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DEVELOPMENT OF NANOTECHNOLOGIES FOR CURD DESSERTS AND FRUIT AND VEGETABLE CRYO-ADDITIVES FOR THEIR PREPARATION AS BAS ENRICHERS, STRUCTURE-FORMING AGENTS, AND COLORANTS

Розроблено новий спосіб та нанотехнологію сиркових десертів для здорового харчування, які включають як інновацію механічну обробку сирного зерна, що супроводжується процесами механоактивації та неферментативного каталізу казеїн-кальцій-фосфатних комплексів в нанорозмірну форму. Розроблено нанотехнологію кріодобавок із плодів та овочів, які використані в сиркових десертах як збагачувачі біологічно активними речовинами (БАР), натуральні структуроутворювачі та барвники. Застосування кріодобавок дає можливість виключити необхідність використання харчових домішок та синтетичних добавок Сиркові десерти знаходяться в нанорозмірній формі та відрізняються високим вмістом натуральних БАР плодів та овочів (β-каротину, фенольних сполук, дубильних речовин, хлорофілів, L-аскорбінової кислоти), розчинних пектинових речовин.

Як основу сиркових десертів використовували знежирений кисломолочний сир. Як сировину для плодоовочевих кріодобавок використовували каротиновмісні плоди (гарбуз, абрикоси, обліпиха), цитрусові (лимон з цедрою), топінамбур, шпинат, яблука.

Гомогенізацію сиру розглянуто як технологічний прийом, що призводить до отримання гомогенної структури та до процесів механоактивації і механолізу – руйнування молекул білку до окремих складових. При цьому відбувається збільшення масової частки вільних α-амінокислот та простих пептидів, розмір яких становить від 0,3 до 1,5 нм. Показано, що 40…45 % зв'язаних α-амінокислот трансформуються у вільну легкозасвоювану форму за рахунок механокрекінгу білку та його компонентів з мінеральними речовинами.

Розроблені плодоовочеві кріопасти є джерелом унікального комплексу натуральних БАР: фенольних сполук (1…2,1 %), каротиноїдів (32,6…45,6 мг в 100 г), L-аскорбінової кислоти (102…260 мг в 100 г), хлорофілів (800…1680 мг в 100 г).

У порівнянні з вихідною сировиною плодоовочеві кріопасти відрізняються високим вмістом розчинних пектинових речовин та за вмістом БАР перевищують якість свіжої сировини в 2,5…3,5 рази за рахунок вилучення при отриманні кріопаст прихованих неактивних форм у вільну форму.

Розроблені сиркові десерти за вмістом БАР перевищують відомі аналоги

Ключові слова: нанотехнологія, сиркові десерти, плодоовочева сировина, механоліз, механокрекінг, гомогенізація, кріообробка, α-амінокислота, БАР

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1. Introduction

Food requirements changed both for consumers and for companies involved in their production and sales in international practice nowadays [1–3].

The main requirement for food is maximum naturalness, presence of ingredients and substances, which improve health, as well as absence of traditional food additives and synthetic components [4, 5].

High technologies with innovations, which make it possible to save the highest content of biologically active substances of fresh raw materials, occupy a special place among food technologies used in production of healthy food products [6]. There is literally a «boom» in creation of nanotechnologies in various branches of industry, including food, today [7–9]. Development focuses on nanotechnologies for simulated and artificial food products using chemical synthetic components and methods in the food industry.

Currently, there is a wide range of simulated artificial food products, including meat, milk, cereals, some vegetables and others developed. Artificial products are almost the same as natural ones by their taste and organoleptic parameters [10, 11]. There is no data on development of nanotechnologies for production of products of natural raw materials, both plant and animal, avaliable in international practice [4, 5].

The study is expedient, because it relates to the solution of the global problem of reducing immunity in the population [1–3] caused by a deficit (about 50 %) of biologically active substances and protein in diets. There are also problems of hunger (every eighth inhabitant of the Earth is starving) and general deterioration of the ecological situation in the world. It is possible to increase immunity by using of products with a high BAS content (vitamins, β-carotene, chlorophyll, biophlavonoids, polyphenols, protein, pectin, prebiotics, etc.) [1, 2, 6]. The main sources of BAS are fruits, berries, vegetables, medicinal and spicy-aromatic vegetable raw materials. The sources of protein are milk and dairy products. In this regard, people use health-improving products, especially fruits, berries, vegetables and milk, to improve the immune system in the leading countries of the world. Scientists from the leading countries of the world, in particular, from Japan, the USA, Germany, England, the Netherlands, and others, develop technologies for such products. This is one of the priority and relevant scientific areas in the food industry, which is developing rapidly in the world [2, 3, 8].

We know that products made of fruits, vegetables and milk, especially sour milk, are natural products, which contribute to increased immunity and health and inhibit the aging process [1, 2, 12].

Therefore, the study on the development of a «new generation» of functional products for improvement of immunity, such as combined milk and plant products enriched with natural fruit and vegetable biologically active additives, is expedient. The mentioned products are products of the future in the field of healthy nutrition [2, 3, 10].

2. Literature review and problem statement

Dairy and sour milk products occupy a special place among food products. First of all, they are the source of valuable proteins, essential amino acids, which are a building material of cells and tissues in a human body and a source of energy [1–3]. Proteins are main components of any diet. We cannot eliminate or replace them with other ingredients, such as fats or carbohydrates. The essential amino acids, such as lysine, tryptophan, methionine, threonine and valine are the most important and scarce in a daily diet, according to nutritionists. Their sources are milk and dairy products [6, 12]. The latter reduce accumulation of rhodionuclides of cesium and strontium and increase resistance to ionizing radiation. They increase resistance to effects of other adverse factors. They improve blood parameters and prevent formation of tumors in a human body. The population consumes milk and dairy products below the norms of civilized countries by 40 %, according to international statistics [3, 6, 10].

