apples with anthocyanin-containing berries of black currant and cherry*

Title of indicator, mg per 100 g	Name of fruit and vegetable ice cream-sorbets			
	«Purple»	«Berries»	«Cherry»	Analog
Anthocyanin coloring substances, %	0.8±0.1	1.1±0.1	1.3±0.1	0
L-ascorbic acid	202.0±3.6	169.0±2.1	143.5±1.9	5.0±0.2
β-carotene	1.82±0.05	0.91±0.03	0.24±0.1	0
Phenolic compounds (by chlorogenic acid)	926.0±13.3	926.8±15.1	982.5±17.8	30.2±0.9
Phenolic compounds (by rutine)	336.3±4.2	335.7±5.1	338.8±4.8	15.1±0.4
Tannins	732.0±9.8	693.1±8.4	719.0±9.2	25.2±0.7
Soluble pectin substances, %	7.1±0.1	6.5±0.1	6.8±0.1	0.1±0.01
Cellulose, %	2.1±0.01	2.4±0.01	2.2±0.01	1.5±0.1
Protein, %	2.3±0.1	2.8±0.1	1.9±0.1	2.0±0.1
Organic acids, %	2.8±0.1	2.5±0.1	2.7±0.1	2.5±0.1
Overall sugar, %	8.4±0.1	8.2±0.1	8.3±0.1	22.0±0.3
Dry substances, %	20.0±0.5	20.0±0.5	20.0±0.5	25.0±0.5

*Note: * – apples are used as the basic component, the formulation amount of anthocyanin-containing berries is from 10 to 15 %*

Table 3

Content of BAS in the new kinds of fruit and vegetable ice cream-sorbets (a green product range) based on mixtures-mixes from apples, lemons and chlorophyll-containing vegetables (spinach, olives)*

Title of indicator, mg per 100 g	Name of fruit and vegetable ice cream-sorbets			
	«Purple»	«Berries»	«Cherry»	Analog
Anthocyanin coloring substances, %	0.8±0.1	1.1±0.1	1.3±0.1	0
L-ascorbic acid	202.0±3.6	169.0±2.1	143.5±1.9	5.0±0.2
β-carotene	1.82±0.05	0.91±0.03	0.24±0.1	0
Phenolic compounds (by chlorogenic acid)	926.0±13.3	926.8±15.1	982.5±17.8	30.2±0.9
Phenolic compounds (by rutine)	336.3±4.2	335.7±5.1	338.8±4.8	15.1±0.4
Tannins	732.0±9.8	693.1±8.4	719.0±9.2	25.2±0.7
Soluble pectin substances, %	7.1±0.1	6.5±0.1	6.8±0.1	0.1±0.01
Cellulose, %	2.1±0.01	2.4±0.01	2.2±0.01	1.5±0.1
Protein, %	2.3±0.1	2.8±0.1	1.9±0.1	2.0±0.1
Organic acids, %	2.8±0.1	2.5±0.1	2.7±0.1	2.5±0.1
Overall sugar, %	8.4±0.1	8.2±0.1	8.3±0.1	22.0±0.3
Dry substances, %	20.0±0.5	20.0±0.5	20.0±0.5	25.0±0.5

*Note: * – apples are used as the basic component; their formulation amount in mixtures-mixes is up to 70 %*

Table 4

Content of BAS in the new kinds of fruit and vegetable ice cream-sorbets (a yellow-orange product range) based on mixtures-mixes from carotene-containing plant raw materials (apricot, sea buckthorn, pumpkin)* and apples

