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STUDYING THE COMPLEX OF BIOLOGICALLY ACTIVE SUBSTANCES IN SPICY VEGETABLES AND DESIGNING THE NANOTECHNOLOGIES FOR CRYOSUPPLEMENTS AND NANOPRODUCTS WITH HEALTH BENEFITS

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Визначено комплекс БАР пряних овочів (коренів імбиру, селери та хрону, часнику), які відрізняються від іншої рослинної сировини високим вмістом ненасичених реакційно активних фіторечовин. До складу належать леткі ароматичні речовини, низькомолекулярні та високомолекулярні фенольні сполуки. Останні є природними антиоксидантами, консервантами та мають бактерицидну та імуномодулюючу дію. Встановлено, що пряні овочі відрізняються значною кількістю пребіотичних речовин (целюлози, пектину та білку) та невисоким вмістом цукрів. Наявність в складі 100 г пряних овочів перерахованих БАР в кількості, що здатна задовольнити добову потребу в них організму людини надає, на думку авторів, свіжим пряним овочам лікувально-профілактичні властивості.

Розроблено нанотехнології оздоровчих заморожених добавок та нанопродуктів із пряних овочів, в яких повністю зберігаються вітаміни, ароматичні речовини, фенольні сполуки та інші БАР свіжої сировини. Крім того, при розробці нанотехнологій були виявлені та вилучені приховані (зв'язані) форми БАР у вільний легкозасвоюваний стан. Масова частка зазначених речовин в 2,5…3,2 рази більша, ніж в свіжих овочах, що контролюється стандартними хімічними методами. Як інновацію при розробці технологій запропоновано використовувати кріообробку сировини, яка включає кріогенне «шокове» заморожування та дрібнодисперсне низькотемпературне подрібнення (механоліз).

Переваги полягають в тому, що вдалось отримати заморожені пряні овочі, які за вмістом натуральних ароматичних речовин та фітокомпонентів (фенольних сполук, поліфенолів та інших БАР) перевищують свіжі пряні овочі в 2…2,5 рази. Відпрацьовані технологічні режими на стендовому напівпромисловому устаткуванні та розроблені технології оздоровчих добавок в формі дрібнодисперсного пюре та заморожених пряних овочів. Із застосуванням отриманих заморожених продуктів та добавок із пряних овочів розроблено широкий асортимент оздоровчих продуктів, які за якістю перевищують відомі аналоги

Ключові слова: кріогенна обробка, пряні овочі, комплекс БАР, оздоровчі добавки, нанопродукти, механоліз, приховані форми БАР

1. Introduction

The relevance of this study relates to the necessity of resolving such global problems as hunger and a 50 % deficit of biologically active substances (vitamins, minerals, phytocomponents, etc.) in food diets [1–3]. Every eighth inhabitant of the Earth is starving [1]. The necessity to resolve the specified problems is growing more important because of the deteriorating environmental situation and the decrease in the immunity of the Ukrainian population, as well as many other countries. Consuming the products with high BAS content can strengthen immunity [1, 4]. The main source of natural BAS are fruits, vegetables, spice-aromatic, medicinal plant raw materials, etc. [4]. In this regard, development of health products and supplements made from fruits and vegetables, aimed at strengthening immunity [5, 6], is one of the priority and urgent scientific areas in the food industry. This field has been developing actively throughout the world. The following leading countries pay the greatest attention to the development of this area: Japan, USA, Canada, Germany, the Netherlands [7, 8].

One of the main natural sources of plant BAS is spicy vegetables (SV), particularly, roots of celery («golden root»), ginger, horseradish, and garlic. The specified types of SV stand out against other types of plant material by the high content of aromatic substances, phenolic compounds, and other healing substances. People in many countries of the world use them in their diet. The spicy vegetables retain their useful properties maximally when consumed fresh. Significant losses (from 20 to 80 %) of volatile aromatic, phenolic compounds, and other BAS [9] occur during processing and storage of spicy vegetables.

In this regard, it is a relevant task to search for the technological methods that make it possible to maximally preserve the BAS from raw materials when developing health supplements and nanoproducts from spicy vegetables with a high content of aromatic substances, phenolic compounds and other BAS.

2. Literature review and problem statement

Traditionally, people consume fresh spicy vegetables and use them as condiments in a dried form when cooking various types of culinary products (first courses, meat, fish products). Among the products that include spicy vegetables, sauces-dressings, sauces-dips, marinades for meat and fish are popular among people [3, 4]. People, however, do not use SV widely in their diet despite a significant content of such unique phytocomponents in spicy vegetables as aromatic substances (essential oils, phenolic compounds, tannins, phytoncides), which have medicinal properties, [3, 4]. There are no products for mass consumption with spicy vegetables as the main raw material. This is explained by the lack of advertising in mass media about healing properties of spicy vegetables and about the recommended norm of consumption in diets.

Difficulties in the processing of spicy vegetables, when using traditional thermal methods, relate to the significant losses of volatile and other BAS. Therefore, it is a relevant task to search for technological methods that make it possible to preserve and stabilize quality of fresh SV after processing them into various types of supplements and food products.

