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# THE NEW ABOUT CAROTENOIDS DURING THE REFRIGERATED PROCESSING OF CAROTENE-CONTAINING VEGETABLES AND BERRIES WITH THE USE OF CRYO- AND MECHANICAL DESTRUCTION

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*The method of refrigerated processing carotenoid herbal materials into nanostructured frozen puree is developed. This process includes the use of complex influence of cryogenic "shock" freezing and low-temperature grinding to raw materials. It allows us to get a fine-dispersed additives with a record content of carotenoids and other biologically active substances in a free form (2,5-3,5 times more than it is liberated from the state bound with biopolymers by means of traditional methods of extraction from plant raw material).*

***Keywords:*** *cryogenic freezing, carotenoids, carotene-containing vegetables, fine-dispersed grinding, mechanoactivation, cryodestruction, hydrophilic carotenoid form.*

# НОВЕ ПРО КАРОТИНОЇДИ ПІД ЧАС ХОЛОДИЛЬНОЇ ПЕРЕРОБКИ КАРОТИНОВМІСНИХ ОВОЧІВ ТА ЯГІД ІЗ ВИКОРИСТАННЯМ КРІОМЕХАНОДЕСТРУКЦІЇ

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*Розроблено холодильний спосіб переробки каротиновмісної рослинної сировини в наноструктуроване заморожене пюре, який включає використання комплексного впливу на сировину процесів кріогенного «шокового» заморожування та низькотемпературного подрібнення, що дозволяють отримати тонкодисперсні добавки з рекордним вмістом каротиноїдів та інших БАР у вільній формі (у 2,5…3,5 рази більше, ніж вивільняється із зв'язаного з біополімерами стану за умови використання традиційних методів екстракції з рослинної сировини).*

***Ключові слова:*** *кріогенне заморожування, каротиноїди, каротиновмісні овочі, тонкодисперсне подрібнення, механоактивація, кріодеструкція, гідрофільна форма каротиноїдів.*

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# НОВОЕ О КАРОТИНОИДАХ ПРИ ХОЛОДИЛЬНОЙ ПЕРЕРАБОТКЕ КАРОТИНОСОДЕРЖАЩИХ ОВОЩЕЙ И ЯГОД С ИСПОЛЬЗОВАНИЕМ КРИОМЕХАНОДЕСТРУКЦИИ

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*Разработан холодильный способ переработки каротиносодержащего растительного сырья в наноструктурированное замороженное пюре, который включает использование комплексного воздействия на сырье процессов криогенного «шокового» замораживания и низкотемпературного измельчения, позволяющих получить тонкодисперсные добавки с рекордным содержанием каротиноидов и других БАВ в свободной форме (в 2,5…3,5 раза больше, чем высвобождается из связанного с биополимерами состояния при использовании традиционных методов экстракции из растительного сырья).*

***Ключевые слова:*** *криогенное замораживание, каротиноиды, каротинсодержащие овощи, тонкодисперсное измельчение, механоактивация, криодеструкция, гидрофильная форма каротиноидов.*

**Introduction.** One of the most progressive methods of processing and preserving fruit and berries in international practice is freezing, which provides the most complete preservation of vitamins and other biologically active substances. Approximately 350 million tonnes from all the world food resources equal to nearly 4500 million tons are subjected to refrigerated processing. The decisive factor determining the quality of frozen foods is the freezing speed. The best characteristics of a shelf life and a quality after heating are typical for fast-frozen foods [4].

Nowadays there are two technologies of fast freezing in the world such as "shock" freezing (using the cold air's draught) and cryogenic "shock" freezing (using the liquified gas). The first of them is widely used in food processing industry. The second one (cryogenic technology) exceeds "shock" freezing using cold air flow. It provides super-fast freezing of a product due to the direct influence of cryogen (cryogenic liquid) on freezable food. Environmentally friendly liquefied nitrogen or carbon dioxide can be used as cryogen [2; 5].

Despite the obvious advantages of cryogenic "shock" freezing compared with a freezing by cold air flow such as ultra-fast freezing speed 3...10 times faster, minimal moisture losses after heating 5...10 times less, the use of environmentally safe natural (non-synthetic) cryogens. Nowadays neither in Ukraine nor in the CIS countries cryogenic freezing has found a wide practical application in the food industry. Now it is being experimentally developed. In the world practice the improvement of the technology of manufacturing fast frozen products is directed towards the transition from the technology of "shock" freezing to the technology of cryogenic freezing. That is why the development of the fast freezing technology based on the use of gaseous or liquid nitrogen as cryogen is actual.

