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EXPLORING THE PROCESSES OF CRYOMECHANODESTRUCTION AND MECHANOCHEMISTRY WHEN DEVISING NANO-TECHNOLOGIES FOR THE FROZEN CAROTENOID PLANT SUPPLEMENTS

V. Pogarska
Doctor of Technical Sciences, Professor
State Prize laureate of Ukraine*
E-mail: viktoria.pogarskaya@ukr.net

R. Pavlyuk
Doctor of Technical Sciences, Professor
State Prize laureate of Ukraine
Honored figure of Science and Technology in Ukraine*
E-mail: ktppom@ukr.net

N. Timofeyeva
Director
Public utility company «Children's Food production facility»
Gagarina ave., 41-B, Kharkiv, Ukraine, 61001
E-mail: kdp2010@yandex.ua

L. Bilenko
Deputy Director of Learning Support
Kharkiv Trade-Economic Colledge of
Kyiv National University of Trade and Economics
Klochkivska str., 202, Kharkiv, Ukraine, 61045
E-mail: Leonida_Bilenko@list.ru

T. Stukonozhenko
Postgraduate Student*
E-mail: ktppom@ukr.net

*Department of Technology processing of fruits, vegetables and milk
Kharkiv State University of Food Technology and Trade
Klochkivska str., 333, Kharkiv, Ukraine, 61051

Виявлено закономірності та механізми комплексної дії процесів глибокої переробки каротинвмісної рослинної сировини заморожування та кріомеханодеструкції на збереження і вилучення каротиноїдів, зв'язаних в нанокомплексах з біополімерами, у вільну та гідрофільну форми. Встановлено, що при розробці нанотехнологій кріопюре відбувається екстракція β-каротину у вільну форму в 3...3,5 рази більше, ніж у вихідній сировині

Ключові слова: кріомеханодеструкція, нанотехнології, каротиноїди, рослинні добавки, руйнування нанокомплексів, біополімери, зв'язані форми

Выявлены закономерности и механизмы комплексного действия процессов глубокой переработки каротинсодержащего растительного сырья, замораживания и криомеханодеструкции на сохранение и извлечение каротиноидов, связаных в нанокомплексах с биополимерами, в свободную и гидрофильную формы. Установлено, что при разработке нанотехнологий криопюре происходит экстракция β-каротина в свободную форму в 3...3,5 раза больше, чем в исходном сырье

Ключевые слова: криомеханодеструкция, нанотехнологии, каротиноиды, растительные добавки, разрушение нанокомплексов, биополимеров, связанные формы

1. Introduction

Provision of population with rational and balanced nutrition is one of the most important problems of mankind. It is much more complicated by the fact that the dynamics of growth of the total population of the Earth is larger than the possibility of providing for the food products that are necessary for life activity, affordable in price and traditional for the given region. According to the estimates of scientists, to date, about 50 % of the world population is beyond poverty and are starving [1, 2]. To address the global problem of hunger, various countries of the world initiated the programs, within which various kinds of artificial powdered foods, such as milk, meat, flour, cereals, vegetables, etc. were developed [3]. The technology of their production include various kinds of food supplements (flavorings, thickeners, taste enhancers, structure forming agents, colorants, preservatives, etc.). This made it possible, when using substandard or artificial raw materials, to obtain products, which by their physical appearance and flavor are almost indistinguishable from natural products, but are affordable by price. The main disadvantage of such products is causing harm to the human body due to applying in their formulation of food supplements and substandard raw materials But, in spite of this, to date, the volumes of industrial production of powder products, alternative to traditional food, are growing. Powder industry attains significant distribution and is spread not only in the countries where the population is starving. but also in the developed countries of the world [4].

Another global problem in international practice is the deficit in food diets of vitamins, carotene, minerals, proteins, and other biologically active substances (BAS) [1]. They are responsible for the health and working capacity of people. The need for them, including population of Ukraine, is satisfied only by 50 % [1, 2, 5]. There are imbalances in food rations and there is a shortage of 50 % of basic food products, including milk, meat, fish, fruits and berries, that is, those products that contribute to improving health of the population [6]. The situation is complicated by the fact that the entire Earth faces deterioration of the environmental situation, which in turn leads to the deterioration of health and reduced immunity of the population. Improving immunity is possible by regular consumption of food products that are distinguished by high BAS content, which include vitamins (C, C, B group, etc.), carotenoids, mineral substances, phenolic compounds, bioflavonoids [7]. These also include dietary fiber – indigestible components of foods – prebiotics and, in particular, pectin substances, cellulose, etc. [7]. When living under ecologically unsafe conditions, the indicated BAS must enter the human body in the amount that exceeds daily rate of consumption by 1.5...2 times [8]. In this regard, in the leading countries of the world, widely distributed are functional health products, especially made of fruits, vegetables, berries. They are high in BAS content. This problem at present is given considerable attention to in the papers of scientists, nutritionists, etc. [9–11].