Title of indicator, mg per 100 g	Name of fruit and vegetable ice cream-sorbets				
	"Orange lime»	"Caro-tene»	"Caroton»	"Orange aprikot»	Analog
β-carotene	22.8±0.7	20.4±0.6	28.9±0.8	25.8±0.7	0
L-ascorbic acid	135.1±4.1	153.6±4.6	112.6±3.6	123.8±3.4	2.0±0.1
Phenolic compounds (by chlorogenic acid)	597.5±17.9	775.8±23.3	541.5±16.2	569.4±17.2	25.5±1.1
Phenolic compounds (by rutine)	169.2±5.1	276.2±8.2	158.4±5.4	163.8±5.1	18.4±0.7
Tannins	508.4±15.2	619.3±18.6	452.9±15.8	480.6±18.4	35.1±1.3
Soluble pectin substances, %	6.8±0.2	6.1±0.2	5.0±0.2	5.9±0.3	0.1±0.01
Cellulose, %	1.1±0.1	0.8±0.1	1.1±0.1	1.1±0.1	1.2±0.1
Protein, %	1.8±0.1	1.5±0.1	2.1±0.1	2.0±0.1	1.0±0.1
Organic acids, %	2.0±0.1	1.1±0.1	1.4±0.1	1.5±0.1	2.0±0.1
Overall sugar, %	7.8±0.5	6.1±0.3	6.8±0.1	6.8±0.1	16.2±0.6
Dry substances, %	20.0±0.5	20.0±0.5	20.0±0.5	20.0±0.5	23.3±0.7

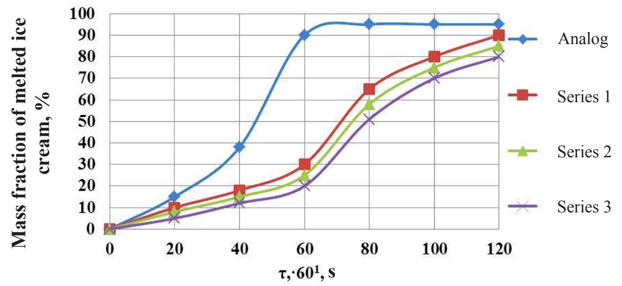
*Note: * – the formulation amount of mixtures-mixes from carotene-containing plant raw materials (apricot, sea buckthorn, pumpkin) ranges from 70 to 80 %*

Thus, we have developed the new types of sorbets that differ from the traditional ones by the absence of synthetic food additives during production, by using, as a raw material, the mixes from fruit, berries, vegetables, whose cryogenic treatment, as well as nanotechnologies, make it possible to obtain products with the record content of BAS. The new sorbets with the record content of natural BAS are positioned as the wellness products "NatureSuperFood" and are recommended for the immunoprophylaxis of population.

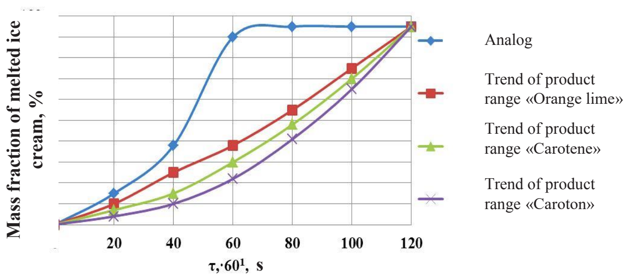
The task of this work also included studying the structural-mechanical properties of the obtained new kinds of ice cream-sorbets of different colors (green, yellow-orange, and pink). The structural-mechanical properties were investigated for such indicators of ice cream as the rate of melting and density. A comparison with analogs is shown in Fig. 2, 3.

It should be noted that the application of the new technique for producing ice cream-sorbets from fruit, berries, vegetables using cryogenic treatment and mechanolysis leads to a decrease in the melting rate of ice cream by 2–3 times in comparison with analog (Fig. 2).

The highest density is reached by mixtures of the new kinds of fruit and vegetable ice cream- sorbets in 9…10 minutes into the process of freezing, while in the production of ice-cream-analogue the highest density is achieved in 11…12 minutes (Fig. 3). It is shown that the new kinds of ice-cream-sorbets, whose production does not employ any artificial structure-forming agents, have the higher indicators for density in comparison with analogs, production of which implies the use of different kinds of food additives. Thus, density of ice cream sample-analog is 65…67 %, while the indicator for density in the new kinds of fruit and vegetable ice cream-sorbets is higher and ranges from 75 % to 80 % (Fig. 3). It should be noted that the high indicators for density and the process of structure-formation and stabilization of the structure of finely dispersed fruit and vegetable sorbets is due solely to the application of components of fruits (pectin, protein), using such technological methods as the cryogenic "shock" freezing and finely dispersed shredding.