Among the products from carotene-containing vegetables and berries a special attention has to be paid to the convenience foods in the form of puree, including the frozen foods, which can be administered into the various food products (creams, jellies, desserts, sambucs, ice cream, cheese desserts and food products for infants). They can be used as enrichers of natural carotenoids and other biologically active substances which are simultaneously food coloring agents, thickeners and structure-builders. In Ukraine there is a shortage of these additives. That is why it is actual to develop cryotechnology of carotenoid additives in the form of a frozen puree including carotene-containing vegetables and berries (CCVB) with a high degree of carotenoids preservation, some of which are in a hydrophilic form. The speed and the final freezing temperature are the decisive factors determining the quality of frozen products.

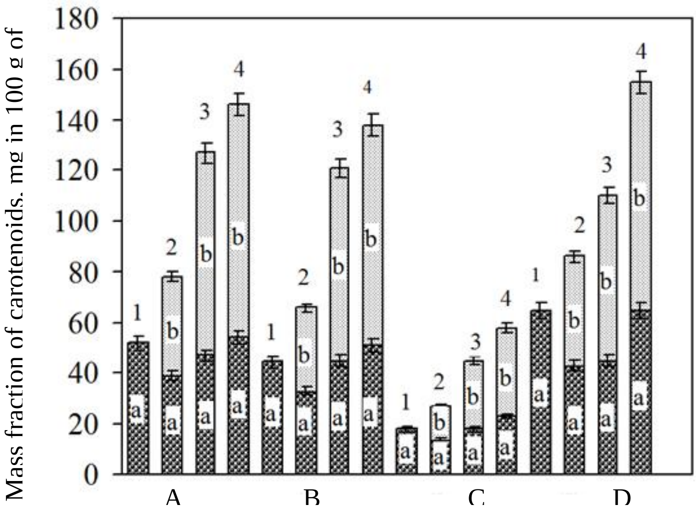
There is almost no literature data concerning the effect of freezing to carotenoids in carotene-containing vegetables and berries. They are limited mainly by the statement of carotenoid losses in some freezing modes and during the storage of frozen foods for some species of herbal materials at low temperatures. Our task was to identify the influence patterns and mechanisms of freezing (with slow and high speed during the cryogenic "shock" freezing), and low-temperature grinding on the safety of carotenoids and activation of its hydrophilic properties during the processing of carotene-containing vegetables and berries.

**Objects and research methods** are technological processes of refrigerated processing (low-temperature freezing and grinding) of carotene-containing vegetables and berries during the preparation of frozen herbal additives. In this research conventional physical-chemical, chemical, spectroscopic methods and the methods of mathematical processing of experimental data with the use of computer technologies were used. The researches were carried out in a scientific-research laboratory of "Innovative cryo- and nanotechnologies of herbal additives and healthful products" of the Chair of the technology of fruits, vegetables and milk processing of Kharkov State University of Food Technology and Trade.

**Results and discussion.** The influence of freezing with slow speed (0,1, 0,2° C/min) to the temperature -18...-20° C and cryogenic "shock" freezing with the speed 1, 2, 5, 10, 20, 30, 40, 50° C/min to the temperature -32, -35, -40° C with the use of nitrogen gas on carotenoids of CCVB (carrot, pumpkin, sweet pepper, sea buckthorn), and other biologically active substances (L-ascorbic acid, low molecular phenolic compounds, tannins) was studied. The cryogenic "shock" freezing was provided with the use of a cryogenic software freezer, which was developed and produced jointly by the National Aerospace University "KhAI" and Kharkov State University of Food

Technology and Trade. Fine-dispersed grinding of the frozen CCVB was carried out on the low-temperature chopper-activator (made in France).

We are the first in international practice who established the common factors of carotenoid (CR) growth and transformation during the freezing at different speed and fine low-temperature grinding of CCVB. It was shown that comparing with raw materials (fresh CCVB) during freezing the quantitative increase of carotenoid mass fraction (2,0...2,5 times) occurs, depending on freezing speed and the form of CCVB (picture 1). It was found that at low temperature grinding and delivery of cryopuree from CCVB allowed to obtain even greater (3...3,5 times) mass fraction of carotenoids that depends on the type of CCVB [1; 3].