Promising raw materials when obtaining products for health food are carotene-containing vegetables, berries, fruits, such as pumpkin, carrot, tomato, sweet pepper, apricot, buckthorn, etc. Carotene-containing vegetable raw materials enjoy considerable demand from the population of various countries of the world, especially in Japan, the USA, Germany, Canada and others. Carotene-containing vegetable raw materials differ from other types in high content of carotenoids, phenolic compounds (rutin, catechin, oxycinnamic acids, etc.), polyphenols, tanning and other BAS. As is known, they have immunomodulatory, antioxidant, detoxic and antitumor effect [12–14]. According to research into the field of molecular biology by famous scientists vitaminologists George Whipple, Klaus Oberbeil and others, consumption of natural plant carotenoids with food products is a reliable protection of human organism against cancer and other diseases [15]. Carotenoids in the human body put out free oxidative radicals and protect cells from harmful viruses, bacteria and other pathogens. Therefore, regular consumption of food high in carotenes is considered by leading vitaminologists to be a reliable protection of human health and working ability [15].

Carotene-containing vegetables, fruits, berries are widely used in Ukraine in individual and mass food sectors (restaurants, culinary shops at supermarkets). They are also used at the industrial enterprises of processing and food industry when manufacturing various kinds of canned foods (juices, concentrates, purees, drinks, sauces, side dishes, desserts, fillings, frozen mixtures, etc.). It is known that traditional mentods of their processing lead to significant losses in BAS (from 20 to 80 %) [7, 9].

2. Literature review and problem statement

According to the UNESCO data, the international forecast "Food of the 21st century" defines one of the most progressive methods of processing and preserving fruits and vegetables, adopted in international practice, as freezing [16, 17]. Low temperatures provide the most complete retention of vitamins and other BAS. Now experts point to increasing share of cold and quick-frozen food in the diet of the population of the Earth. Their production per capita in countries such as England, France, Germany, Japan, the USA is from 40 to 100 kg annually. Over the last 5–10 years, Ukraine has also witnessed the dynamics of increasing the production and expanding the range of products of deep or "shock" freezing. A wide range of quick-frozen food products is manufactured. The amount of frozen and cooled products is growing every year. Today, of the existing world food supply that, including fish and seafood, is about 4500 million tons, the frozen and cooled products account for about 350 million tons [4].

Currently, there are two technologies for quick freezing of products in the world: "shock" (by a flow of cold air) and cryogenic (by liquefied gas) [7]. The first of them is widespread in the food and processing industry. "Shock" freeze is based on quick cooling of the product by increasing the speed of heat removal, which is achieved by the integrated impact of two factors:

1) lowering temperature of environment in the freezer, operated by synthetic refrigerants, to "shock" temperature (–30...–35 °C);

2) increasing motion of coolant, which in this case is cold air. The end of the freezing process is reached when the temperature inside a product –12...–18 °C [7].

The second (cryogenic) technology (by liquefied gas) by effectiveness far exceeds the "shock" one and provides super-fast freezing of the product due to direct effect of the cooling agent (cryogenic fluid) on the products that are being frozen. These include environmentally safe liquefied nitrogen or carbon dioxide.

In spite of the obvious advantages of cryogenic freezing over the "shock" one, which include: 3–4 times larger rate of freezing, 5–10 times lower loss of moisture after warming, as well as using while freezing environmentally friendly natural (not synthetic) refrigerants, in Ukraine, at present, cryogenic freezing is not practically applied in the food industry [4].

Nowdays, the world practice of improving refrigerating equipment and technology for the production of quick-frozen products is aimed at the transition from traditional chamber (refrigerating) to apparatus freezing. For this purpose, they use quick-refrigeration equipment, as well as gradually abandon the application of synthetic refrigerants (freons, halons).

In this case, replacing them with the natural environmentally safe refrigerants (nitrogen, carbon dioxide) is implied, as well as the transition from the technology of "shock" to the technology of cryogenic "shock" freezing [18–20].

Widespread use of technology of cryogenic freezing of food in Ukraine until now has been limited because of the difficulties related to the necessity of using specialized equipment (fast-refrigerating cryogenic plants, cryo-refrigerating chambers, nitrogen-filling stations). In addition, there is a lack of information about the technology of obtaining liquid nitrogen and its use when freezing fruits, berries, vegetables, paste-like supplements from them, as well as the functional products for health food with their use. In Ukraine, the application of cryotechnologies when freezing, storing and processing vegetable raw materials is at the stage of experimental development. According to data from leading international experts on refrigeration technology, of the existing refrigerants, which are used for freezing, the most suitable for freezing food products is liquid nitrogen. It is characterized by low boiling temperature, chemical and biological inertness, safety at work [19, 21]. As for the scientific literary data on the effect of low temperatures at freezing and crushing fruits and vegetables on the quality of raw materials, mass share of biopolymers and BAS, then such data are limited and even contradictory. The majority of available data in the scientific literature is devoted to studying effect on the quality of vegetable raw materials exposed to high temperatures (pasteurization, sterilization, thermal drying, etc.). However, the benefits of cryogenic freezing and crushing, as already noted, are absolutely clear. In this regard, it is important to develop scientific foundations for the technologies of frozen carotenoid finely dispersed plant supplements, based on the application of methods of deep processing with the use of gaseous or liquid nitrogen as a cooling agent, accompanied by the processes of mechanochemistry and cryodestruction and the use of obtained nano-supplements in the development of technology for the health food products.

