

*Представлено дослідження хімічного складу ягід журавлини. Визначено фракційний склад органічних кислот, цукрів та фенольних речовин, що містяться в продуктах переробки журавлини. Експериментально підтверджено позитивний вплив ферментативного каталізу на вилучення фенольних речовин та якість соку з журавлини. Встановлені раціональні умови проведення ферментативного каталізу. Запропоновано комплексну переробку ягід журавлини з використанням соку в технології фруктових соусів, а вичавок сокового виробництва – у технології безалкогольних напоїв та м'ясних паштетів*

*Ключові слова: ферментні препарати, фенольні сполуки, леткі ароматичні речовини, журавлина, сік, соус, напої, паштети*

*Представлено исследование химического состава ягод клюквы. Определены фракционный состав органических кислот, сахаров и фенольных веществ, содержащихся в продуктах переработки клюквы. Экспериментально подтверждено положительное влияние ферментативного катализа на извлечение фенольных веществ и качество клюквенного сока. Установлены рациональные условия проведения ферментативного катализа. Предложена комплексная переработка ягод клюквы с использованием сока в технологии фруктовых соусов, а выжимок сокового производства – в технологии безалкогольных напитков и мясных паштетов*

*Ключевые слова: ферментные препараты, фенольные соединения, летучие ароматические вещества, клюква, сок, соус, напитки, паштеты*

# STUDY OF THE CHEMICAL COMPOSITION OF CRANBERRY AND THE USE OF BERRIES IN FOOD TECHNOLOGY

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## 1. Introduction

Competitiveness of food products increases due to improvement of their consumer properties, diversification and introduction of new technologies, which are designed with a view to modern advancements in science and technology.

An important issue is to improve quality of food and to ensure rational use of raw materials in processing industries [1].

In recent years, the food industry has begun to focus on using natural food components, which are completely non-toxic and are capable of improving biological and consumer value of a finished product.

In world practice, manufacturers widely use natural juices, local spice-aromatic, wild raw materials, and other plant materials rich in essential micronutrients for the production of beverages of high biological value and beverages of functional purpose [2].

Berries, fruits, vegetables, and their products are natural sources of biologically active supplements (BAS). They positively affect metabolic processes in the human body, prevent obesity and play an important role in prevention and treatment of diseases of cardiovascular and nervous systems.

Wild berries, including cranberry, which have a high content of phenolic compounds, vitamin C, tocopherol, iodine, organic acids, etc. occupy a special place among them [3].

Studies into chemical composition of cranberry began at the beginning of the last century and are still conducted by researchers from North America, Canada, Finland, Norway, China, Japan, Belarus, Russia and many other countries [4]. There was no much research into chemical composition of cranberry, in particular technological potential of phenolic substances, in Ukraine.

Modern technologies make it possible to produce food products from cranberries. However, they do not use diverse and useful technological supplies of phytochemicals in full. Imperfection of technological processes, lack of information on chemical composition and therapeutic and preventive properties of cranberries, inappropriate use of waste products limits the processing of berries.

Current and promising tasks are the studies aimed at examining biologically active complex of cranberries, substantiation of the choice of biocatalysis as the most effective way of extraction of phenolic substances from raw materials into finished products during processing, rational use of

waste products and creation of food products with higher biological value based on them.

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## 2. Literature review and problem statement

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An analysis of literature revealed that data on the chemical composition of cranberries of wild and cultural varieties in some cases are given without the indication of particular variety [5, 6]. Cranberry synthesizes a certain range of chemical compounds dependent on many factors: ambient temperature, light flux, soil composition, relative humidity, oxidative stress, etc. [7]. Accordingly, the chemical composition of European cranberry (moor berry) that grows in Ukraine requires careful research.

Scientific research and publications of recent years [2–3, 8] testify to a growing interest of specialists in the use of cranberries as a source of functional ingredients. Cranberries have therapeutic and prophylactic properties [8]. The use of berries positively affects work of cardiovascular, nervous, digestive and immune systems [9].

They are widely used for treatment of atherosclerosis, thrombophlebitis, kidney and urogenital diseases, and diabetes [10].

Studies into chemical composition of cranberry confirm the content of a wide range of nutrients and biologically active substances in its composition, but they all are controversial because of complex phytochemistry of cranberries.