One of the promising directions for obtaining health foods made from fruits and vegetables is to use freezing [5–7]. Freezing of food products is one of the most progressive techniques for processing and preserving food raw materials as indicated in the «Nutrition in 21st Century» international forecast by UNESCO [8, 9]. The most effective technique of freezing, which provides the highest degree of preservation of vitamins and other BAS, is the rapid «shock» freezing by a cold airflow [5, 6]. The disadvantage of the method of freezing is a significant loss of cellular juice and vitamins during defrosting after storage for 6 months [6–8]. Cryogenic «shock» freezing is widespread in leading countries of the world. It differs from the traditional freezing by the application of cryogenic liquids (particularly, liquid nitrogen, carbon dioxide, etc.) [6, 10, 11]. The cryogenic method of freezing is not widely adopted in Ukraine. In addition, there are no designed cryogenic technologies of fruit and vegetable processing, which would make it possible to maximally preserve BAS. There are no studies into physical-and-chemical and biochemical processes, the processes of cryodestruction and mechanodestruction processes at cryorefrigeration of fruits, vegetables and purees made from them.

The quality of raw materials, when studying the influence of traditional «shock» freezing of vegetables, is understood as the texture and organoleptic indicators of a product (physical appearance, taste and aroma, consistency) [10]. For the most part, researchers study thermophysical characteristics, specific heat capacity, thermal conductivity of a product at various freezing rates, including cryogenic [11]. Studying the kinetic processes of freezing, changes in the quality of food products, makes it possible to forecast storage duration and the shelf life of frozen products, including products of an animal origin [12]. In terms of examining the effect of freezing and storage of frozen vegetables on BAS content, data from the scientific literature mostly address determining the losses of BAS loss [13]. Continuous search for and development of new technologies for cooling and freezing of food products [14] is underway. It was established [14] that the faster the freezing rate, the better the quality of food products and the lesser the loss of cellular juice during defrosting [14]. Gaseous nitrogen performs a role of an inertial medium when cooling food products: its presence prolongs the storing time of cooled products. In addition, there are data on the effect of freezing modes on a cellular structure of plant raw materials, cellular juice loss, BAS content, and color variation at defrosting [15]. Paper [16] studied the influence of low and ultralow freezing temperatures on the quality of food products at subsequent defrosting [16]. It was established that the lower temperature when freezing a product, the better the quality. However, in parallel, this leads to an increase in the cost of a product. The scientific literature provides guidance, forecasts for the development of food industry in the 21st century [17]. Freezing is considered to be one of the most progressive techniques for processing and storing plant and animal food raw materials [18]. It was established [18] that the maximum losses of the mass fraction of ascorbic acid and color changes occurred in the samples of vegetables stored at −10 °C. The authors showed that the rate of loss of ascorbic acid in the samples stored at −10 °C was three times higher than that in samples stored at −18 °C. It was shown that the higher the rate and the shorter the duration of freezing of vegetables, the smaller the disruption of cellular structure and the loss of cellular juice at defrosting [19]. There is very little information in the scientific literature about the influence of cryogenic processing, both in the case of cryogenic «shock» freezing and in the case of grinding of frozen vegetables, including the spicy ones; it is mainly of a contradictory non-systematic nature. The exceptions are the results of fundamental and applied studies into the influence of cryogenic freezing and finely dispersed shredding of fruits and vegetables obtained at the Kharkov State University of Nutrition and Trade [7]. The obtained results of research work over the period of 1983–2006 were implemented at the enterprises of Ukraine, Russia, and Latvia. Particularly, the scientists developed cryogenic nanotechnologies for frozen fruits [7] and carotene- [5] and chlorophyll-containing [6] vegetables, which made it possible not only to preserve vitamins and other BAS, but also to discover the hidden forms bound to biopolymers (2...2.5 times higher than in fresh products) [5–10]. The studies revealed mechanisms that occur in this case in frozen products. They showed that frozen fruits and vegetables outperform the fresh ones for BAS content by 2...2.5 times [5, 6, 8]. The studies also found hidden forms of proteins [9], pectin substances [7] in frozen (or thermally treated) and finely dispersed shredded mushrooms, fruits and vegetables. The mass fraction of the specified substances is 1.5...5.0 times higher than that in the starting raw materials [7, 9]. The research also showed that the destruction of biopolymers occurs, by 50–70 %, into monomers in this case. As for the freezing of spicy vegetables and finely dispersed ground spicy vegetables, there is no relevant information in the scientific literature. There is a suggestion to use as the innovation a cryogenic treatment of spicy vegetables (roots of celery, ginger, horseradish, and garlic). Cryogenic treatment involves a comprehensive action of cryogenic «shock» freezing and the finely-dispersed low-temperature shredding of raw materials. The comprehensive effect of these technological techniques is accompanied by the processes of cryodestruction, mechanoactivation and non-enzymatic catalysis of plant materials. In comparison with fresh spicy vegetables, the mass fraction of BAS in the obtained frozen products and frozen puree is larger by 2...3.5 times. It is not possible to obtain the specified quality of products when using traditional methods. This made it possible to develop cryogenic nanotechnologies of health supplements in the form of finely dispersed puree and frozen spicy vegetables.

3. The aim and objectives of the study

The objective of this study is to identify a complex of BAS in spicy vegetables and to design nanotechnologies for health supplements and nanoproducts using the cryogenic treatment, particularly, cryogenic «shock» freezing and finely dispersed grinding applying liquid and gaseous nitrogen. The spicy vegetables we used are roots of ginger, celery, horseradish, and garlic.