Authors of present work have been digging deep in this direction for over 30 years and are actually the founders of the new direction in the food industry of the USSR and Ukraine – cryogenic technologies and equipment (cryogrinding and drying) [4, 7]. In addition, Authors of present article have discovered alternative methods for grinding and obtained the new generation of frozen and homogeneous pastes, finely dispersed powders with a record content of vitamins and other BAS. On the basis of the new generation of finely dispersed supplements, we have developed technologies for natural functional health products, which are implemented in the production at the enterprises of Ukraine, Russia, Latvia [18, 20].

Traditional methods of processing plant raw materials lead to a significant loss of vitamins and other BAS in the original raw materials (from 20 to 80 %) [7, 9]. That is why it is relevant to devise high technologies, including nanotechnologies, which can make the process of treating food raw materials more efficient. In addition, they will allow maximum saving and extraction of target components of the original (fresh) vegetable raw materials (biologically active substances and nutrients). The technologies in question should be resource-efficient, waste-free and less energy-intensive. The main objective in the development of high technologies for processing vegetable raw materials is the study of influence of different kinds of technological methods on the natural micro-and nano-scale objects (cells, pores, capillaries). Also important is the research into influence on the nano complexes of BAS with various types of biopolymers, on the sophisticated complexes of the biopolymers themselves and their transformation into the more bio-accessible easily-digestible form. The main purpose of the implementation of the newest technologies is obtaining fundamentally new food products with the characteristics that cannot be achieved by using traditional methods. The most progressive methods of processing vegetable raw materials currently in use in the international practice are freezing and cryogenic grinding. They have not been widely applied in Ukraine as yet. In addition, there is a shortage in Ukraine of both the frozen supplements, including made of traditional plant raw materials (carrot, pumpkin, tomato, sweet pepper, apricot, buckthorn, etc.), and the functional health food products from them [9]. The scientific literature lacks systemized data on studying the processes of freezing, cryomechanodestruction and mechanochemistry in the development of nanotechnologies in the processing of plant raw materials into finely dispersed frozen supplements, with the exception of the results that were obtained by Authors of present work. The available literature data are of fragmented contradictory character.

Among the products from the carotene-containing plant raw materials (CCPR), a special place is occupied by supplements – semi-finished products in the form of pastes, purees, frozen products. Thet can be introduced as colorings – enriching agents with natural carotenoids and other BAS into various foods (cheese, toppings for confectionery products, creams, gels, desserts, sambuca, juices, ketchups, sauces, baby food, etc.). There is a shortage of such supplements in Ukraine. In this regard, it is relevant to develop the cryotechnology of carotenoid supplements in the form of frozen puree from CCPR that differ in high degree of preservation of carotenoids [9–11].

Overview of data in the periodic literature over the past 10 years has revealed that systematized data are lacking at present on the impact of cryogenic freezing and fine grinding on β-carotene, its transformation into the hydrophilic form in the processing of fruits and berries, except for the papers of Authors of present article. The main part of the available literature data mostly addresses the processes of crystal formation, heat mass transfer when freezing and storing the products in a frozen state. In addition, the research are devoted to finding the cryoprotectors, which are necessary to introduce into the product when freezing in order to reduce the loss of cellular juice at warming [20].

The literature data on the influence of freezing on carotenoids of fruits and vegetables are limited to mostly stating the carotenoid losses, both during particular modes of freezing and when storing the frozen food for certain kinds of vegetable raw materials at low temperatures [9–11]. Data on the detection of modes of freezing, which allow saving and more fully extracting carotenoids from plant raw materials and transforming them into water-soluble form, are missing in the scientific literature.

In this regard, the task of present work included theoretical and experimental detection of regularities and mechanism of influence of refrigeration (at slow speed and high speed of cryogenic freezing with the application of cryogenic fluid) to the final temperature in a product −32...−35 °C, as well as low-temperature grinding of carotene-containing vegetables, fruits, berries in the course of their processing on the preservation of carotenoids and the activation of their hydrophilic properties.

3. The aim and tasks of the study

The aim of present work is to study the impact of processes of cryomechanodestruction and mechanochemistry on the preservation and transformation of carotenoids in the development of nanotechnologies for the frozen carotenoid plant finely dispersed supplements.