a



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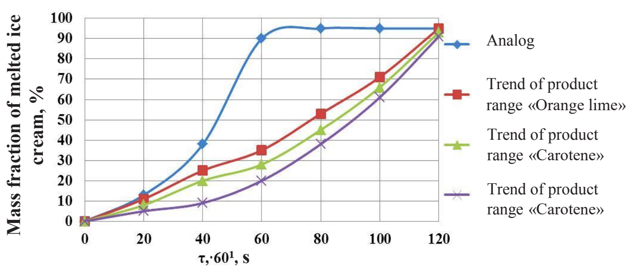

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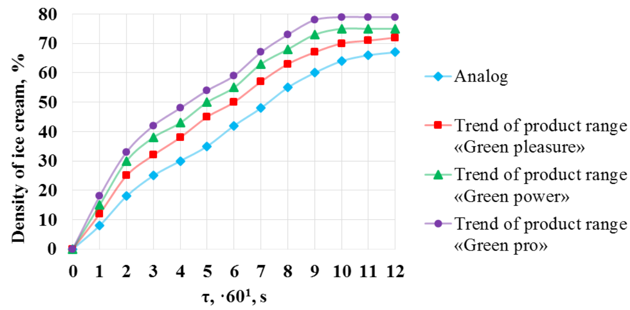
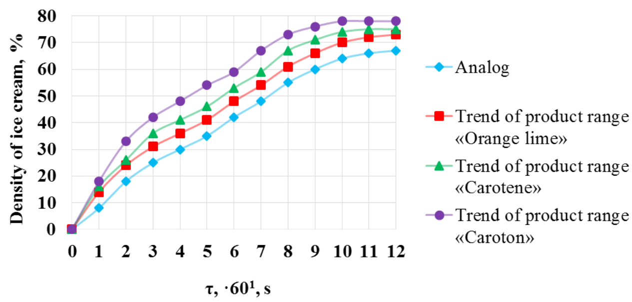
Fig. 2. Melting rate of the new kinds of fruit and vegetable ice cream-sorbets, obtained by using the cryogenic "shock" freezing and mechanolysis, compared with analog: *a* – sorbets from chlorophyll-containing vegetables; *b* – sorbets from carotene-containing plant raw materials; *c* – sorbets from anthocyanin-containing berries

The stabilizing effect of inactive (hidden) forms of pectin substances from fruits and vegetables, which in the course of cryogenic treatment and mechanolysis are transformed into active form (soluble pectin), on the formation of texture of the new kinds of ice cream-sorbets has been confirmed by the method of IR spectroscopy (Fig. 4).

An increase in the intensity of infrared spectra of the examined samples of sorbets in the frequency domain from 3,000 cm^{-1} to 3,600 cm^{-1}, is characteristic of valence fluctuations of the functional groups –OH, taking part in the formation of hydrogen bonds. Formation of hydrogen bonds occurs due to the extraction in large quantities and the transformation of pectin substances from fruits, berries, vegetables from the inactive into the active (high-methoxylated) form. The acquired data correlate with the texture of the new kinds of fruit and vegetable sorbets, which is denser, in comparison with analog, in terms of texture of the product, as well as their structural-mechanical properties (degree of density, melting rate).



a



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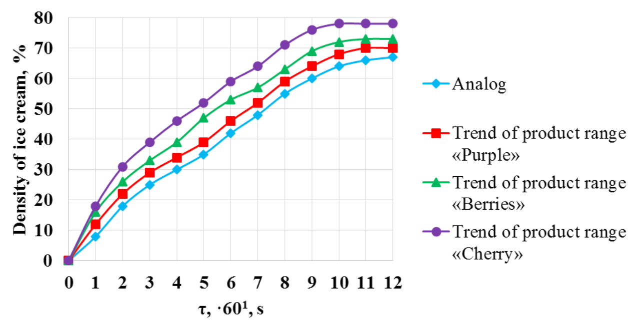

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Fig. 3. Density of the new kinds of fruit and vegetable ice cream-sorbets, obtained by using the cryogenic "shock" freezing and mechanolysis, compared with analog: *a* – sorbets from chlorophyll-containing vegetables; *b* – sorbets from carotene-containing plant raw materials; *c* – sorbets from anthocyanin-containing berries