It is necessary to solve the following tasks to achieve the objective:

– to determine a complex of phytocomponents of biologically active substances (unsaturated plant aromatic substances, low molecular phenolic compounds (for rutin) and oxycinnamic acids; polyphenols – tannins, prebiotics (cellulose, pectin, protein), organic acids, etc.;

– to study the effect of cryogenic «shock» freezing at high rates until reaching different resulting temperatures in spicy vegetables and purees on the enzymatic and biochemical processes;

– to examine the influence of the processes of cryomechanochemistry, non-enzymatic catalysis during cryogenic treatment of spicy vegetables and when obtaining a nanopuree on the activation and inactivation of oxidative enzymes and retention of BAS (aromatic, phenolic, and tannic substances);

– to design the nanotechnologies for health supplements and nanoproducts from spicy vegetables that would employ cryogenic treatment, to investigate the quality of nanopuree and frozen spicy vegetables, to compare with analogues, and to develop nanoproducts with the application of health supplements and frozen products (sauces-dips, sauces-dressings, confectionery fillings – «Pan-Cake», nanodrinks, nanosorbets, marinades, etc.).

4. Materials and methods of the study

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

The scientific research was carried out at the Kharkiv State University of Nutrition and Trade (KhSUNT, Ukraine) at the Department of Technology for Processing of Fruits, Vegetables, and Milk. We performed experimental study at the research laboratory for the «Innovative cryo- and nanotechnologies of plant supplements and health-improving products» at the indicated department. The photograph of the equipment used during experimental study is given in paper [6]. We carried out cryogenic «shock» freezing in a fast-freezing experimental apparatus using as a refrigerant and an inert medium liquid and gaseous nitrogen. The apparatus serves to freeze products with a hard shell, as well as liquid products placed in special containers. The fast freezing apparatus makes it possible to change temperature in a freezer chamber in the range from −5 °C to −100 °C. The temperature of gas medium in a freezer chamber should be set manually. The device maintained it automatically throughout the experiment. It was possible to change it at any stage of the experiment if necessary. We froze spicy vegetables at a high rate from 0.5 to 10 °C per minute to the resulting temperatures inside a product of −18 °C, −25 °C, −32 °C, −35 °C. We chose the temperature of minus 60 °C as the optimum temperature in the chamber of the freezing apparatus for freezing the spicy vegetables.

We used the Robot Couper homogenizer-shredder (France) for finely dispersed grinding of spicy vegetables [6].

We manufactured nanoproducts (sauces-dressings, sauce-dips, snacks and fillings) applying the health supplements from spicy vegetables using the UNOX SPA steam convector, XVC series. The above equipment makes it possible to manufacture products in their own juice without using a vegetable oil; that makes it possible to preserve the natural taste and nutrients of fresh raw materials. Depending on the design features, a steam convector can carry out culinary treatment of products employing different treatment modes: wet steam, dry heat, overheated steam, regulated steam. Preparation of each meal in a steam convector machine proceeds without external intervention, without a need for watering or manual removal of moisture.

The materials used in the course of experimental studies are described in detail in [20].

5. Results of studying the BAS complex of spicy vegetables and the design of nanotechnologies for health supplements and nanoproducts

We selected fresh spicy vegetables (roots of ginger, celery, horseradish, and garlic), which are known for their healing, therapeutic and prophylactic properties, to develop nanoproducts and frozen supplements in the form of a puree. We determined the complex of BAS-phytocomponents of spicy vegetables (volatile unsaturated aromatic substances, low molecular phenolic compounds (for rutin and oxycinnamic acids), high molecular phenolic (tannic) substances (by tannin), L-ascorbic acid). In addition, we controlled minerals (K, Ca, Mg, P, Fe), prebiotics (cellulose, pectin, protein) and organic acids in spicy vegetables. According to Table 1, the specified complex of BAS of fresh spicy vegetables are the unsaturated aromatic substances. Their mass fraction depends on the type of vegetable and makes up from 46 to 172 by the number of aroma (in ml of Na thiosulfate). In addition, the complex of BAS of spicy vegetables includes low molecular phenolic compounds (for rutin) – from 75 to 101.4 mg per 100 g, oxycinnamic acids (by chlorogenic acid) – from 0.3 to 0.6 %, and high molecular tannins – from 0.35 to 0.4 %.

The BAS complex of spicy vegetables also includes L-ascorbic acid. Its mass fraction makes up from 28.3 to 82.3 mg in 100 g dependent on the type of spicy vegetables. Horseradish roots have the highest content of L-ascorbic acid (up to 82.3 mg per 100 g), roots of celery have the smallest content (up to 34.2 mg per 100 g). Spicy vegetables contain also prebiotics, particularly cellulose in the range of 1.0 to 4.2 %, pectin from 0.8 to 1.3 %, and protein from 2.2 to 6.5 %. In addition, spicy vegetables have a significant amount of minerals K, Ca, Mg, P, and others and not high content of simple digestible sugars (from 1.6 to 6.6 %). As we can see from Table 1, spicy vegetables have high BAS content and low content of sugars and proteins. Therefore, spicy vegetables are low-calorie foods.