However, the disadvantage of the chemical composition of dairy products is a low content of biologically active substances, in particular, of vitamin C, β-carotene, α-tocopherol and chlorophyll. In addition, low levels of natural phytocomponents, i. e. antioxidants, geroprotectors, such as low molecular weight phenolic compounds (catechins, flavonol glycosides, polyphenols, etc.) and terpenoids [1–3]. The sources of the mentioned substances are plant raw materials (fruits, berries, vegetables, medicinal and spicy-aromatic plants) and products of beekeeping. The idea of creation of a combined dairy and sour milk products with herbal supplements that have high BAS content for immunization and health promotion arose originally in Japan after the tragedy in Hiroshima and Nagasaki [1–3]. Scientists in Western Europe, America and other countries pick it up then [6, 12]. Today, the number one nutrition problem in the world is creation of combined milk-and-plant products, especially sour milk products. We know that the state of the immune system of a human body depends on the state of the intestine by 80 %, and we know the role of lactic acid bacteria from sour milk products in the maintenance of the intestine in a healthy state [1, 6].

Sour milk products combined with herbal additives (bioyoghurts, biokefirs, bio curdled milk, curd desserts) are the main products for immunological prophylaxis and health promotion of the population [1, 6, 12]. The composition of such fermented products includes useful lactic acid bacteria in active state and natural vitamins and antioxidants of plant materials. The most popular among these products are combined fruit and vegetable curd desserts with curd in their basis. Their main disadvantages are a low content of BAS and presence of various types of food additives [6, 13, 14].

There are objective difficulties in production of combined fruit and vegetable desserts based on curd. The reasons of the difficulties are:

– using of various types of artificial food additives (thickeners, structure formers, stabilizers, colorants, aromizers, transgenic fats, etc.), which are harmful to a human body [14–16];

– using of natural fruit and vegetable fillers (jams, jam, bases, confitures, jam, preserves, frozen fruits and vegetables (at –18 °C), etc.) of low quality and with low BAS contents [14–18];

– deficit of high-quality natural fruit and vegetable fillers for enrichment of food products with natural BAS in the market [19–21];

– a short shelf life of curd desserts (36 hours at a temperature of +4...+6 °C and 14 days at a temperature of +1...+2 °C), etc. [6, 20].

It is possible to explane the listed difficulties, which arise in production of fruit and vegetable curd desserts, by a low living standard of the population and a need to use cheaper products of low-quality, artificial raw materials and food additives. The presence of the latter in the composition of products leads to a decrease in the defenses of a human body, allergies, various types of diseases and, as a consequence, a decrease in life expectancy.

The cause of difficulties, which arise in production of fruit and vegetable curd desserts aimed at improvement of health of the population, is also a lack of fundamentally new approaches, ideas and innovations for resolution of the mentioned problems in international practice. In this regard, it is important to expand the range of health-improving curd desserts with natural additives and fortifiers of fruits and vegetables. In addition, the search for and development of new innovative technological methods for production of fruit and vegetable additives with a high BAS content is relevant. The option for the solution to the mentioned disadvantages and difficulties in production of curd desserts for healthy nutrition can be using of natural fruit and vegetable raw materials in production. It is promising to use traditional types of fruit and vegetable raw materials known for their therapeutic and prophylactic properties. Such raw materials include: pumpkin, sea buckthorn, apricots, lemons with a rind, apples, spinach, Jerusalem artichokes, etc.

It is necessary to find and offer unique methods for processing of fruits and vegetables into additives, i. e. fillers for curd desserts, in order to solve the problem of obtaining of fruit and vegetable curd desserts, which improve health. Therefore, we consider the study on the development of technologies of fruit and vegetable additives, which should not only be carriers of BAS – fortifiers, but also to act as structure formers, gelling agents, colorants and aromatizers at the same time, as the promising study. This will give possibility to reduce or eliminate a need for artificial food additives in production of curd desserts. Authors of papers [7, 19, 20] proposed this approach axactly. There was a new method for production of fruit and vegetable fine-dispersed frozen additives (pastes) proposed with the use of cryogenic processing of raw materials as an innovation in creation of curd desserts for healthy nutrition. It included cryogenic «shock» freezing with the use of liquid and gaseous nitrogen and low-temperature grinding [7, 8, 22]. Researchers found that using of cryoprocessing leads to significantly less cellular juice loss and BAS loss during defrosting of fruits and vegetables for certain types of fruit and vegetable raw materials [23, 24]. In addition, a texture of frozen fruit and vegetable sorbets (cold desserts) and puree preserves better [25–28]. Reseracher established that the higher is the freezing rate of plant products, the better is preservation of vitamins and other BAS [29, 30].

The structure of products forms differently when using finely dispersed cryo-additives made of fruits and vegetables in production of curd desserts, than when using traditional food additives. Biochemical, enzymatic and oxidative processes occur differently. This fact requires additional research.

Scientisits used the recommendations of FAO/WHO for creation of health-improving combined desserts of curd and cryo-additives of fruits, vegetables and natural spice extracts. In addition, they used recommendations of well-known scientists in the field of vitaminization of food products and functional products [31–33]. We can make a conclusion on their therapeutic and preventive action in accordance with the above recommendations based on the analysis of a chemical composition of food products. We can relate the products, which contain 50...70 mg of ascorbic acid, 5...6 mg of β-carotene, 25...50 mg of P-active phenolic compounds per 100 grams, to the products, which improve human health.