To achieve the set aim, the following tasks were to be solved:

– to study the influence of cryogenic "shock" freezing on the preservation of carotene in carotene-containing vegetables, fruits and berries;

– to examine the influence of comprehensive action on the carotene-containing vegetable raw materials of the processes of deep treatment, which include cryogenic "shock" freezing and finely dispersed grinding, on the preservation and transformation of β-carotene into the free and hydrophilic form;

– to explore the effect of cryotreatment of carotene-containing vegetable raw materials on the preservation of L-ascorbic acid;

– to compare quality of nanostructured frozen nanopuree from carotene-containing plant raw materials to the quality of frozen and fresh raw materials.

4. Materials and equipment used during experimental research

The study was carried out with the use of carotene-containing vegetables, fruits and berries, including carrot, pumpkin, sweet pepper, tomato, apricot, buckthorn, frozen nanopuree made of them, and the products (nanojuices, gel, nanosorbets). The method for determining parameters (β-carotene, L-sscorbic acid, phenolic substances, polyphenols of the examined samples, namely, carrot, pumpkin, tomato, sweet pepper, apricot, buckthorn, and cryopuree from them, as well as carotenoid nanojuices, gel, nanosorbets) is described in paper [21].

5. The study of processes of cryomechanodestruction and mechanochemistry in the development of nanotechnologies for the frozen carotenoid plant supplements

The main thing in the development of nanotechnologies for carotenoid plant supplements using cryogenic refrigeration and finely dispersed grinding was not only to preserve carotenoids and L-ascorbic acid, but also to more fully extract from the raw materials their hidden shapes and partially transform carotenoids from hydrophobic into the hydrophilic form. It turned out to be possible due to the cryogenic treatment of raw materials, their cryodestruction, cryomechanoactivation and non-fermentive catalysis-mechanolysis.

We established the patterns of growth and transformation of the carotenoid carotene-containing raw materials during cryogenic freezing at high speed and low-temperature grinding of the frozen raw materials. It is shown that at cryogenic freezing, in comparison with the original raw materials (fresh vegetables and berries), there is a quantitative increase in the mass share of carotenoids, which depending on the speed of freezing and the type of carotene-containing raw materials (CCPR) is 2.0...2.5 times larger than in the original raw material (Fig. 1). That is, it is demonstrated that, compared to fresh raw materials, frozen carotene-containing fruits, berries and vegetables contain 2,0...2,5 times more of carotene. It was found that at low-temperature grinding of cryogenically frozen CCPR, while obtaining cryopuree, there occurs even larger substantial increase in the mass proportion of carotenoids, which depending on the type of CCPR is 3...3.5 times (Fig. 2). In parallel, the mass share of carotenoids (CR) increases, which are in the water-soluble form (WF), that is, the hydrofillic properties activation occurs. Ratio between the fat soluble form (FF) and WF of carotenoids in the frozen product is: 1:1 (at slow speed of freezing) and 1:1.5...1.7 (at cryogenic freezing and low-temperature grinding).

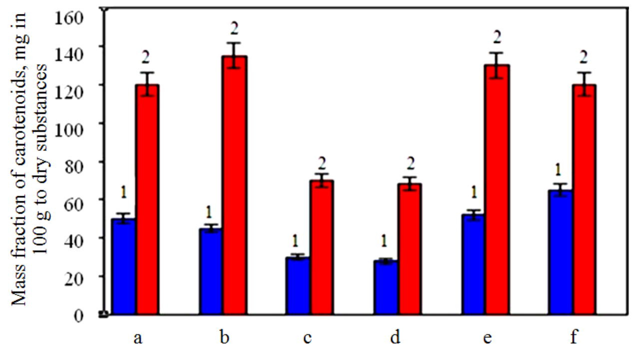

Fig. 1. Impact of cryogenic "shock" freezing at high speed (20 °C/min) on β-carotene of carotene-containing vegetables, fruits and berries, where: 1 – original fresh vegetables, fruits and berries; 2 – frozen at high speed to –35 °C; a – carrot, b –pumpkin, c – tomato, d – sweet pepper, e – apricot, f – buckthorn

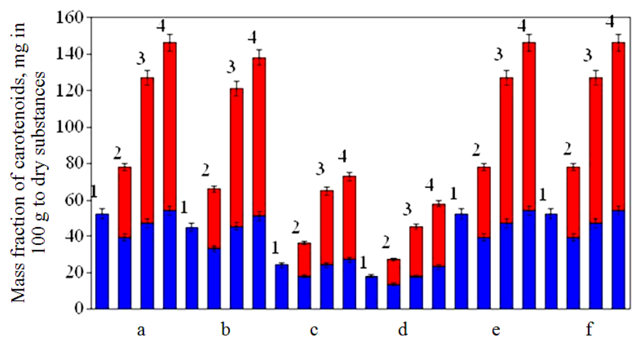

Fig. 2. Impact of freezing and low-temperature grinding of carotene-containing vegetables, fruits, berries on carotenoids: 1 – original (fresh) carotene-containing vegetable raw materials; 2 – CCPR, frozen at slow speed to –18...–20 °C; 3 – CCPR, frozen at high speed (20 °C/min.)) to –35 °C; 4 – CCPR, after low-temperature grinding; ■ – fat soluble form of CR; ■ – water-soluble form of CR; a – carrot, b –pumpkin, c – tomato, d – sweet pepper, e – apricot, f – buckthorn

We detected a mechanism of cryotreatment of raw materials (Fig. 3), which may explain the effect of increasing and transforming the carotenoids into hydrophilic form when freezing. At cryogenic freezing, during crystal formation, there is a destruction of nano complexes of biopolymers with carotenoids (proteins, cellulose, pectin substances, starch) and transition of part of the carotenoids from the bound by biopolymers form into free from by breaking the hydrogen bonds, weakening of induction interaction, etc.