Thus, we established the presence of the unique complex of BAS when studying the chemical composition of fresh spicy vegetables. A mass fraction of individual BAS in spicy vegetables – phytocomponents (phenolic compounds, aromatic substances, L-ascorbic acid) can satisfy daily or 0.5 of daily needs of the human body. The mentioned complex of BAS-phytocomponents renders fresh spicy vegetables their healing, medicinal properties (particularly, according to the scientific literature, antioxidant, detoxifying, antitumor action), contributes to strengthening of the immune system, vessels of heart and brain, and others.

We know that one of the main factors in processing of fruits and vegetables to various health supplements and food products that affect a degree of preservation of vitamins and phytocomponents – phenolic, aromatic substances and other BAS, including freezing, is inactivation of oxidative and hydrolytic enzymes. The latter contribute to destruction and oxidation of BAS of plant material and cellular juice loss. A use of various technological techniques for inactivation of enzymes (blanching, short-term immersion in water, cooking, vacuum treatment, preservation in solutions of lemon, ascorbic acid, pasteurization, etc.) are well studied. As for the influence of low temperatures on activity of enzymes during freezing, there are many issues that are studied not enough and remain open, and data obtained are controversial. We know that frozen vegetables and fruits lose a significant amount of BAS (from 40 to 50 %) and there are significant losses of cellular juice during defrosting after 6 months of storage in refrigerated chambers at –18 °C. Many Ukrainian and foreign scientists detected an effect of freezing (traditional, «shock») and freezing storage on loss of BAS and cellular juice during defrosting for different types of raw materials. In this regard, it is important to identify modes of technological processing during freezing of fruits and vegetables, which lead to irreversible denaturation and coagulation of protein globule of enzymes. In addition, it is relevant to search for processing modes during freezing, which enable blocking of active centers of enzymes. The mentioned block will not let an enzyme activity to resume during defrosting. We used cryogenic «shock» freezing in the development of nanotechnology of supplements of spicy vegetables in the form of frozen fine dispersed purees. Cryogenic «shock» freezing differs from traditional freezing by the use of high freezing rates (from 2 to 10 °C/min) and lower resulting temperatures in a frozen product (–32...–35 °C). Traditional «shock» freezing means the freezing of vegetables to –18 °C in a product. If necessary, we can subject frozen vegetables to finely dispersed low-temperature grinding.

Table 1

Content of biologically active phytocomponents, prebiotics and minerals in fresh spicy vegetables

Characteristic	Spicy vegetables			
	celery root	ginger root	horseradish root	garlic
Aromatic substances (by the number of aroma of Na thiosulfate)	46.4...50.2	120.4...135.0	150.6...172.0	144.5...160.1
Low molecular phenolic compounds (for chlorogenic acid), mg per 100 g	315.2...345.6	380.6...395.6	564.2...580.6	305.2...328.4
Flavanol glycosides (for rutin), mg per 100 g	102.3...124.6	92.2...101.4	75.2...89.2	80.4...95.2
High molecular phenolic (tannin) substances, mg per 100 g	375.6...400.2	350.6...375.6	381.4...420.2	345.2...390.2
Ascorbic acid, mg per 100 g	31.4...35.0	35.6...42.3	60.2...82.6	28.3...34.2
Mineral substances (ash content)	1.2...1.4	1.0...1.3	1.0...1.4	1.5...1.8
Potassium, mg per 100 g	395...430	362...415	520...579	260...300
Calcium, mg per 100 g	65...80	75...92	80...119	90...120
Magnesium, mg per 100 g	25...35	35...50	40...60	30...50
Phosphorus, mg per 100 g	30...45	50...72	80...139	100...140
Cellulose, %	1.2...2.2	2.7...4.2	2.8...4.0	1.0...1.4
Protein, %	2.2...2.5	2.4...3.2	2.5...3.0	4.0...6.5
Pectin substances, %	0.9...1.2	0.9...1.3	1.0...1.3	0.8...1.0
Total sugar, %	1.6...3.0	1.7...2.9	4.0...5.6	3.0...3.9
Glucose + Fructose, %	2.5...3.4	2.6...3.2	2.0...4.0	3.2...5.0
Organic acids, %	0.1...0.2	0.1...0.2	0.1...0.2	0.1...0.2
Dry matter, %	12.5...14.0	22.0...26.0	23.0...25.0	30.0...32.0

The crystalline structure formed in intensive cryogenic processing of spicy vegetables during a «shock» freezing (with a use of gaseous nitrogen) and fine dispersed grinding differs from typical one of traditionally frozen puree. In addition, enzymatic and non-enzymatic, as well as oxidative processes and BAS changes, changes in biopolymers, and nanoassociates (or nanocomplexes) proceed differently. The listed processes with a use of cryogenic «shock» freezing at –35 °C (in the middle of a product) compared with shock freezing at –18 °C will occur in different ways, which requires additional research. In this regard, the task of the work was to study an influence of cryogenic processing with a use of cryogenic equipment for freezing and fine dispersed low temperature grinding on enzymatic and biochemical processes in spicy vegetables. We carried out cryogenic processing by liquid and gaseous nitrogen as a refrigerant and an inert medium. We carried out a comparison with the traditional «shock» freezing and grinding.

This work, for the first time, studies the features of enzymatic, biochemical and cryomechanical processes in the development of nanotechnology for supplements in the form of frozen finely dispersed puree of spicy vegetables using the cryogenic «shock» freezing and low temperature grinding.