3. The aim and objectives of the study

The objective of the study is to develop nanotechnology for curd desserts by processing of curd using mechanolysis of casein-calcium-phosphate complex into nanoform without the use of food additives. This will be possible due to the use of cryo-additives obtained based on nanotechnology of cryo-additives made of fruits and vegetables as natural BAS fortifiers, thickeners, colorants and aromatizers in production of curd desserts.

We set the following tasks to achieve the objective:

– application of non-fermentative catalysis and mechanolysis of casein-calcium-phosphate complex into nanosized form during homogenization and using of fruit and vegetable cryo-additives as BAS fortifiers, structure-formers, colorants and aromatizers for new types of curd desserts in production of curd desserts;

– investigation of an influence of the processes of mechanical destruction and mechanolysis on molecules of curd protein and transformation into some of its component α-amino acids at fine-grained grinding and obtaining of curd desserts in nanoscale form;

– investigation of the BAS complex (β-carotene, L-ascorbic acid, chlorophyll, phenolic compounds and polyphenols) and prebiotics in fruit and vegetable fresh raw material and in cryo-additives made of it and obtained by cryogenic nanotechnology as natural fortifiers for curd desserts;

– development of formulations and nanotechnology for curd desserts for healthy nutrition due to enrichment with cryo-additives made of fruits and vegetables in nanosized form and extracts of natural spices.

4. Materials and methods to study the development of nanotechnologies for health-improving curd desserts

4. 1. Materials and equipment used in the experimental study

We carried out the study at the «Innovative Cryotechnology of Plant Supplements and Health Products» research laboratory at the Department of Technology for Processing of Fruits, Vegetables, and Milk at the Kharkiv State University of Nutrition and Trade (KHSUNT, Ukraine). We used model experiments with finely dispersed grinding of low-fat curd made with the use of fine grinders (without the use of cold) «Robot Coupe» (France), «ThermoMix TM 5» (Germany).

We used modern cryogenic bench equipment at the department of KHSUNT for cryogenic «shock» freezing when obtaining fine grinded cryo-additives of fruits and vegetables. That was a software cryogenic «shock» freezer with liquid and gaseous nitrogen used as a refrigerant and inert medium. The temperature in the freezing chamber was from –60 °C to –100 °C. We froze fruits, berries, and vegetables to different end temperatures in a product at different high rates. We used «SIRMAN» (Italy) and «Robot Coupe» (France) grinders for fine-dispersed low-temperature grinding.

We used fresh fruit and vegetable raw materials, such as pumpkin, apricots, sea buckthorn, spinach, Jerusalem artichokes, lemons with rind and apples in the study.

We also used extracts of natural spices and medicinal plant materials, such as coriander, melissa, cardamom, chicory root and lemon rind.

4. 2. Methodologies for determining the parameters of investigated samples

We used the mass fraction of protein as a criterion for assessment of the quality of curd (raw) and fine-grained curd. We controlled the mass fraction of bound and free α-amino acids and the mass fraction of fat and dry matter at the same time.

We determined the quality by the content of basic BAS and prebiotics in fresh fruits, berries, and vegetables. We controlled contents of the following BAS: β-carotene, L-ascorbic acid, *a* and *b* chlorophylls, low molecular weight phenolic compounds; flavanol glycosides and tannins. In addition, we determined prebiotics (inulin, protein and pectin), a mass fraction of sugar, organic acids and others.

There are more detailed materials and methods of research, as well as methods for determination of parameters of the studied samples in works [6–8].

5. Results of development of nanotechnologies for health-improving curd desserts and fortifying fruit and vegetable cryo-additives for their production

The basis for production of health-improving curd desserts is curd with complete protein, which contains all essential amino acids (lysine, tryptophan, leucine, isoleucine, methionine, valine, threonine and phenylalanine) in a balanced amount. The disadvantage of curd is incomplete assimilation of protein by a human body, because curd undergoes a partial transition of casein-calcium-phosphate complex into an insoluble and slightly soluble form during heat treatment [6, 10]. In this regard, it is necessary to apply such technological techniques, which contribute to destruction of protein molecules to individual components, in production of curd desserts. We used fine-grained grinding and homogenization of curd mass as a sour milk base for this purpose. This gives possibility to transform a significant portion of protein into separate α-amino acids contained in the easily digestible form.

We used natural fine grinded cryo-pastes of carotene-containing raw materials (apricots, sea buckthorns, pumpkins), lemons with rind, spinach, apples and Jerusalem artichokes, which were developed by authors as an innovation in the development of combined fruit and vegetable curd desserts. We used cryo-pastes as natural BAS fortifiers, structure-formers, gel formers, natural colorants and aromatizers. We proposed and developed cryo-paste technologies with the use of cryogenic «shock» freezing and fine-grained grinding as innovations.

We considered homogenization as a technological method, which leads not only to obtaining of a homogeneous structure of a product, but also to the processes of mechanical degradation and destruction of protein molecules to its low molecular weight components (α-amino acids). In this case, enrichment of curd products with useful low molecular weight substances of curd occurs. The mass fraction of free amino acids, simple peptides, etc., which are easily digestible for a human, increases (Fig. 1).