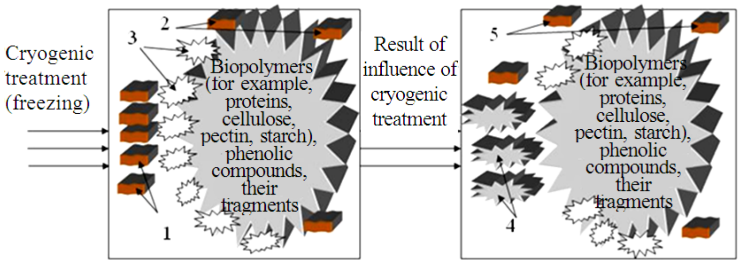

Fig. 3. Schematic representation of the mechanism of influence of cryotreatment of carotene-containing vegetables, fruits, berries on the preservation and formation of water-soluble carotenoid forms: 1 — CR in free form; 2 — CR in the bound by biopolymers state; 3 — hydrophilic groups of fragments of biopolymers, phenolic compounds; 4 — water-soluble complexes of carotenoids (CR-protein, CR-cellulose, CR-pectin, CR-phenolic compounds, etc.); 5 — CR that passed from the bound by biopolymers state into free form

By water-soluble forms of CR we understand water-soluble complexes (associates) of CR with biopolymers (protein, cellulose, pectin, starch, etc.), phenolic compounds or their fragments that have hydrophilic properties due to the hydrofillic groups (NH_2^-, SH^-, OH^-, COH^-, CH^-), which are included into their composition. In addition, when freezing, there may occur the formation of water-soluble forms of CR due to the formation of complexes between CR and biopolymers (protein, carbohydrates, etc.), phenolic compounds and their fragments that have hydrophilic properties (Fig. 3).

In parallel, we studied the impact of speed of freezing and low-temperature grinding on L-ascorbic acid. It is shown (Fig. 4) that in comparison with the original raw materials (fresh CCPR) when freezing at slow speed, there occurs the reduction in mass fraction of ascorbic acid, which, depending on the type of CCPR, is 20...23 %. It was established that during cryogenic freezing to temperature –35 °C, there is an increase in the mass fraction of ascorbic acid by 20...25 %, and at low finely dispersed grinding (depending on the type of CCPR) – an increase in content by 2.0...2.5 times compared to the original (fresh) carotene-containing vegetables, fruits, and berries.

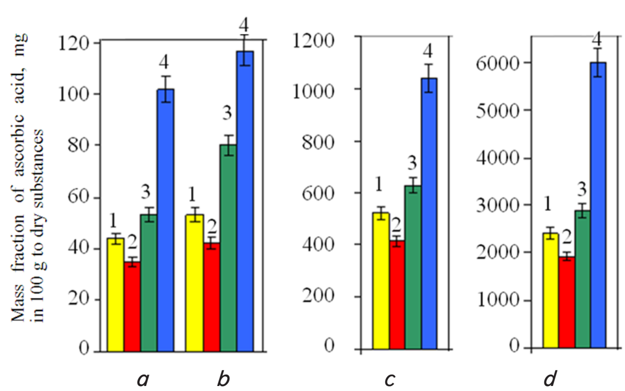

Fig. 4. Effect of freezing and low-temperature grinding of carotene-containing vegetables on ascorbic acid: 1— original (fresh) carotene-containing plant raw materials; 2 — CCPR, frozen at slow speed to –18...–20 °C; 3 — CCPR, frozen at high speed 20 °C/min. to –35 °C; 4 — CCPR, after low–temperature grinding; *a* — carrot, *b* — pumpkin, *c* — tomato, *d* — sweet pepper

Thus, it is established that the use of freezing results, in comparison with the original raw materials (fresh CCPR), in the increase in the content of carotenoids, the mass share of which, depending on the speed of freezing, increases by 1.5...2.5 times, as well as in the activation of their hydrofillic properties – transformation of part of the carotenoids (50 %) into water-soluble form. It is demonstrated that, unlike the traditional way of freezing at slow speed, the use of cryogenic freezing contributes to an increase in the mass fraction of not only carotenoids, but ascorbic acid as well, whose content in a quick-frozen product increases, depending on the type of CCPR, by 20...25 %. It is established that the application of finely dispersed low-temperature grinding while obtaining cryopastes results in comparison with the original (fresh) CCPR in the increase in mass proportion of carotenoids by 3.0...3.5 times and ascorbic acid – by 2.0...2.5 times.