**Picture 1. The influence of low-temperature freezing and grinding of carotene-containing vegetables and berries to carotenoids: 1 – raw (fresh) carotene-containing vegetables and berries; 2, 3 – CCVB frozen at slow (2) speed to -18...-20° C and at high (3) speed 10° C/min to -35° C; 4 – CCVB which were frozen to -35º C after low-temperature grinding; a, b – fat-soluble (a) and soluble (b) forms of CR; A – carrot, B – pumpkin, C – sweet pepper, D – sea buckthorn.**

At the same time mass fraction of CR in a water-soluble form is increasing. It means the activation of CR hydrophilic properties. The relation between fat-soluble and water-soluble forms of carotenoids in the frozen product is 1:1 (if the speed of freezing is slow) and 1:1,5...1,7 (in case of cryogenic "shock" freezing and a low-temperature grinding).

The mechanism of increasing and transformation of carotenoids to the hydrophilic form during freezing was discovered. In our opinion, it is the destruction of carotenoid complexes with biopolymers (proteins, cellulose, pectins, starch) and the transition of some carotenoids from the bound form to the free one due to the destruction of hydrogen bonds and weakening of inductive interaction. Besides, both during freezing and heat processing water-soluble CR forms can be formed due to the creation of complexes between the CR and biopolymers (proteins, carbohydrates, etc.), phenolic compounds and their fragments with hydrophilic properties [1**;** 5].

It is shown that frozen carotene-containing vegetables and berries, by their quality, and content of carotenoids, exceed raw vegetables 2,0...2,5 times, but frozen fine dispersed cryopurees –3,0...3,5 times (Table).

Table

**Comparative characteristics of quality of fresh and frozen carotene-containing vegetables and berries and fine dispersed cryopuree from them**

| Product name | Mass fraction of | | | |
|---|---|---|---|---|
| | L-ascorbic acid, mg/100 g | phenolic compounds (for chlorogenic acid) mg/100 g | flavonol glycosides (for routine) mg per 100 g | carotene, mg per 100 g |
| Carrot | 8,2 | 146,0 | 50,1 | 7,5 |
| Frozen carrot (pieces) | 12,5 | 196,0 | 74,2 | 14,6 |
| Carrot cryopure | 18,3 | 242,2 | 104,8 | 20,8 |
| Fresh pumpkin | 5,0 | 88,1 | 43,1 | 8,0 |
| Frozen pumpkin (pieces) | 8,2 | 126,9 | 69,4 | 16,4 |
| Pumpkin cryopure | 11,2 | 177,2 | 92,0 | 28,8 |
| Fresh sweet pepper | 300,4 | 120,3 | 29,6 | 2,9 |
| Frozen sweet pepper (pieces) | 450,2 | 175,2 | 42,1 | 5,6 |
| Sweet pepper cryopure | 753,8 | 207,5 | 53,3 | 9,7 |
| Fresh sea buckthorn | 201,5 | 640,0 | 92,2 | 25,0 |
| Frozen sea buckthorn (berries) | 300,4 | 860,2 | 142,3 | 48,2 |
| Sea buckthorn cryopure | 405,6 | 1289,2 | 198,2 | 70,0 |

**Conclusions.** As a result, the experimental data allowed us introduce a new influence of freezing and low-temperature grinding processes during the processing of herbal materials to carotenoids and activation of their hydrophilic properties. The use of freezing and low temperature grinding during the processing of carotene-containing materials leads to destruction of carotenoid complexes with biopolymers, which is manifested in the increase of mass fraction of carotenoids (2,0...2,5 times depending on the speed of freezing and 3,0...3,5 times during the low temperature grinding), and also the activation of the hydrophilic properties – transformation of a portion (50...70%) of carotenoids into a water-soluble form. Such technological methods as cryogenic "shock" freezing and fine-dispersed low temperature grinding during the processing of CCVB was used in developing the technology of frozen carotenoid semises – additives – colorings – enrichers with natural BAS and carotenoids, half of which is in water-soluble form. Furthermore, new additives can be used in the manufacture of various food products as natural structurants and thickeners.

On the base of these results, the technology, technological schemes and regulatory documentation for a frozen carotenoid additives were created and approved at the Ministry of Health of Ukraine (ТУУ 10.3-01566330-281:2013). The technologies and pilot scale batches of new additives and the products with their use (JSC "Khladoprom" SPF "FIPAR" SPP "Cryas-1") were approbated in a production environment.

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