We showed that significant disaggregation of nanocomplexes and mechanical degradation of proteins to free α-amino acids occurs at homogenization of curd. The number of the latter increases by 1.6...3.5 times when grinding curd (Fig. 1). We confirmed the revealed pattern by gas-liquid chromatography at Microtechna 339 amino acid analyzer (Czech Republic) in the study of the mass fraction of individual α-amino acids found both in the bonded form and in the free form. We revealed that significant mechanical degradation and mechanocracking (destruction) of biopolymers occur during homogenization of curd. This leads to a significant reduction in bound α-amino acids (by 25...45 %) and an increase in the mass fraction of free α-amino acids (by 1.6...3.5 times) and organic acids. This evidences violation of not only quaternary and tertiary structure, but also destruction of protein biopolymer chains to individual amino acids and release of organic acids, that is, destruction of secondary and primary structure of protein. Exceptions are free amino acids, namely, methionine and tyrosine. Their amount increases by 9 % and 40 %, respectively (Fig. 1).

The obtained patterns indicate that homogeneous curd has a more easily digestible form, since 28...45 % of α-amino acids of protein transform from the bound form to the free form. Therefore, its absorption by a human body is much better. The obtained curd mass has nanostructured nanosized form and differs significantly from its analogues. The size of α-amino acid molecules of the obtained curd mass is from 0.3 to 1.5 nm. Compared to the traditional curd mass, the size of the particles is several times smaller, and the digestibility of living organisms is several times higher. The obtained results make it possible to present the influence of homogenization on the quality of a product in a new way.

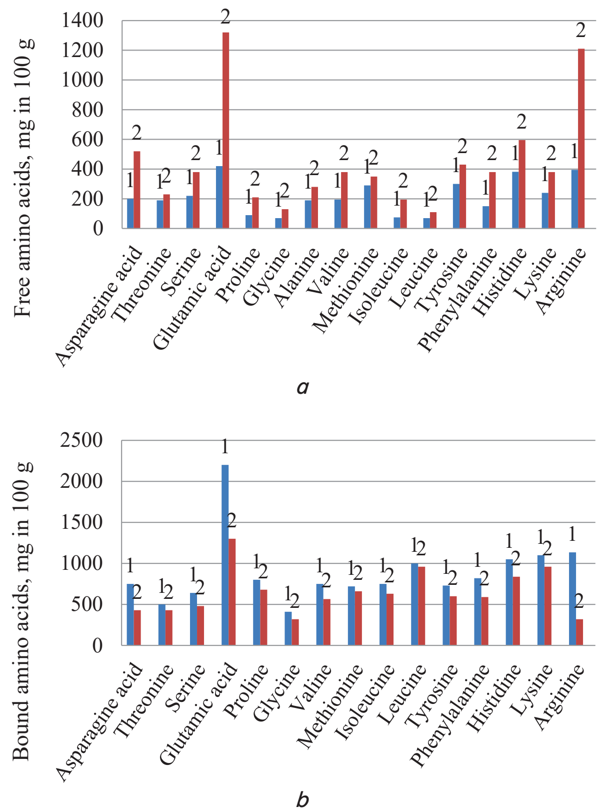


Fig. 1. Influence of mechanical degradation and mechanolysis processes on the content of bound (*a*) and free (*b*) amino acids of casein-calcium-phosphate complex of low-fat curd when obtaining homogenized curd mass in nanosized form: 1 – raw curd (curd grains); 2 – curd after fine grinding (homogenization)

In parallel, we carried out the research using the method of spectral analysis (Fig. 2). There are significant differences in the position of the wide characteristic absorption band in the frequencies of 2,900...3,600, 3,590...3,650 cm^{-1} traced in the infrared spectrum of curd grains (1) and grinded curd (2) after homogenization. The latter are characteristic for valence fluctuations of OH-groups of intermolecular and intermolecular hydrogen bonds.

There is a significant decrease in the intensity of the mentioned characteristic absorption bands in homogeneous curd. This indicates destruction of hydrogen bonds in protein nanocomplexes, as well as in nanocomplexes of various low molecular compounds with biopolymers and organic acids, lipids, minerals, alcohols, ketones and aromatic compounds. The obtained results are consistent with the data obtained by chemical methods of research. In addition, there is a decrease in bound moisture and an increase in free moisture. Thus, we observe a decrease in the absorption spectra in curd after homogenization in the frequency range of 3,300...3,500 cm^{-1}, which are characteristic for valence fluctuations of NH-groups involved in hydrogen bonds. This fact testifies also to destruction of quaternary, tertiary, secondary and primary structure of the biopolymer-casein, as well as destruction of hydrogen bonds and protein mechanolysis to free amino acids in homogenization.

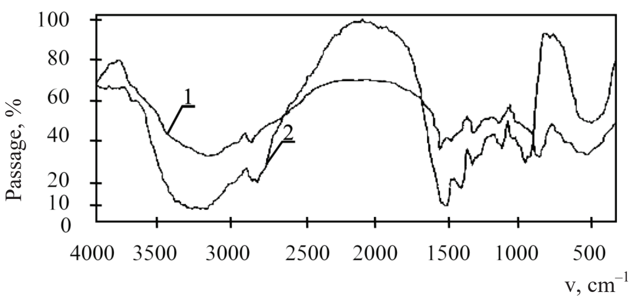


Fig. 2. Infrared spectra:
1 — curd grains; 2 — curd mass in the nanosized form obtained with the use of processes of mechanical destruction and mechanolysis at homogenization

We can observe peaks of these fluctuations in homogeneous curd in the frequency range of 3,000...3,200 cm^{-1}, which is characteristic for valence fluctuations of CH-groups in spectra of aromatic compounds. This fact indicates the release of aromatic compounds, that is products of lactic fermentation in preparation of homogenized curd. In addition, there is an increase in the relative fraction in the carboxylic acid region, which indicates an increase in the amount of free organic acids formed as a result of detachment of the latter from biopolymers, in the region of 2,500...3,000 cm^{-1} of the infrared spectrum of homogeneous curd. There is also a peak in the frequency range of 2,920...2,850 cm^{-1}. This corresponds to valence fluctuations of CH_3-groups and indicates the release of aromatic substances of terpenoid nature. There is also an intensive absorption in the area of 2,000...2,500 cm^{-1}. A wide band in this range indicates presence of valence fluctuations of NH_2- and NH_3- groups and an increase in the mass fraction of free α-amino acids. There is also an increase of free amino acids in the range of 1,030...1,360 cm^{-1}. The results of the study obtained by infrared spectroscopy confirm the assumption on disaggregation and destruction of casein-calcium-phosphate complexes of curd products, destruction of the protein structure with detachment of free amino acids, and a decrease in the molecular weight of protein (almost two-fold).