The obtained experimental data allow us to present anew the impact of the processes of cryogenic freezing and low-temperature grinding in the processing of vegetable raw materials on carotenoids and activation of their hydrofillic properties. The mechanism of influence of the processes of freezing and low-temperature grinding in the processing of raw carotene-containing materials is in the cryodestruction of nano complexes of carotenoids with biopolymers, destruction, mechanocracking of the bonds between BAS and biopolymers, which leads to the increase in mass proportion of carotenoids (by 1.5...2.5 times, depending on the speed of freezing and by 3.0...3.5 times at low-temperature grinding), as well as the activation of their hydrofillic properties – transformation of the part (50...70 %) of carotenoids into water-soluble form, Fig. 5, 6.

By water-soluble forms of CA we understand water-soluble complexes (associates) of CR with biopolymers (protein, cellulose, pectin, starch, etc.), phenolic compounds or their fragments that have hydrophilic properties due to the hydrophilic groups (NH_2^-, SH^-, OH^-, COH^-, CH^-), that are included into their composition.

Cleavage during finely dispersed grinding of water-soluble complexes (associates) of CR with the fragments of biopolymers, phenolic compounds that have hydrophilic properties.

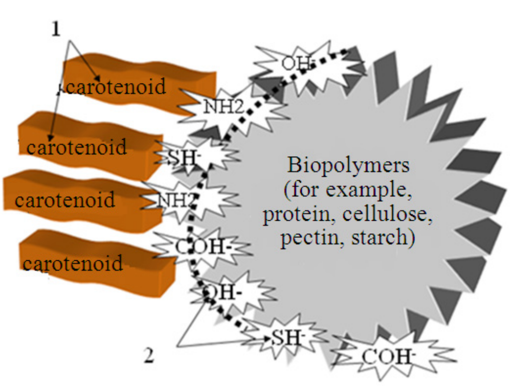

Fig. 5. Schematic representation of the process of cryomechanochemistry process — the mechanism of formation and growth of water-soluble forms* of carotenoids at cryogrinding of carotene-containing vegetables, fruits, berries: 1 — CR in the bound by biopolymers form; 2 — fragments of biopolymers, phenolic compounds, which include hydrophilic groups

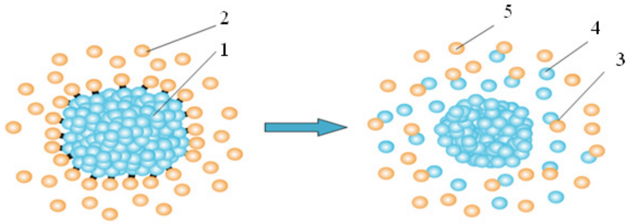

Fig. 6. Schematic representation of the mechanism of influence of cryotreatment (freezing and finely dispersed grinding) on the destruction and mechanolysis of nano complexes – protein – carotenoids with the formation of water-soluble forms of carotenoids and amino acids, where: 1 – biopolymer of protein; 2 – carotenoid; 3 – carotenoids with the fragments of protein (certain amino acids); 4 – free amino acids; 5 – free carotenoids

Such technological techniques as cryogenic freezing and low-temperature grinding during processing the carotene-containing vegetable raw materials were applied for the scientific substantiation of nanotechnology for the frozen carotenoid supplements – colorants – enrichers of carotenoids, half of which is in the water-soluble form.

Below is a comparative analysis of the content of β-carotene and other BAS in fresh and cryofrozen carotene-containing vegetables and berries at high speed freezing and nanostructured puree made from them (Table 1).

It is shown that supplements from carotene-containing vegetables and berries in the form of frozen finely dispersed purée, obtained by the nanotechnology, by the content of β-carotene and other biologically active substances (ascorbic acid, phenolic compounds, tannins) significantly outperform the original raw materials and the known world analogues. They have a fundamentally new chemical composition than those obtained by traditional technology. Practically all BAS in nanopuree are in the nanodimensional form, which are easily absorbed by the human body. It is known that the size of molecules of the listed biologically active substances in the obtained supplements from CCR are in the range from 0.5 to 1.5 nm. It is demonstrated that supplements from carotene-containing vegetables by the content of β-carotene exceed the original raw material by 3–3.5 times, by the content of L-ascorbic acid – by 2–2.2 times, by the content of phenolic substances by 1.7–1.8 times, tannin – by 1.5–1.7 times (Table 1). 100 g of nanopuree from carrot, pumpkin, buckthorn, apricot contain 5 to 6 daily dozes of β-carotene, needed by human body. In addition, the carotenoid supplements also contain a significant amount of ascorbic acid, from ¼ to 1 daily need of the human body.