As we can see from Table 2, enzymatic processes in spicy vegetables occur in different ways at cryogenic «shock» freezing and at finely dispersed grinding. We established the activation of oxidative enzymes (peroxidase and polyphenol oxidase) of spicy vegetables during cryogenic «shock» freezing with high rates at freezing to –18 °C. The activity of enzymes was 1.3...1.4 times higher than for initial fresh raw materials. We showed also that activity of oxidative enzymes increases in 2.5...4.5 times (for peroxidase) and 2.3...3.3 times (for polyphenol oxidase) at further fine dispersed low temperature grinding of frozen vegetables.

That is, at low temperatures, activation of enzymes is similar to activation of enzymes in heat treatment of plant raw material. The established activation in cryogenic processing is a result of cryodestruction processes and a more complete extraction of enzymes from a bound state, as well as activation by small crystals of ice of active centers of enzymes. We established that complete inactivation of oxidative enzymes occurs during cryogenic «shock» freezing of spicy vegetables with a use of high rates to temperature in the middle of the product of –32...–35 °C. We established mechanisms of the process. We used the obtained results in development of nanotechnologies of supplements in the form of frozen fine dispersed purees and frozen vegetables.

Table 2

Influence of temperature of cryogenic «shock» freezing and low temperature grinding on activity of oxidative enzymes of spicy vegetables

Product	Activity			
	peroxidase		polyphenol oxidase	
	ml 0.01 N iodine to DM	% to starting material	ml 0.01 N iodine to DM	% to starting material
Celery root				
Fresh (initial raw material)	28.3	100	26.7	100
Frozen to –18 °C	37.4	135.4	34.5	134.2
Cryopaste from celery root frozen to –18 °C	86.6	311.8	82.0	325.3
Cryogenically «shock» frozen to –35 °C	0	0	0	0
Cryopaste from celery root cryogenically «shock» frozen to –35 °C	0	0	0	0
Ginger root				
Fresh (initial raw material)	40.6	100	32.7	100
Frozen to –18 °C	55.5	136.6	40.2	135.2
Cryopaste from ginger root frozen to –18 °C	125.3	305.2	136.0	318.6
Cryogenically «shock» frozen to –35 °C	0	0	0	0
Cryopaste from ginger root cryogenically «shock» frozen to –35 °C	0	0	0	0
Horseradish root				
Fresh (initial raw material)	90.5	100	23.8	100
Frozen to –18 °C	120.4	130.5	40.1	131.2
Cryopaste from horseradish root frozen to –18 °C	407.7	450.5	54.6	229.1
Cryogenically «shock» frozen to –35 °C	13.5	15.0	0	0
Cryopaste from horseradish root cryogenically «shock» frozen to –35 °C	15.5	17.0	0	0
Garlic				
Fresh (initial raw material)	28.0	100	13.6	100
Frozen to –18 °C	37.2	134.8	18.8	130.2
Cryopaste from garlic frozen to –18 °C	62.4	252.5	37.5	275.7
Cryogenically «shock» frozen to –35 °C	0	0	0	0
Cryopaste from garlic cryogenically «shock» frozen to –35 °C	0	0	0	0

We established falsity of the existing opinion about a low content of aromatic substances (essential oils, ketones, aldehydes and phytoncides) and low molecular BAS in spicy vegetables in hidden (bound) forms by biochemical, chemical and spectroscopic research methods. We established that grinded spicy vegetables take full storage of vitamins, aromatic substances, phenolic compounds. and other BAS at cryogenic «shock» freezing (with a use of liquid and gaseous nitrogen) to temperature in a product of –32...–35 °C at high rates (from 0.5 to 10 °C/min). In addition, cryogenic processing of spicy vegetables helps to extract hidden (bound) forms of BAS. We showed that there is a more complete extraction of BAS. Their mass fraction in frozen products is 1.5...2.6 times higher than that in fresh vegetables (Table 3, Fig. 1).

We can see that the quality of frozen spicy vegetables exceeds the quality of fresh vegetables and the quality of known analogues by 1.8...2.6 times. The increase occurs due to the more complete extraction of BAS, particularly, aromatic volatile substances, phenolic compounds, tannins, L-ascorbic acid from a bounded with biopolymers form to the free form.

Table 3

Influence of cryogenic «shock» freezing and low temperature grinding of spicy vegetables on BAS content when obtained from supplements in the form of puree