An increase in the intensity of infrared spectra in the frequency domain is from 1,800 cm^{-1} to 3,000 cm^{-1}. That testifies to the intermolecular rearrangement and formation of complexes of associates and various complexes of compounds (organic acids, in particular, galacturonic acid, proteins, α-amino acids, sugars, alcohols, ketones, etc.). In addition, this process occurs at the expense of biopolymers (pectin, proteins), most of which are in sorbets in the nano-dimensional form, and which are capable of structure formation and gel formation. The specified increase in intensity indicates a stabilizing action of components in fruit and vegetable raw materials, which act as natural plant structure-forming agents when making fruit and vegetable sorbets using the processes of cryogenic treatment of raw materials and mechanolysis. A combined application of cryogenic "shock" freezing and non-fermenting catalysis (mechanolysis) during low-temperature treatment of raw materials makes it possible to obtain new kinds of fruit and vegetable sorbets without the additional use of artificial stabilizers of structure.

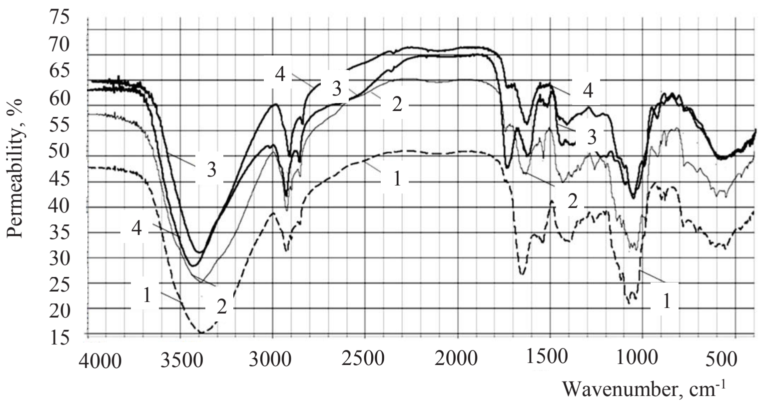

Fig. 4. Comparison of IR-spectra of the new kinds of fruit and vegetable ice cream-sorbets, obtained byusing the cryogenic "shock" freezing and mechanolysis, with analog, where 1 – analog, 2, 3, 4 – new kinds of ice cream-sorbets: 2 — "Green pleasure", 3 – "Green power", 4 — "Green pro"

The new kinds of fruit and vegetable ice cream-sorbets are stored for 12 months without loss of BAS, which is ensured by the complete inactivation of oxidizing enzymes in their production.

The new technique and nanotechnologies for making the wellness products "NatureSuperFood", fruit and vegetable ice cream-sorbets, were validated under industrial conditions at enterprises in the city of Kharkiv (NPP "KRIAS plus", TOV "FM Hladoprom", TOV SUIP "Plus, LTD").

6. Discussion of results of studying the nanotechnologies for making the wellness products "NatureSuperFood", fruit and vegetable ice cream-sorbets with the record content of BAS

The merits of this work are in the fact that we managed to obtain ice cream, specifically sorbets, which, by the content of such BAS as the phytocomponents carotenoids, chlorophylls, anthocyanins, vitamins, etc., outperform analogs by 2...3 times. A new technique and the nanotechnologies for manufacturing ice-cream from natural raw materials, fruits and vegetables with the record content of BAS, have been developed using the cryogenic treatment as innovation. We have discovered in sorbets the hidden forms of BAS and biopolymers (pectin, proteins) in the nano-dimensional form; they act as structure-forming agents, stabilizers of texture, as well as gel-forming agents.

The technological modes of natural sorbets production were tested at the bench semi-finished equipment. The research results obtained would make it possible to consider anew the process of creating a wide range of sorbets – the source of natural phytocomponents, which contribute to strengthening the immunity of the human body. The new sorbets are recommended as unique natural products for immunoprophylaxis of all strata of population.

The results reported in this study are of considerable practical value, both for Ukraine and different countries of the world, as the planet Earth faces a shortage of food products, especially those of natural origin, as well as dietary supplements, with a high content of BAS, while a significant part of the population is starving. However, despite the healing properties of BAS in plant raw materials (such as fruits, berries, vegetables, mushrooms, etc.), the biological potential (vitamins and various components (phenolic compounds, polyphenols, carotenoids, chlorophylls, pectin substances and other prebiotic substances, etc.)), which Nature gave to fruit and vegetables, is used only in part. It is known that they are digested fresh by the human body by 30...40 % at most. Thus, there are significant losses of the biological potential of useful food raw materials – fruit, berries, vegetables, both during processing and consumption. At the same time, each year, losses on the planet Earth amount to hundreds of billion of tons.