In cranberries, there are polyphenolic compounds – anthocyanins, leucoanthocyanins, catechins. The mentioned substances increase the activity of enzymes and improve vascular elasticity. Flavonoids and a full range of triterpene acids make cranberries a leader among products to be consumed in avitaminosis. Cranberry pectin forms solid compounds with heavy and radioactive metals and is excreted from the body [11]. Paper [12] shows that the regular use of cranberry products reduces the risk of gastric ulcer due to obstruction of the action of *Helicobacter pylori* bacteria.

Cranberries contain sugar (4–5 %), fiber (up to 2 %), pectin (1.4 %), organic acids (2.4 %), ascorbic acid, B vitamins, nicotinic acid, trace elements (iodine, iron, copper, manganese, silver) [2, 9, 13].

Cranberries can be stored fresh until the next harvest in wooden barrels filled with water [13].

A number of publications on improvement of the technology of food products with a use of cranberries and products of processing increased in recent years.

The developed technologies of production of functional beverages (nonalcohol, acidic, kvass), where cranberries are used as a biological active ingredient, make possible to refuse the use of synthetic flavors and preservatives [8, 13]. Also, there were developed technologies of yogurt production [8], yogurt was enriched with products of processing of cranberries, which contained a complex of antioxidant substances.

It is recommended to use cranberry puree, which is obtained by blending with sharp steam, to improve the nutritional value of confectionery products [12]. A well-known method of obtaining *halva* for health support purpose is the use of a composition of powders of cranberry and black chokeberry [14].

A development of the technology of production of canned condensed milk with the use of fruit and berry syrups of cranberries and blueberries is described in paper [15]. Recent scientific studies point to the expediency of using cranberry

puree in the manufacture of finishing semi-finished products of extended shelf life, with increased nutritional value [16].

The most traditional method of cranberries processing is the extraction of juice. However, a significant part of the polyphenolic compounds remains in pressed skins during production of juices, and existing technologies for the cranberry processing do not allow the integrated use of raw materials.

In addition, there are no data on studies on changes in the chemical composition and BAS in cranberries under the influence of enzyme preparations. The determinative value in the stability mechanism of the polyphenolic complex of wild berries is a fractional composition of raw polyphenols, which is influenced by a region of cultivation and technological methods of processing of raw materials, but there is no data on investigation of the effect on the extraction of phenolic substances of combination during fermentolysis of endo- and exo-enzyme activity.

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## 3. The aim and objectives of the study

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The aim of present work is to study chemical composition of cranberry gathered in Ukraine and the use of products of their processing in food technologies.

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

- investigation of peculiarities of the chemical composition and content of BAS in cranberries collected on the territory of Ukraine and products of their processing;
- identification of the composition of phenolic substances, organic acids, sugars, as well as volatile compounds of berries, juice and squashes of cranberries;
- investigation of the effect of combination at fermentolysis of endo- and exoferment activity on the extraction of phenolic substances;
- suggestion of complex processing of cranberries.

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## 4. Materials and methods to study basic physical and chemical indicators of cranberry and products of processing

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For the research, we used cranberries, which were gathered in the western and northern regions of Ukraine.

The objects of the study were cranberry berries, juice, pressed skins, as well as fruit sauce, nonalcohol beverages and meat pastes made using cranberry processing products.

We carried out determination of basic physical and chemical parameters of the investigated raw material according to commonly accepted methods: dry matter – by the method of arbitration drying, acidity – by volume titration, vitamin C – by iodometric method, phenolic substances – by the Folin-Ciocalteu method in terms of gallic acid.

A work [20] presents more detailed standardized methods of research of physical and chemical indicators of cranberries and products of their processing, as well as a method of chromatographic studies for the identification of phenolic substances, organic acids and sugars.

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## 5. Results of study of the content of biologically active substances in cranberry and cranberry juices

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We analyzed cranberries at a stage of consumer ripeness. They were spherical, red colored, they had sour, specific

taste and aroma characteristic of cranberries according to organoleptic parameters.

Study into the chemical composition of cranberries showed that they contain: water – 86...87 %, dry matter – 13.2 %, sugar – 3.65 %, pectin – 0.77 %, protopectin – 0.35 %, fiber – 1.80 % and have rather high titrated acidity (2.5 %). Carbohydrates are significant components of organic compounds of cranberries. Cranberry polysaccharides consist mainly of pectin substances and fiber. The obtained data corresponds to researches of other scientists [2, 9, 13].