Product	Mass fraction							
	aromatics (by the number of aroma)		phenolic compounds (for chlorogenic acid)		tannins (for tannin)		L-ascorbic acid	
	ml of Na thiosulfate	starting material	mg per 100 g	starting material	mg per 100 g	starting material	mg per 100 g	starting material
Celery root								
Fresh	50.2	100.0	320.0	100.0	400.2	100.0	32.0	100.0
Frozen to –18 °C	45.0	90.1	310.0	98.2	380.0	95.0	30.8	96.2
Frozen to –18 °C and finely-dispersed ground	62.4	120.4	392.0	125.6	450.4	125.1	41.8	130.6
Frozen to –35 °C	128.6	251.5	480.0	150.0	592.0	145.0	65.8	205.6
Frozen to –35 °C and finely-dispersed ground	161.7	322.2	540.0	171.2	600.6	180.2	86.9	271.7
Ginger root								
Fresh	120.4	100.0	395.0	100.0	350.0	100.0	42.0	100.0
Frozen to –18 °C	110.8	92.0	377.2	95.5	343.7	98.2	39.9	95.2
Frozen to –18 °C and finely-dispersed ground	157.0	130.4	508.8	128.8	438.9	125.4	55.6	132.4
Frozen to –35 °C	211.9	176.0	632.8	160.2	544.6	155.6	70.8	168.6
Frozen to –35 °C and finely-dispersed ground	313.1	260.1	720.5	182.4	623.7	178.2	87.7	208.9
Horseradish root								
Fresh	172.0	100.0	564.0	100.0	380.4	100.0	70.2	100.0
Frozen to –18 °C	155.5	90.4	497.5	88.2	346.9	91.2	59.9	85.4
Frozen to –18 °C and finely-dispersed ground	190.2	110.6	595.6	105.6	414.3	108.9	71.3	101.6
Frozen to –35 °C	255.6	148.6	802.6	142.3	572.9	150.6	122.4	174.4
Frozen to –35 °C and finely-dispersed ground	284.5	165.4	894.5	158.6	628.4	165.2	140.8	200.5
Garlic								
Fresh	160.4	100.0	305.4	100.0	345.2	100.0	30.2	100.0
Frozen to –18 °C	148.2	92.4	287.1	94.0	312.1	90.4	26.9	89.2
Frozen to –18 °C and finely-dispersed ground	170.9	106.6	337.5	110.5	388.4	112.5	31.9	105.6
Frozen to –35 °C	241.2	150.4	444.1	145.4	471.9	136.7	41.1	136.2
Frozen to –35 °C and finely-dispersed ground	258.6	161.2	520.7	170.5	570.3	165.2	59.1	195.6

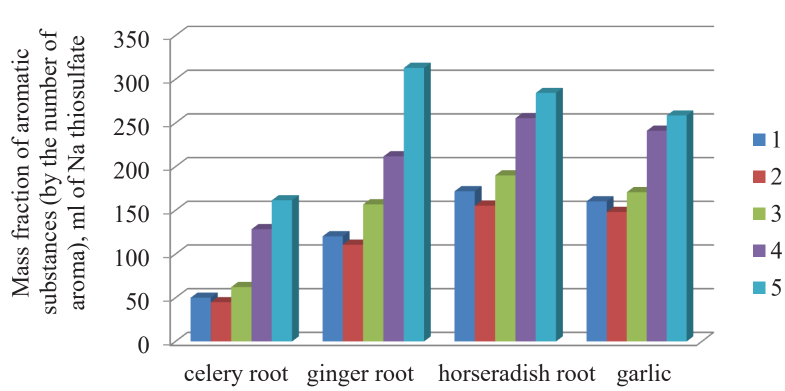

Fig. 1. Influence of cryogenic «shock» freezing and finely dispersed low-temperature grinding on the content of aromatic substances when obtaining the nanostructured puree from roots of celery, ginger, horseradish, and garlic, where 1 — fresh vegetables, 2, 3 — frozen to –18 °C (2) and finely dispersed ground spicy vegetables (3), 4, 5 — frozen to –35 °C (4) and finely dispersed ground spicy vegetables (5)

We should note that no loss of cellular juice occurs during defrosting of spicy vegetables. This indicates a complete inactivation (analogous to oxidizing enzymes) of hydrolytic, cytolytic and proteolytic enzymes. The obtained data of studies of frozen spicy vegetables became the basis for development of cryogenic technology of frozen spicy vegetables and purees of them. We showed also that there is an even more complete (by 1.7...2.2 times) extraction of hidden forms of low molecular BAS (Table 3, Fig. 3) in fine dispersed grinding of frozen spicy vegetables. We extracted the largest amount of volatile aromatic substances from roots of celery (3.2 times), because of its morphological structure and chemical composition characteristics.

We revealed also that there is a slight loss of BAS (from 2 to 10 %) at freezing the spicy vegetables to a temperature of –18...–20 °C. BAS losses at the specified temperatures of freezing a product occur due to the activation of oxidative enzymes. The enzymatic activity of spicy vegetables frozen to a temperature of –18...–20 °C is 30...35 % higher than that of fresh vegetables (Table 2). The spectroscopic method in the study of infrared spectra (Fig. 2) confirmed the results of experimental studies obtained by chemical methods.