The new direction in the deep processing of fruit and vegetables into sorbets, proposed in this study, would make it possible to maximaly utilize the biological potential inherent to them, which is similar to increasing the crop yield of fruit and vegetable raw materials by several times. The developed new wellness products "NatureSuperFood", sorbets, are intended for industrial production both at large enterprises and at small establishments, including restaurant business and trade, etc.

7. Conclusions

1. We have scientifically substantiated and experimentally proven a possibility of using the cryogenic "shock" freezing and cryomechanolysis at finely dispersed shredding of fruits and vegetables as the innovative method for structure formation and for obtaining fruit and vegetable ice cream-sorbets with the record content of BAS. A combined effect of these factors leads to the activation and extraction of hidden BAS from fruits and vegetables into a free form (by 2.5...3.5 times larger than that in fresh raw materials), as well as the transformation of pectin (70 %) from inactive form into active form.

2. We have developed a new technique, the nanotechnologies and technological schemes, for making the wellness products "NatureSuperFood", fruit and vegetable ice cream-sorbets, using the cryogenic treatment of raw materials, which make it possible to obtain a product with unique characteristics. The technological modes to produce ice-cream-sorbets were tested at the bench semi-industrial equipment. A special feature of the technology for sorbets production is the use of natural ingredients only (fruits, berries, vegetables), as well as the absence of artificial food additives (stabilizers, thickeners, emulsifiers, synthetic colorants, etc.). The nanotechnologies make it possible to not only retain in sorbets the vitamins and other BAS from original raw materials, but also to provide for the extraction the hidden inactive bound forms of BAS from raw materials into the free nanoform. The new kinds of sorbets are in the nano-dimensional form and are distinguished by the high content of natural biologically-active substances from fruits and vegetables (β-carotene, chlorophylls, phenolic compounds, anthocyanins, aromatic substances, etc.). In addition, the new kinds of sorbets differ in high content of soluble pectin substances that act natural thickeners and structure-forming agents. That makes it possible to eliminate the need to use modified and synthetic additives in food.

3. We have developed the formulations, and studied the quality and content of BAS in 3 kinds of fruit and vegetable ice cream from chlorophyll-containing, carotene-containing and anthocyanin-containing fruits, berries, vegetables; a comparison with analogs was conducted. Natural vegetable raw materials (fruits, berries, vegetables) that are in the manufacture of the new kinds of ice cream, specifically sorbets, act as “five in one”: a source of BAS, a thickener, a structure-forming agent, a colorant, and a flavor enhancer. It is shown that the new kinds of fruit and vegetable ice cream-sorbets have original taste and aroma of the natural product and are different from existing analogs by the record content of L-ascorbic acid, β-carotene, chlorophylls *a* and *b*, phenolic compounds, tanning substances, which are in the nanoform in a product. 100 g of the new kinds of ice cream, sorbets, contain from 1.5 to 2 daily dosage of the specified substances.

4. It was established that structural-mechanical properties of the new kinds of ice cream, sorbets, derived from a mixture of fruits, berries, vegetables, by using cryogenic treatment, outperform their analogs for such indicators as the rate of melting and density. It was shown that even though the new kinds of ice-cream-sorbets are made without the use of food additives – structure-forming agents and stabilizers of structure, their melting rate in comparison with analog is 2 times slower, and the degree of density is higher by 20...25 %. The process of structure-formation and stabilization of the structure of fruit and vegetable ice cream-sorbets occurs through the use of components of fruit and vegetable raw materials – pectin, cellulose, protein, which are transformed during cryogenic treatment of raw materials from inactive form into the active nanoform. The stabilizing effect of the latter has been confirmed by the method of IR spectroscopy.