Thus, we detected the influence of mechanical destruction, mechanical activation and mechanolysis processes on fine-dispersed grinding on casein-calcium-phosphate complexes by means of chemical and spectroscopic methods of research. In addition, we established an increase in the content of free and reduced bound amino acids of protein, the content of free amino acids during obtaining of curd products in the nanosized form and disclosed the mechanism of this process.

The next task was to study the complex of biologically active phytocomponents and prebiotics in fruit and vegetable cryopastes proposed for use as innovations in production of curd desserts for healthy nutrition. This made it possible to exclude a need for traditional food additives in production of curd desserts.

We established that cryopastes of the studied fruits, berries and vegetables are the source of unique complexes of natural biologically active phytocomponents with a predominant number of low molecular weight and high molecular weight phenolic compounds. The mass fraction of phenolic compounds ranges from 1 % to 2.1 % in dependence on a type of raw material (Table 1).

Table 1

The content of biologically active phytocomponents and prebiotics in fresh fruits and vegetables and cryopastes made of them ($n=3$, $P\geq 0.95$)

Product	Mass fraction, mg per 100 g						Mass fraction of soluble pectin, %
	β-carotene	*L*-ascorbic acid	phenolic compounds (by chlorogenic acid)	phenolic compounds (by routine)	tannins (by tannin)	*a* and *b* chlorophylls	
Fresh apricots	10.1	54.9	315.5	71.0	261.2	0	1.5
cryopaste	32.6	145.1	556.3	122.4	490.3	0	7.4
Fresh sea-buckthorn	14.5	98.2	550.1	98.1	438.6	0	1.3
cryopaste	45.2	260.4	923.4	172.6	801.4	0	6.9
Fresh pumpkins	11.8	42.3	270.2	62.3	263.2	0	1.1
cryopaste	45.6	102.2	491.4	104.6	436.1	0	4.8
Fresh lemons	0.2	90.3	120.3	75.0	320.2	0	2.0
cryopaste	0.4	220.4	210.2	132.4	548.4	0	7.7
Fresh apples	0.1	70.8	538.2	164.2	365.6	0	1.5
cryopaste	0.2	180.0	980.3	385.1	746.2	0	7.4
Fresh Jerusalem artichokes	0.1	20.4	350.0	240.0	300.0	0	1.9
cryopaste	0.2	35.8	680.2	460.2	540.1	0	7.5
Fresh spinach	7.2	70.4	338.2	104.2	375.6	850.2	0.9
cryopaste	25.4	180.6	580.3	185.1	740.2	1,680.1	15.4

In cryopastes, we controlled forms of phenolic compounds, which have healing properties (in particular, routine, chlorogenic acid, tannins, quercetin) and for determination of which there were reliable chemical methods of research included in DSTU. We showed that the mass fraction of *L*-ascorbic acid in 100 g of fruit and vegetable cryopaste is from 102 mg in pumpkin cryopaste to 260 mg in cryopaste of sea buckthorn (Table 1). Carotenoid cryopastes of pumpkins, sea buckthorn and apricots differ by the highest levels of β-carotene. Its mass fraction ranges from 32.6 mg (in apricot cryopaste) to 45.6 mg (pumpkin cryopaste) per 100 g, respectively. We should note that the required daily portion in β-carotene is 5...6 mg per day for a human body according to the formula of rational and balanced nutrition. That is, carotenoid cryopastes contain from 6.5 to 9 daily needs of β-carotene. One tablespoon of carotenoid cryopaste (10 g) contains the required daily portion of β-carotene for a human body. 100 g of spinach cryopaste contains from 850 mg to 1,680 mg of a and b chlorophylls. In addition, fruit and vegetable cryopastes contain a significant amount of prebiotic substances (pectin, cellulose and protein). The mass fraction of soluble pectin ranges from 4.8 % to 7.7 %, cellulose – from 2.5 to 5.0 %, protein – from 1.5 to 4.5 %.

The established complexes of BAS contained in cryopastes of fruits and vegetables determine their comprehensive therapeutic and prophylactic effect on a human body. In particular, they strengthen vessels of heart and brain and the immune system. They act as detoxicants, antioxidants, antibacterial and prophylactic substances.

We found also hidden inactive forms of biologically active substances and biopolymers (in particular, pectin) in fresh fruits and vegetables (by 3...5 times). The study showed that the mass fraction of BAS (phenolic compounds, tannins, *L*-ascorbic acid, β-carotene, a and b chlorophylls) in fine-grinded fruit and vegetable cryopastes is 2.5...3.5 times more than in fresh fruit, berries and vegetables (Table 1). The obtained fruit and vegetable cryopastes differ from the existing additives by the highest BAS content. They are in nanoscale form, and they have no analogues. We propose to use new additives in production of curd desserts for healthy nutrition as BAS fortifiers, structure-formers, gel formers and natural colorants. The use of the obtained cryopastes in production of curd desserts makes possible to eliminate a need for the use of harmful traditional food additives.