The main part of soluble dry matter in cranberries is sugar, which is represented exclusively by hexoses – glucose and fructose (Table 1). Fructose predominates in cranberries. There is also sorbitol in the composition, which content is 11 % of total sugars content. The presence of sorbitol indicates therapeutic and prophylactic properties of this raw material.

Table 1

Composition of organic acids and sugars in cranberries, mg/100 g (n=3, p<0.05)

Organic acids			Sugars		Polyalcohol
citric acid	malic acid	succinic acid	glucose	fructose	sorbitol
1,662	965	312	1,683	1,819	382

In addition to sugars, presence of organic acids determines taste properties of raw material (Table 1). It is established that citric acid dominates in cranberries, and there are also malic and succinic acids. Succinic acid can act as a restoring agent and a radical-acceptor agent responsible for antioxidant protection.

Results of experimental studies confirmed that cranberries have rather high index of biological activity. They contain L-ascorbic acid, coloring and phenolic substances (Table 2).

Table 2

Content of biologically active substances in cranberries (n=3, p<0.05)

Content, mg/100 g			Biological activity, cond. unit act.
L-ascorbic acid	coloring agents*	phenolic substances	
16.60	48.70	90.00	2,840.00

Note: \* – a list of cyanidin

The main indicator, which characterizes antioxidant activity of cranberries, is a presence of phenolic substances (FS), among which coloring ones prevail (Table 2).

However, only a part of physiologically functional ingredients in berries is placed in cellular juice and turns into a soluble part during processing. A significant proportion, due to the ability of structural biopolymers of berries, which is a basis of cell walls, is in a bound state. They form protein-carbohydrate-phenolic complexes, among which polysaccharides (cellulose, hemicellulose, pectin) and phenolic compounds predominate. They are localized in skin and cell wall of raw material. This fact affects juice content of raw material and this is an obstacle to the release of useful ingredients of berries into a soluble part. The most effective way to break integrity of mentioned natural biopolymers is complex action for pretreatment of enzymes that simultaneously have pectolytic and cellulolytic action.

Previous studies identified the effectiveness of a use of multienzyme compositions (MEC) of enzyme preparations

based on enzymes of pectophoetidine and celotrine for cranberry processing. Pretreatment modes are: MEC – 1:7 (Pectophoetidine P20x: Celotrine G3x), temperature 50 °C, duration 60 minutes [18].

We carried out investigation to determine the effect of the combination method at the fermentolysis of endo- and exoenzyme activity. Investigation covered various ways of fermentolysis of a squash and their effect on destruction of cranberry structural biopolymers and extraction of phenolic and anthocyanin substances from raw material. The enzyme complex was introduced into a prepared squash and kept for 60 minutes at a fermentation temperature of 50 °C (F1). A squash was warmed to a temperature of 85±5 °C, cooled to fermentation temperature and introduced a complex of enzymes (F2). A squash was fermented at a temperature of 50 °C, warmed to a temperature of 85±5 °C, cooled and pressed (F3).

Control sample was raw juice after mechanical grinding.

Research determined the phenolic composition of cranberries in different methods of enzymatic catalysis (Table 3) and composition of anthocyanins glycosides in raw material and juices made of it (Table 4).

It was established that for the maximum extraction of phenolic substances, the best results are achieved at the simultaneous action of endo- and exoenzymes with subsequent inactivation of their action after fermentation process is completed (method F3). In this treatment, the transfer of phenolic substances to juice is 97.4 % of their content in raw material. For phenolic substances, F3 method provides the highest results for flavones and their derivatives and anthocyanins. In the case of oxycuric acids, we can achieve the maximum extraction by the action of enzymes with inactivation of their own enzymes of raw material (method F2).

We determined that anthocyanins predominate among flavonoids in berries, the content is 64 % of the content of phenolic compounds. Detected flavones and their derivatives: myrecetin-3-O-arabinozide (6.69 mg/100 g), quercetin-3-O-galactoside (10.07 mg/100 g), quercetin-3-O-arabinozide (1.84 mg/100 g), quercetin-3-O-ramozide (3.86 mg/100 g), camphterol-3-O-glycoside (1.31 mg/100 g), camphoryl derivatives (0.67 mg/100 g).