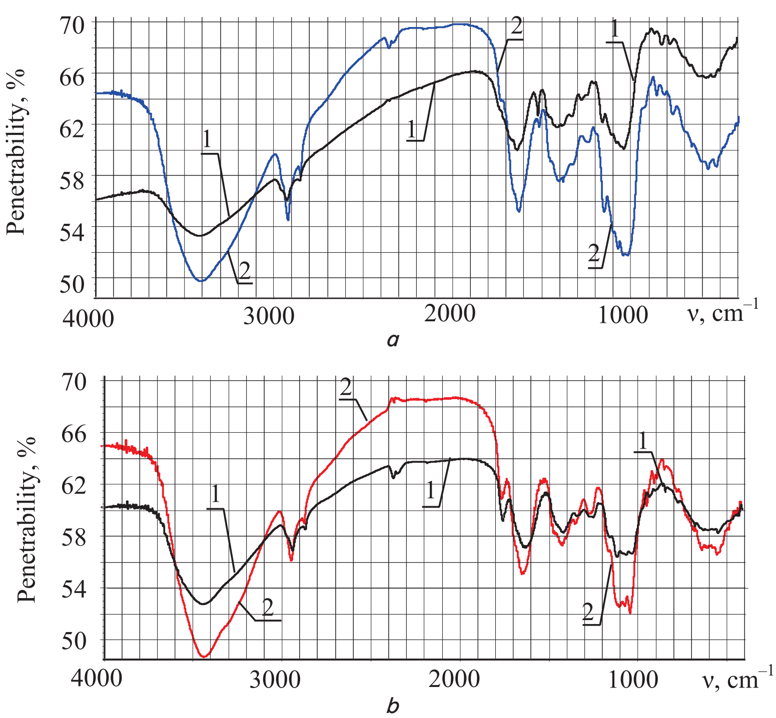

Fig. 2. Infrared spectra of roots of celery, ginger, and finely dispersed frozen purees obtained from them using the cryogenic «shock» for the frozen and finely dispersed low-temperature grinding: *a* — roots of celery, *b* — roots of ginger; 1, 2 — spicy fresh vegetables (1) and purees (2)

The comparison of IR spectra of fine dispersed purees of spicy vegetables of roots of celery and ginger and fresh vegetables indicates that there is a decrease in intensity of spectra in the frequency range from 3,200 to 3,650 cm^{-1}. This region is characteristic for valence fluctuations of functional groups –OH, which participate in formation of intermolecular and intra molecular hydrogen bonds. These bonds are parts of free and bound water, «biopolymer-BAS» nanocomplexes such as phenolic compounds, tannins, sugars, amino acids, and other BAS. This indicates destruction of mentioned hydrogen bonds, cryo-and mechanical degradation of «biopolymer-BAS» nanocomplexes, disaggregation and mechanolysis of biopolymers or associatives and nanocomplexes with low molecular BAS. In addition, there is an increase in intensity of spectra in the frequency region υ=2,900...1,600 cm^{-1}, υ=1,750...1,720 cm^{-1}, υ=1,470...1,355 cm^{-1}, υ=550...450 cm^{-1}, which are characteristic for valence fluctuations of the functional groups $-CH_3$, $-NH_2$, $-NH_3$, –C–O–, as well as for unsaturated double bonds. This indicates that there is a significant increase and transition of low molecular BAS, particularly aromatic substances, phenolic compounds, from the bound hidden form to the free from at cryogenic processing and fine dispersed grinding in raw material.

Based on the experimental data obtained, we developed nanotechnologies of supplements of spicy vegetables in the form of fine dispersed puree and frozen spicy vegetables in the form of chopped pieces. The new technologies differ from traditional one by the fact that they completely exclude heat treatment of vegetables and a use of liquid and gaseous nitrogen as a refrigerant and an inert medium. Technologies include cryogenic «shock» freezing at high rates (from 0.5 to 10 °C per minute) to lower temperatures in the middle of a product –32...–35 °C than during traditional «shock» freezing (to –18...–20 °C). The new technologies make it possible to receive frozen spicy vegetables and purees from them with a record amount of aromatic, phenolic and other biologically active substances. The mass fraction of BAS in the new products exceeds the amount of BAS in fresh vegetables by 2...3.2 times, as well as the amount of BAS in the Ukrainian and foreign analogues (Table 3, Fig. 3). We can see that there is no loss of cellular juice during defrosting. Complete inactivation of oxidative enzymes provides a longer storage life of spicy vegetables, which is 12 months without BAS loss during storage and defrosting. There are various types of health-improving products with a high content of natural BAS developed with a use of frozen spicy vegetables and purees of them. Such as dressing sauces, sauces-dips, confectionery fillings, particularly «PanCake», nanodrinks, snacks, spices for meat and fish dishes, spicy additives in nanosorbets, etc. We tested the new technologies under industrial setting at NPP «KRIAS» (Ukraine), LLC «KhPK» (Ukraine), «FIPAR» (Ukraine), etc. We have devised and received the approval of TU and TI for «Frozen Spicy Vegetables and Purees made from them» from the Ministry of Health of Ukraine, permitting their use for manufacturing the health-improving products.

6. Discussion of results of studying the BAS complex of spicy vegetables and designing the nanotechnologies for health supplements

The advantage of the study is obtaining of frozen spicy vegetables, which exceed fresh spicy vegetables by 2...2.5 times in the content of natural aromatic substances and phyto-components – phenolic compounds, polyphenols, and other BAS. We discovered the hidden forms of BAS of spicy vegetables. We worked out the technological modes and developed technologies for health supplements in the form of fine dispersed purees of spicy vegetables and frozen spicy vegetables. It became possible, by using the obtained frozen foods and spicy supplements, to develop a wide range of health products that exceed known analogues in terms of quality.

The obtained research results give possibility to get a new look at the freezing of fruits, vegetables and fine dispersed frozen purees of them. It is worth to note that each plant material is a very complex heterogeneous fine dispersed system, which includes up to 1,000 different substances. In addition, fruits and vegetables are breathable foods. During processing and storage of fruits and vegetables there are complex enzymatic, biochemical, chemical, and other processes that we need to be able to manage. The development of nanotechnology with a use of cryogenic processing of spicy vegetables includes innovations, a special approach, which constitute the «know-how» of this development.