References

1. Strategy on Diet, Physical Activity and Health: report of a Joint WHO/FAO/UNU. Expert Consultation. Geneva: World Healt Organization, 2010.
2. Influence of the processes of steam-thermal cryogenic treatment and mechanolysis on biopolymers and biologically active substances in the course of obtaining health promoting nanoproducts / Pavlyuk R., Pogarska V., Kakadii I., Pogarskiy A., Stukonozhenko T. // Eastern-European Journal of Enterprise Technologies. 2017. Vol. 6, Issue 11 (90). P. 41–47. doi: https://doi.org/10.15587/1729-4061.2017.117654
3. Exploring the processes of cryomechanodestruction and mechanochemistry when devising nano-technologies for the frozen carotenoid plant supplements / Pavlyuk R., Pogarska V., Timofeyeva N., Bilenko L., Stukonozhenko T. // Eastern-European Journal of Enterprise Technologies. 2016. Vol. 6, Issue 11 (84). P. 39–46. doi: https://doi.org/10.15587/1729-4061.2016.86968
4. Developing the cryogenic freezing technology of chlorophyll-containing vegetables / Pavlyuk R., Poharskyi O. S., Kaplun O. A., Losieva S. M. // Eastern-European Journal of Enterprise Technologies. 2015. Vol. 6, Issue 10 (78). P. 42–47. doi: https://doi.org/10.15587/1729-4061.2015.56111
5. Nauchnye osnovy zdorovogo pitaniya / Tutel’yan V. A. et. al. Moscow: Izdatel’skiy dom «Panorama», 2010. 816 p.
6. The effect of cryomechanodestruction on activation of heteropolysaccaride-protein nanocomplexes when developing nanotechnologies of plant supplements / Pavlyuk R., Pogarska V., Balabai K., Pavlyuk V., Kotuyk T. // Eastern-European Journal of Enterprise Technologies. 2016. Vol. 4, Issue 11 (82). P. 20–28. doi: https://doi.org/10.15587/1729-4061.2016.76107
7. Technology of healthy processed cheese products without melting salts with the use of freezing and non-fermentative catalysis / Pavlyuk R., Pogarska V., Yurieva O., Skripka L., Abramova T. // Eastern-European Journal of Enterprise Technologies. 2016. Vol. 5, Issue 11 (83). P. 51–61. doi: https://doi.org/10.15587/1729-4061.2016.81415
8. Studying the complex of biologically active substances in spicy vegetables and designing the nanotechnologies for cryosupplements and nanoproducts with health benefits / Pavlyuk R., Pogarskaya V., Cherevko O., Pavliuk V., Radchenko L., Dudnyk E. et. al. // Eastern-European Journal of Enterprise Technologies. 2018. Vol. 4, Issue 11. P. 6–14. doi: https://doi.org/10.15587/1729-4061.2018.133819
9. Stringer M., Dennis K. Ohlazhdennye i zamorozhennye produkty. Sankt-Peterburg: Professiya, 2004. 492 p.
10. Sinha N. K., H’yu I. G. Nastol’naya kniga po pererabotke plodoovoshchnoy produkcii. Sankt-Peterburg: Professiya, 2014. 912 p.
11. Development of nanotechnology of fine frozen champignon puree (agaricus bisporus) / Pavliuk R. Yu., Poharska V. V., Matsipura T. S., Maksymova N. P. // Eastern-European Journal of Enterprise Technologies. 2015. Vol. 6, Issue 10 (77). P. 24–28. doi: https://doi.org/10.15587/1729-4061.2015.56145
12. Marshall R. T., Goff H. D., Hartel R. W. Ice Cream. Springer, 2012. 371 p. doi: https://doi.org/10.1007/978-1-4615-0163-3
13. Clarke C. The Science of the Ice Cream. Royal Society of Chemistry, 2015. 234 p.
14. Fructan stability in strawberry sorbets in dependence on their source and the period of storage / Topolska K., Filipiak-Florkiewicz A., Florkiewicz A., Cieslik E. // European Food Research and Technology. 2016. Vol. 243, Issue 4. P. 701–709. doi: https://doi.org/10.1007/s00217-016-2783-0
15. Yangilar F. Effects of Green Banana Flour on Ice Cream’s Physical, Chemical and Sensory Properties // Food Technology and Biotechnology. 2015. Vol. 53, Issue 3. P. 315–323. doi: https://doi.org/10.17113/ftb.53.03.15.3851