We developed formulations and technologies for new curd desserts for healthy nutrition (orange-yellow line) based on nanostructured homogenized curd with fine dispersed cryo-additives made of carotene-containing berries and vegetables, citruses, and Jerusalem artichokes. «Carotella», «Oranzhon», «Caroton» and «Svitlyachok» desserts differ from their analogues by higher levels of β-carotene and other BAS. In addition, we developed curd desserts with natural chlorophyll-containing cryo-additives made of spinach, apples, and Jerusalem artichokes (green line). The obtained curd desserts relate to healthy food and have no analogues. Formulations of curd desserts contain 5 % of sugar and 5 % of butter.

Curd desserts get spoiled quickly. Thus, we can store them for 36 hours at a temperature of +4...+6 °C, and for 14 days at 0...+2 °C. We suggested using additives of natural spices and medicinal spice-aromatic raw materials in the form of hydro-alcoholic extracts to increase the shelf life of curd desserts. We used cardamom, coriander, melissa, root chicory and lemon rind as raw materials for production of extracts. These raw materials contain natural preservatives, detoxicants and substances with bactericidal and bacteriostatic action, due to the high content of aromatic substances and phenolic compounds and tannins.

We developed nanotechnology for fruit and vegetable curd desserts for healthy nutrition based on the study results. The new curd desserts differ from traditional ones, because their production includes mechanical processing of curd grains accompanied by processes of mechanical activation and non-enzymatic catalysis of casein-calcium-phosphate complex in the nanosized form (Fig. 3). As an innovation in production of curd desserts, we used fruit and vegetable cryo-additives in easily digestible form as BAS fortifiers, structure-forming agents, and colorants. This made it possible to exclude a need for food additives and synthetic additives. We added extracts of natural spices to curd desserts for BAS enrichment and prolongation of the shelf life. The addition of the mentioned extracts increased the shelf life twice. We determined and substantiated rational parameters of the technology and developed a technological scheme (Fig. 3). We selected equipment and developed normative documentation (projects of technical specifications, technical requirements). We performed tests under production conditions.

We studied the quality of new fruit and vegetable desserts on the content of BAS (Tables 2, 3). We revealed that fruit and vegetable desserts have the original taste and aroma of a natural product and a natural pronounced color. In addition, the new curd desserts differ from the existing desserts by higher levels of natural BAS (β-carotene, chlorophyll, phenolic compounds, L-ascorbic acid and tannins) and prebiotics in a soluble and easily digestible form.

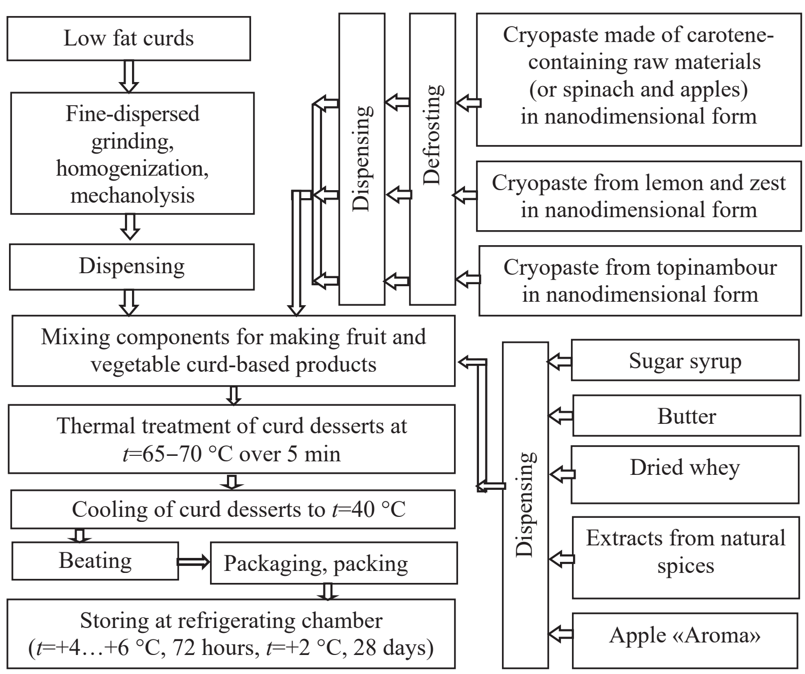


Fig. 3. Principal technological scheme of the nanotechnology for production of natural curd products for healthy nutrition enriched with cryo-additives of fruits and vegetables and extracts of spices and aromatic herbs

Table 2

Quality of the orange-yellow line of health-improving fruit and vegetable curd desserts*

Name of parameter, mg per 100 g	Name of a health-improving fruit and vegetable curd dessert				
	«Carotella»	«Orangon»	«Caroton»	«Svitlyachok»	Analogue
β-carotene	5.4±0.2	5.5±0.1	4.0±0.1	5.3±0.1	0
L-ascorbic acid	18.2±1.8	31.0±1.0	20.0±1.2	18.5±2.4	2.0±0.1
Phenolic compounds (by chlorogenic acid)	108.0±4.5	121.1±5.2	106.0±2.5	111.6±3.1	5.2±0.1
Phenolic compounds (by routine)	15.2±0.5	5.4±0.2	16.1±0.9	15.8±0.6	0
Tanning agents (by tannin)	105.0±2.0	18.2±0.2	125.3±1.7	109.8±1.9	25.4±1.2
Soluble pectin substances	0.9±2.1	1.0±0.1	0.9±0.1	1.0±0.1	0
Cellulose, %	0.5±0.01	0.6±0.01	0.4±0.01	0.6±0.01	0
Protein, %	18.0±0.2	18.4±0.5	18.2±0.7	18.3±0.5	6.4±0.2
Free amino acids, %	9.0±0.2	9.2±0.5	9.8±0.5	9.2±0.5	0
Bound amino acids, %	9.0±0.2	9.2±0.4	8.4±0.4	9.1±0.4	0
Total sugar, %	5.9±0.1	5.3±0.1	5.6±0.1	5.5±0.1	15.0±0.1
Fat, %	5.0±0.1	5.0±0.1	5.0±0.1	5.0±0.1	5.0±0.1
Dry matter, %	35.2±0.1	35.6±0.1	35.3±0.1	35.3±0.1	28.0±0.1