Disadvantages, difficulties and features of processing of spicy vegetables include losses (from 20 to 80 %) of volatile aromatic substances, which have unique healing properties. The latter are due to presence of BAS in them, which are difficult to create artificially. Aromatic compounds of spicy vegetables are not a single substance, but a group (or a mixture) of different chemical nature of biologically active unsaturated volatile substances. Volatile substances include ketones, aldehydes, higher alcohols, terpenoids, esters, flavonoids, tannins and other substances that are components of spicy vegetables. These substances are natural antioxidants, detoxicants, immunomodulators and preservatives in development of a wide range of products for a healthy diet.

The volumes of vegetable cultivation are up to 200 thousand tons per year in Ukraine. Importing resolves the problem of shortage of spicy vegetables of domestic production. Thus, an increase in the cultivation and harvesting of spicy vegetables and the development of processing technologies for supplements and products that make it possible to preserve the healing BAS of fresh raw materials are important tasks.

The proposed method of cryogenic processing and non-enzymatic catalysis (mechanical destruction of nanocomplexes of biopolymers with low molecular BAS) of spicy vegetables retains aromatic substances and other BAS from the starting raw materials and prevents the processes of destruction. The new method is a method of deep treatment. This makes it possible to extract the bound (hidden) forms of aromatic substances and other BAS from spicy vegetables, which have antioxidant, detoxicating, immunomodulatory and preserving effect, and to obtain products with a strong flavor.

In the future, we plan to develop a line of high quality products for the healthy diet with a stable texture and a long storage life applying the obtained supplements from spicy vegetables in the form of frozen finely dispersed purees. These products include juice nanodrinks, sauces-dressings, sauces-dips and salty fillings for confectionery, snacks, combined milk-and-plant products, etc. We plan to conduct a research employing the chemical, physical-chemical, spectroscopic, microbiological and other research methods for the development of such types of products.

7. Conclusions

1. We determined the complex of BAS-phytocomponents of spicy vegetables. We established that the specified BAS complex consists of unsaturated reactive-active aromatic substances (from 46 to 172 by the number of aroma (in ml of Na thiosulfate), low molecular phenolic compounds (from 0.3 to 0.6 %), high molecular polyphenols (from 0.35 to 0.4 %). The latter are the natural antioxidants, preservatives, which have bactericidal and immunomodulatory effects. Spicy vegetables also contain a significant number of prebiotics, particularly, cellulose (from 1.0 to 4.2 %), pectin (from 0.9 % to 0.4 %), protein (from 1.8 to 6.5 %), and low sugar content (from 1.6 to 6.6 %). The presence of BAS in the composition of 100 grams of spicy vegetables in the amount that is able to satisfy a daily need of the human body, according to authors, provides fresh spicy vegetables with therapeutic and prophylactic properties.

2. We established that enzymatic processes in spicy vegetables occur in different ways during traditional «shock» freezing (to –18 °C), cryogenic «shock» freezing (to –32...–35 °C) and finely dispersed low temperature grinding. We detected the greater activation of oxidative enzymes (peroxidase and polyphenol oxidase) of spicy vegetables, by 1.3...1.4 times, during cryogenic «shock» freezing to –18 °C in comparison with raw material. We also showed that there is a much greater activation of oxidative enzymes at subsequent finely dispersed low-temperature grinding of frozen vegetables. The activity of enzymes increased by 2.5...4.5 times (for peroxidase) and by 2.3...3.2 times (for polyphenol oxidase). We revealed the mechanisms of these processes. We also established that the inactivation of oxidative enzymes occurs at the cryogenic «shock» freezing of spicy vegetables that employs high rates to a temperature in the middle of a product of –32...–35 °C. We defined the inactivation mechanisms. We used the obtained results to develop the nanotechnologies of frozen spicy vegetables and health-improving finely dispersed supplements made from them.

3. We established that the use of liquid and gaseous nitrogen makes it possible to preserve vitamins, aromatic substances, phenolic compounds, polyphenols and other BAS in full during cryogenic «shock» freezing at high rates (from 0.5 to 10 °C/min) to the temperature in a product of –32...–35 °C. The use of cryogenic treatment contributes to the more complete (by 1.5...2.5 times) extraction of BAS of fresh spicy vegetables from the hidden, bound with biopolymers, form. The quality of frozen spicy vegetables exceeds the quality of fresh vegetables and the quality of analogues by 1.5...2.5 times. We revealed the hidden forms of aromatic and phenolic compounds in spicy vegetables. We showed that the extraction of hidden forms of low molecular BAS is better when applying the finely dispersed grinding of frozen vegetables. It is greater by 1.7...2.2 times.

4. We developed the nanotechnologies for cryogenic «shock» freezing of spicy vegetables in the form of chopped pieces and finely dispersed purees. The new technologies make it possible to obtain frozen spicy vegetables and supplements in the form of finely dispersed frozen purees with a record amount of aromatic, phenolic compounds, and other BAS. The quantity of BAS in the new technologies of supplements and frozen spicy vegetables exceeds the mass fraction of BAS in fresh spicy vegetables and in the Ukrainian and foreign analogues by 2...3.2 times. Our study showed that there are no cellular juice losses during defrosting when using the new technologies for frozen spicy vegetables. This is explained by the complete inactivation of oxidative and hydrolytic enzymes of spicy vegetables during cryogenic treatment.

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