The composition of phenolic compounds of cranberries contains oxycinnamic acids. There are caffeic acid (18.47 mg/100 g) and vanillin acid (0.99 mg/100 g) in the composition.

Table 4 shows that glycosides of cyanidin and glycosides of peonidin with three carbohydrates – glucose, galactose and arabinose represent anthocyanins of cranberries represent cranberry anthocyanins.

Glycosides of peonidin predominate in cranberries with a share of 61.0 % of a total content of anthocyanins. Peonidin-3-O-galactoside predominates among glycosides of peonidin, its content is 13.94 mg/100 g (32 % of a total content of anthocyanins), the content of peonidin-3-O-arabinozide is 8.12 mg/100 g (18.7 %) and peonidin-3-O-glucoside – 4.32 mg/100 g (10.0 %). The share of cyanidin glycosides is 39 % of the total content of anthocyanins, cyanidin-3-O-galactoside predominates, its content is 8.12 mg/100 g, the content of cyanidin-3-O-arabinozide is 7.50 mg/100 g, with the lowest content – cyanidin-3-O-glucoside – 1.40 mg/100 g.

It was necessary to determine the content of aromatic compounds in juices to better investigate the chemical composition of cranberry. There were 54 compounds detected, 53 of which were identified and their quantitative composi-

tion (mg/dm<sup>3</sup>) was determined. Fig. 1 shows chromatogram of volatile aromatic compounds in cranberry juice.

Phenolic compounds in cranberry and cranberry juices, mg/100 g (n=3, p≤0.05)

Name of sample	Groups of phenolic substances	Content, mg/100 g	% of PhS content	Predominant representative	Content, mg/100 g	% of PhS content
Berry	Oxycinnamic acids	19.46	21.62	Caffeic acid	18.47	20.52
K1		23.31	25.90		21.30	23.67
F1		22.83	25.37		21.06	23.40
F2		23.42	26.02		21.52	23.91
F3		22.77	25.30		20.73	23.03
Squash		29.00	32.22		27.76	30.84
Berry	Flavones and their derivatives	24.44	27.16	Quercetin-3-O-galactoside	10.07	11.19
K1		22.02	24.47		8.36	9.29
F1		21.80	24.22		8.46	9.40
F2		23.52	26.13		9.12	10.13
F3		24.84	27.60		9.70	10.78
Squash		57.29	63.66		22.17	24.63
Berry	Anthocyanins	43.40	48.22	Peonidin-3-O-galactoside	13.94	15.49
K1		31.44	34.93		10.06	11.18
F1		34.26	38.07		10.84	12.04
F2		34.50	38.33		11.03	12.26
F3		37.40	41.56		11.87	13.19
Squash		77.97	86.63		24.79	27.54

Table 3

is (by almost 2 times) higher than the control sample.

The use of MES increases produce of juice to 75 %, but part of raw material goes to waste. A share of squash is up to 25 %. Squash is a promising source of a natural complex of BAS (Table 3, 4), its biological activity is 1m920 units. act., which indicates the expediency of its further processing.

Cranberry juice obtained by enzymatic catalysis was used in the production of fruit sauces. The determined rational ratio of the prescription components is as follows in the composition of a sauce: cranberry juice – 30 %, banana puree – 60 %, extract of cranberry squash – 10 %. Blending banana puree with cranberry juice made it possible to obtain a composition with the required structural parameters. The quality of fruit sauce is given in Table 6.

The development of receipts of non-alcohol carbonated beverages included a use of cranberry water-alcohol extracts.

There were the following directions of development of nonalcohol carbonated beverages:

- use of cranberry extracts only;
- use of cranberry extracts with the addition of flavors identical to natural;
- use of extracts of cranberry and water-alcohol tinctures of spicy aromatic raw material (monarda).

Table 7 shows quality indicators for nonalcohol beverages.