*Note: * – we used cryo-additives of pumpkins and lemons with rind («Carotella»); cryo-additives of sea buckthorn and lemons with rind («Orangon»); cryo-additives of apricots and lemons with rind («Caroton»); cryo-additives of pumpkins, lemons with rind and Jerusalem artichokes («Svitlyachok») as fortifying additives in production of new types of health-improving fruit and vegetable curd desserts of the orange-yellow line*

Table 3

Quality of the green line of health-improving fruit and vegetable cheese desserts*

Name of parameter, mg per 100g	Name of health-improving fruit and vegetable curd dessert			
	«Green power»	«Green pleasure»	«Green pro»	Analogue
A and b chlorophylls	31.0±1.1	28.8±0.9	32.1±1.2	0
L-ascorbic acid	250.0±7.5	212.4±7.1	242.6±7.3	0
β-carotene	3.0±0.01	2.8±0.01	2.5±0.01	0
Phenolic compounds (by chlorogenic acid)	132.4±4.1	140.0±4.2	145.4±4.3	0
Phenolic compounds (by routine)	25.4±0.8	26.2±0.8	27.1±0.9	0
Tanning agents (by tannin)	148.6±4.5	150.2±4.8	145.6±4.2	0
Soluble pectin substances, %	0.9±0.05	1.0±0.01	0.8±0.01	0
Protein, %	18.0±1.0	19.1±0.9	18.8±0.8	6.4
Bound amino acids, %	9.5±0.3	9.4±0.2	9.5±0.3	0
Free α-amino acids, %	9.3±0.2	8.7±0.3	9.0±0.2	0
Total sugar, %	6.0±0.01	6.1±0.01	5.9±0.01	15.0±0.5
Fat, %	5.1±0.01	5.0±0.01	5.0±0.01	5.0±0.01
Dry matter, %	35.2±0.1	35.6±0.1	35.3±0.1	28.0±0.1

*Note: * – we used cryo-additives of spinach, citruses, apples, and Jerusalem artichokes as fortifying additives in production of new types of health-improving fruit and vegetable curd desserts of the green line*

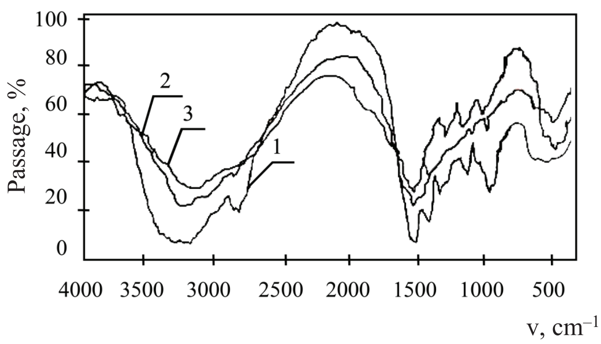
We can see that the new desserts contain complete protein (about 18 %). Its large part is in the form of free α-amino acids. In addition, new types of curd desserts relate to healthy food, as they contain a significant amount of BAS, which contribute to the strengthening of immunity. There is the required daily portion of β-carotene (5.0...5.5 mg), chlorophylls (212.0...250.0 mg) and low molecular weight phenolic compounds (by routine – 25.0...28.0 mg) per 100 g of the curd desserts. In addition, 100 g of the desserts contain 1/4 of the required daily portion of complete protein (18.0...18.9 g) (Tables 2, 3).

We established that the new types of curd desserts contain natural *L*-ascorbic acid. Its content ranges from 28.8 to 32 mg per 100 g in green curd desserts. It is about of 0.5 of the required daily portion of vitamin C. The desserts of the orange-yellow line contain from 18 mg to 30 mg per 100 g, which is 1/3 of the required daily portion.

We found that the new curd desserts exceed the known analogues by BAS content. The green line has no analogues. In addition, they do not have any nutritional additives. It is possible to recommend new curd desserts for healthy nutrition with the highest amount of natural BAS for immune prophylaxis of the population (especially for children and elderly persons).

The study showed that we can store new types of fruit and vegetable curd desserts 2 times longer than traditional ones. It is possible to store them for 72 hours at a temperature of +4...+6 °C and 8 days at +2 °C without BAS losses, due to complete inactivation of oxidative enzymes in their production and presence of natural phyto-substances with preservative action.

We confirmed the stabilizing effect of proteins of homogenized curd and pectin substances of cryopastes of fruit and vegetable raw materials on formation of a texture of new types of curd desserts by the method of infrared spectroscopy (Fig. 4).