Thus, the use of processes of cryomechanodestruction and mechanochemistry (cryogenic "shock" freezing and finely dispersed grinding) allows obtaining qualitatively new supplements in the form of frozen nanopuree from carotene-containing vegetables and berries (carrot, sweet pepper, pumpkin, tomato, apricot, buckthorn) with a record-breaking content of BAS in the easily digestible form, which are impossible to obtain using traditional methods. By the chemical composition, the new supplements from carotene-containing plant raw materials possess potential immunomodulatory, antitumor and detoxic effect.

The obtained experimental data presented in present article, served as a basis when developing the cryogenic nanotechnology from CCR in the form of frozen nanopurees. New technologies were verified under production conditions at NPP "KRIAS" (Kharkiv, Ukraine) and NPP "FIPAR" (Kharkiv, Ukraine) and we devised regulatory documentation (TUU 15.3-01566330-306 and TI). Based on it, new kinds of health food were developed (carotenoid health improving rolls for schoolchildren and biscuits, which are implemented in production at KP "Plant of Baby Food" (Kharkiv, Ukraine).

We also developed carotenoid fillings for confectionery products, which are implemented in production at NVF "HPK" (Kharkiv). On the base of carotenoid supplements, there were developed such health improving products as: nanosorbets, curd desserts, nanodrinks, nanojuices, desserts, creams, biokefirs, bioyoghurts, etc.

Table 1

Comparative analysis of the content of β-carotene and other BAS in fresh and cryofrozen carotene-containing vegetables and berries at high speed freezing and nanostructured puree made from them

Product	Mass share (mg per 100 g)			
	β-carotene	L-ascorbic acid	phenolic compounds (by chlorogenic acid)	flavonol glycosides (by rutin)
Fresh carrot	9,8±0,3	10,5±0,2	154±12,1	60,2±3,6
Carrot frozen in pieces	20,4±1,2	20,0±1,5	205±4,8	90,3±6,2
Nanostructured cryopuree from carrot	30,2±2,5	28,6±1,8	290±6,9	110,3±5,8
Fresh pumpkin	10,2±0,4	14,2±0,3	143±11,8	52,0±4,0
Pumpkin frozen in pieces	21,0±1,0	25,3±0,5	200±10,5	70,2±3,8
Nanostructured cryopuree from pumpkin	35,5±2,8	34,8±2,4	250±12,6	85,6±5,2
Fresh apricot	8,5±1,6	40,2±1,8	120,3±10,1	45,4±1,2
Frozen apricot	15,2±1,0	60,5±5,0	150,4±8,2	70,2±5,1
Nanostructured cryopuree from apricot	24,2±2,2	120,3±10,4	180,5±12,1	80,3±3,9
Fresh buckthorn	12,8±0,6	70,2±5,4	160,2±12,1	70,2±5,4
Frozen buckthorn	18,9±1,2	100,4±10,2	203,3±20,2	100,1±10,2
Nanostructured cryopuree from buckthorn	36,8±2,8	215,3±11,2	240,2±25,4	125,2±11,6
Fresh tomato	7,0±0,4	25,4±1,2	125,4±8,2	55,2±1,8
Nanostructured cryopuree from tomato	20,0±1,9	50,2±5,6	260,2±24,8	90,7±15,1
Fresh sweet pepper	5,5±0,1	200,4±20,4	148,2±20,4	85,2±5,8
Fresh sweet pepper frozen in pieces	10,6±0,5	300,0±30,6	190,2±18,0	120,3±7,2
Nanostructured cryopuree from sweet pepper	16,9±1,8	401,2±39,6	250,6±25,6	145,8±10,3

6. Discussion of results of research into influence of cryomechanodestruction and cryomechanochemistry on the activation of extracting hidden forms of carotenoids, L-ascorbic acid from nano complexes with biopolymers when developing the nanotechnologies of supplements from CCR

The influence of cryomechanodestruction was examined on the activation and destruction of heteropolysaccharides – protein nano complexes with carotene and other low molecular BAS such as L-ascorbic acid, phenolic compounds, which in the plant raw materials are in the non-active bound form, when developing the nanotechnologies of plant supplements, including frozen nanopuree form carrot, sweet pepper, pumpkin, tomato, apricot, buckthorn.

The benefits of present research include the fact that, as a result of using comprehensive cryotreatment of raw materials and cryomechanodestruction, nano complexes of biopolymers with low molecular substances such as β-carotene, L-ascorbic acid, low molecular phenolic compounds are destroyed and they pass from the hidden bound form into free soluble easily digestible form – the nanoform. This makes it possible to reveal much more the biopotential of plant cell, tissue and extract from them the hidden forms of biologically active substances with fundamentally new chemical composition and high consumer properties, which might be used when creating healthful food products.