16. Cassava derivatives in ice cream formulations: effects on physicochemical, physical and sensory properties / De Souza Fernandes D., Leonel M., Del Bem M. S., Mischan M. M., Garcia É. L., dos Santos T. P. R. // Journal of Food Science and Technology. 2017. Vol. 54, Issue 6. P. 1357–1367. doi: https://doi.org/10.1007/s13197-017-2533-8
17. The production of ice cream using stevia as a sweetener / Ozdemir C., Arslaner A., Ozdemir S., Allahyari M. // Journal of Food Science and Technology. 2015. Vol. 52, Issue 11. P. 7545–7548. doi: https://doi.org/10.1007/s13197-015-1784-5
18. Goraya R. K., Bajwa U. Enhancing the functional properties and nutritional quality of ice cream with processed amla (Indian gooseberry) // Journal of Food Science and Technology. 2015. Vol. 52, Issue 12. P. 7861–7871. doi: https://doi.org/10.1007/s13197-015-1877-1
19. Innovation in ice cream manufacturing. Shaking a traditional dairy category. URL: http://www.allfoodexperts.com/innovation-in-ice-cream-manufacturing-shaking-a-traditional-dairy-category/
20. Askew K. VERU's 'shock-freezing' tech creates ice cream with 'more taste, less calories'. URL: https://www.foodnavigator.com/Article/2017/10/06/VERU-s-shock-freezing-tech-creates-ice-cream-with-more-taste-less-calories
21. Tuan Pham Q. Freezing time formulas for foods with low moisture content, low freezing point and for cryogenic freezing // Journal of Food Engineering. 2014. Vol. 127. P. 85–92. doi: https://doi.org/10.1016/j.jfoodeng.2013.12.007
22. Landmarks in the historical development of twenty first century food processing technologies / Misra N. N., Koubaa M., Roohinejad S., Juliano P., Alpas H., Inácio R. S. et. al. // Food Research International. 2017. Vol. 97. P. 318–339. doi: https://doi.org/10.1016/j.foodres.2017.05.001
23. The Effect of Storage Temperature on the Ascorbic Acid Content and Color of Frozen Broad Beans and Cauliflowers and Consumption of electrical Energy during Storage (Turkish with English Abstract) // Gida/The Journal of Food. 2015. Vol. 11, Issue 5.
24. Min K., Chen K., Arora R. Effect of short-term versus prolonged freezing on freeze-thaw injury and post-thaw recovery in spinach: Importance in laboratory freeze-thaw protocols // Environmental and Experimental Botany. 2014. Vol. 106. P. 124–131. doi: https://doi.org/10.1016/j.envexpbot.2014.01.009
25. James S. J., James C. Chilling and Freezing // Food Safety Management. 2014. P. 481–510. doi: https://doi.org/10.1016/b978-0-12-381504-0.00020-2
26. Evans J. Emerging Refrigeration and Freezing Technologies for Food Preservation // Innovation and Future Trends in Food Manufacturing and Supply Chain Technologies. 2016. P. 175–201. doi: https://doi.org/10.1016/b978-1-78242-447-5.00007-1
27. Effects of different freezing methods on the quality and microstructure of lotus (Nelumbo nucifera) root / Tu J., Zhang M., Xu B., Liu H. // International Journal of Refrigeration. 2015. Vol. 52. P. 59–65. doi: https://doi.org/10.1016/j.ijrefrig.2014.12.015
28. Tolstorebrov I., Eikevik T. M., Bantle M. Effect of low and ultra-low temperature applications during freezing and frozen storage on quality parameters for fish // International Journal of Refrigeration. 2016. Vol. 63. P. 37–47. doi: https://doi.org/10.1016/j.ijrefrig.2015.11.003
29. The study of bas complex in chlorophyllcontaining vegetables and development of healthimproving nanoproducts by a deep processing method / Pavlyuk R., Pogarska V., Mikhaylov V., Bessarab O., Radchenko L., Pogarskiy A. et. al. // Eastern-European Journal of Enterprise Technologies. 2018. Vol. 2, Issue 11 (92). P. 48–56. doi: https://doi.org/10.15587/1729-4061.2018.127158
30. Development of a new method of storage and maximum separation of chlorophils from chlorophylcontaining vegetables at reception of healthfull nanoproducts / Pavlyuk R., Pogarska V., Mikhaylov V., Bessarab O., Radchenko L., Pogarskiy A. et. al. // EUREKA: Life Sciences. 2018. Issue 2. P. 47–54. doi: https://doi.org/10.21303/2504-5695.2018.00616