Valency fluctuations of groups, cm^{-1}				
OH	NH	CH	S-H	C=O
3645…3500	3500…3300	3350…2850	2600…2550	1750…1720
Valency fluctuations of groups, cm^{-1}				
COOH	CH_3	C–O–	C=N	S=S
1750…1700	1470…1355	1300…1000	1230…1030	550…450

Fig. 4. Infrared spectra of the curd dessert (the analogue) without additives (1) and homogenized raw curd mass obtained using the cryo-additive of sea buckthorn, lemons with rind and cryo-additives of apricots, lemons with rind and extracts of natural spicy-aromatic plant raw materials (2, 3) as fortifiers

We detected an increase in the intensity of infrared spectra of experimental samples of curd desserts in the frequency range from 3,000 cm^{-1} to 3,600 cm^{-1}, which is characteristic for valence fluctuations of functional –OH-groups, which participate in formation of hydrogen bonds. An increase in intensity indicates an increased ability to bond water through formation of hydrogen bonds of proteins and polysaccharides, in particular, pectin substances of fruit and vegetable curd desserts. The obtained data correlate with the texture of new types of fruit and vegetable curd desserts. It is denser in comparison with consistency of analogue curd desserts, as well as with their structural and mechanical properties.

We found an increase in the intensity of infrared spectra in the frequency range of 1,800 cm^{-1} to 3,000 cm^{-1}. This testifies to intermolecular transformation and complex formation of associates and various complexes of compounds (organic acids, in particular, galacturonic acid, proteins, α-amino acids, alcohols, sugars, ketones, etc.). In addition, an increase in intensity occurs at the expense of biopolymers (pectin and proteins), a large part of which is in cryo-additives in the nanoscale form, and which are capable of structure formation and gelling. The indicated increase in intensity indicates the stabilizing effect of the components of additives.

We tested new method and nanotechnology for production of health-improving products, i. e. fruit and vegetable curd desserts, under production conditions at the enterprises of the city of Kharkiv and its region (Ukraine), such as «Bogoduhivsky Molzavod» Ltd., «FM Khladoprom» LLC, «KRIAS Plus» SPE, «Plus LTD» LLC.

6. Discussion of results of studying the development of nanotechnologies for curd desserts and fortifying fruit and vegetable cryo-additives

The advantage of this study consists in the fact that the obtained combined fruit and vegetable curd desserts exceed the known analogues by the content of health-improving natural BAS (carotenoids, chlorophylls, phenolic compounds, polyphenols, ascorbic acid) and prebiotic substances (pectin substances, cellulose). In addition, there are no food additives in the new types of desserts unlike in the existing curd desserts.

We developed a new method and nanotechnology for production of combined fruit and vegetable curd desserts in the nanoscale form with the highest BAS content. We proposed using mechanolysis and non-enzymatic catalysis in homogenization as an innovation in the processing of curd. We also proposed to use cryogenic «shock» freezing and fine-dispersed grinding in production of vegetable fillers for curd desserts. We showed that 40...45 % of bound α-amino acids transform into the free easily digestible form at fine-dispersed grinding (homogenization) of curd. The size of free α-amino acid molecules ranges from 0.3 to 1.5 nm. We revealed the mechanism of the process associated with mechanocracking (destruction of protein molecules to its components).

The study showed that the obtained fruit and vegetable cryopastes exceed raw material by 2.5...3.5 times by BAS content, due to extraction of hidden bound forms from raw materials.

Fruit and vegetable cryopastes used in production of curd desserts act as carriers of BAS, thickeners, colorants and aromatizing agents. The new types of fruit and vegetable curd desserts are unique in their chemical composition due to natural products, which are recommended for immunoprophylaxis for all the population.

The obtained study results made it possible to develop affordable curd desserts of high biological value without using artificial food additives (thickeners, structure-formers, stabilizers, colorants, aromatizers, transgenic fats, etc.), which are harmful to a human body. In addition, the study results have a scientific and practical value, because the proposed direction of deep processing of fruits, vegetables and curd into fruit and vegetable curd desserts for healthy nutrition helps to maximize the biological potential of raw materials.

7. Conclusions

1. Using of non-enzymatic catalysis and mechanolysis in the processing of curd grains leads to the transition of casein-calcium-phosphate complex into the nanosized form during homogenization. The study established possibility of using of fruit and vegetable cryo-additives in production of curd desserts as natural BAS fortifiers, structure-forming agents, and colorants. This has made it possible to exclude a need for using of food additives and synthetic components in production and to obtain new curd desserts with the highest BAS content, which exceeds the known analogues.

2. We established that homogenization of curd leads to a significant degradation of casein-calcium-phosphate nanocomplexes and mechanical degradation of proteins to low molecular weight components, such as α-amino acids, peptides, and dipeptides (by 40... 45 %), due to the processes of mechanocracking.

3. We studied the complex of BAS (β-carotene, *L*-ascorbic acid, *a* and *b* chlorophylls, phenolic compounds, tannins, prebiotics) in cryopastes of fruits and vegetables in comparison with fresh fruit and vegetable raw materials. The study showed that cryopastes contain a significant number of the mentioned BAS and exceed raw material by 2.5...3.5 times, due to the presence of a large number of hidden compounds bonded with biopolymers of BAS forms in fresh raw materials. The obtained data contradict the commonly accepted opinion that plant raw materials contains 5...10 % of BAS in the bound state.

4. We developed formulations and nanotechnologies for new curd desserts and cryopastes of fruit and vegetable raw materials for their production. We studied the content of BAS in curd desserts and compared it with the content of BAS in analogues. We established duration of the shelf life. We showed that new types of fruit and vegetable curd desserts for healthy nutrition have the original taste and aroma of a natural product and differ from analogues by the highest content of BAS, which are in the nanoscale form. 100 g of new types of desserts contain the required daily portion of BAS (in particular, β-carotene, chlorophyll, phenolic compounds, tannins, etc.).

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