A shortcoming in the implementation of the proposed solutions on cryotechnology in the food industry of Ukraine and abroad is that manufacturers of frozen food and supplements, when assessing quality of the finished products, do not come up with the requirements regarding the content of vitamins and other BAS that determine biological value and health improving effect of products. Traditionally, the assessment of products quality in the production and storage is conducted by the organoleptic, physical-chemical, microbiological indicators and the content of toxic substances. When evaluating the quality of frozen food, the main requirements relate to temperature modes of freezing, storing the product, as well as the inadmissibility of processes of re-freezing to prevent significant loss of cellular juice, solids, as well as microbial contamination when unfreezing the product. In this case, the scientific literature mostly address the peculiarities of processes of moisture crystallization. There is a lack of systemized data on the influence of different factors on the preservation of BAS in plant raw materials in the production and storage of supplements and products, including those frozen.

Availabe data deal with the stated losses of carotenoids and other BAS in vegetable raw materials (from 20 to 80 %) during different types of technological treatment when obtaining plant supplements and products. In addition, it is universally accepted that the vegetable raw materials contain 5...10 % of low molecular substances, including biologically active ones, in the form bound with biopolymers.

Results, presented by Authors in the given work, testify to the existence in vegetable raw materials of not 5...10 % but significantly larger amount of BAS (carotenoids, L-ascorbic acid, phenolic compounds, etc.) that are in the hidden, bound by biopolymers, form. Their amount, depending on the type of raw materials and the type of BAS, ranges from 50 % to 350 %. Authors established that the application of processes of cryomechanodestruction allows using the biological potential, built into raw materials, much more effectively. The application of cryomechanodestruction processes at processing vegetable raw materials into supplements and products makes it possible to receive products, the quality of which by the content of BAS exceeds the quality of original raw materials by 1.5...3.5 times.

There are no results in the scientific literature of studies by other authors that indicate the possibility of additional extraction of the hidden, bound with biopolymers, forms of carotenoids and other BAS, and the possibility to obtain a product of higher biological value, in comparison with the original raw materials, with the exception of papers by Authors of present work.

Carotenoid nanosupplements (frozen puree, nanopowders, nanosorbets, nanoicecream), developed by Authors, received two gold medals in the category of health nanoproducts of the future at the International Contest of Culinary Specialists "AgroKookFest" (Kharkiv, October 2016), as well as received a gold medal at the International Culinary Festival BISER MORA and a diploma of Alliance of Cooks of the Mediterranean and European regions (Croatia, March 2015) in the category "Health products of the 21st century." This demonstrates that such food products will find their customer not only in Ukraine but in other countries of the world as well. At present, the work is patent-pending, a program of activities is under way for the purpose of introducing new types of products and technologies of their production to the European and world markets. There are proposals for cooperation from our colleagues from Poland, Sweden, Slovenia, Croatia and other countries.

Further development and continuation of research into this area is to conduct studies on the impact of the processes, which are considered in present work, on the hard-to-solve nano complexes of biopolymers (pectins, cellulose), preservation and creation of micro-organisms, etc. In addition, extending the range of natural products in the nanoform with high BAS content.

7. Conclusions

1. We established patterns of growth and transformation of carotenoids during freezing of carotene-containing raw materials at various high speeds and low-temperature grinding of carotene-containing vegetables. It is demonstrated that at cryogenic freezing, in comparison with the original raw materials (fresh vegetables and berries), there is a quantitative increase in the mass share of carotenoids, which, depending on the speed of freezing and the type of carotene-containing raw materials (CCR), is 2.0...2.5 larger more than in the original raw materials. That is, it is shown that the frozen carotene-containing berries and vegetables contain 2.0...2.5 times more of β-carotene than the fresh ones. We discovered the mechanism of these processes.

2. It was found that during cryogenic freezing and low-temperature grinding and obtaining cryopuree from carotene-containing vegetables and berries, there is an increase in the mass share of carotenoids, which, depending on the type of vegetable raw materials, is 3.0. 3.5 times larger than in the original raw materials. In parallel, the mass fraction of CR increases, which are in the water-soluble form (WF), that is, there occurs the activation of hydrofillic properties of CR. The ratio between the fat soluble form (FF) and WF of carotenoids in the frozen product is 1:1 (at slow speed freezing) and 1:1.5...1.7 (at cryogenic "shock" freezing and low-temperature grinding). We explored mechanisms of the specified processes.

3. It was established that at cryogenic "shock" freezing to temperature minus 35 °C, there is an increase in the mass fraction of ascorbic acid by 20…25 %, and at low-temperature finely dispersed grinding (depending on the type of CCR) – an increase by 2.0…2.5 times compared to the original carotene-containing vegetables.

4. It is demonstrated that supplements from carotene-containing vegetables and berries in the form of frozen finely dispersed purée, obtained by the nanotechnology, by the content of β-carotene and other biologically active substances (ascorbic acid, phenolic compounds, tannins) exceed the original raw materials and the known world analogues. They have a fundamentally new chemical composition than those obtained by traditional technology. Almost all BAS in nanopuree are in the nanodimensional form, which are easily absorbed by the human body. Thus, by the content of β-carotene, supplements exceed by 3.0–3.5 times the original raw materials, by the content of L-ascorbic acid – by 2.0–2.2 times, by the content of phenolic substances – by 1.7–1.8 times, tannins – by 1.5…1.7 times.

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