The total concentration of volatile compounds in cranberry juice is 284.81 mg/dm<sup>3</sup>. There are the following groups: alcohols – 23 compounds (117.41 mg/dm<sup>3</sup>), acids – 8 compounds (115.81 mg/dm<sup>3</sup>), aldehydes – 10 compounds (4.95 mg/dm<sup>3</sup>), ketones – 5 compounds (6.17 mg/dm<sup>3</sup>), ether – 5 compounds (3.99 mg/dm<sup>3</sup>), lactones – 3 compounds (0.78 mg/dm<sup>3</sup>), heterocyclic compounds – 1 (0.38 mg/dm<sup>3</sup>) and 1 unidentified compound (35, 32 mg/dm<sup>3</sup>). Benzyl alcohol (65.70 mg/dm<sup>3</sup>) prevails among the alcohols, benzene (87.53 mg/dm<sup>3</sup>) acid is predominant among the acids. β-methyl ionone (3.39 mg/dm<sup>3</sup>) predominates among ketones. Benzyl acetate (2.14 mg/dm<sup>3</sup>) has the highest content in the ether group. Glutacon anhydride (1.32 mg/dm<sup>3</sup>) predominates among aldehydes. γ-nonalactone (0.33 mg/dm<sup>3</sup>) predominates in the group of lactones.

Table 5 shows the results of the content of organic acids and sugars in cranberry juices obtained in the traditional way and using MES.

The obtained results (Table 5) confirm that enzymatic treatment results in a significant increase in the release of organic acids and sugars to a soluble part of juices. The content of organic acids in comparison with the control sample increases when enzymatic treatment is applied to squash: citric acid – by 1.45 times, malic acid – by 1.34 times, succinic acid – by 1.24 times (Table 5).

The content of main energy components (glucose and fructose) is approximately 50:50 in juice. The content of sorbitol in juices with a use of MES

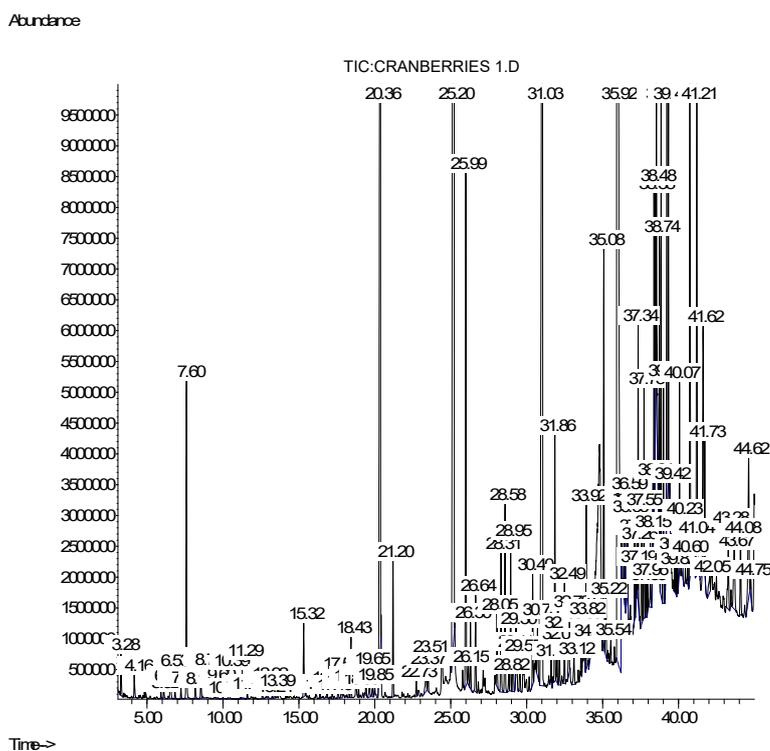


Fig. 1. Chromatogram of volatile aromatic compounds in cranberry juice

Table 4

Composition of anthocyanins glycosides in cranberries and cranberry juices

Name of samples	Representatives of anthocyanins	Mass concentration, mg/100 g	% of PhS content	Predominant representative	Mass concentration, mg/100 g	% of content of anthocyanins
Berry	Peonidin	26.38	29.31	Peonidin-3-O-galactoside	13.94	32.12
K1		19.21	21.34		10.06	23.18
F1		21.29	23.66		10.84	24.98
F2		21.25	23.61		11.03	25.42
F3		23.05	25.61		11.87	27.35
Squash		47.91	53.23		24.79	57.12

Table 5

Content of organic acids and sugars in cranberry juices, mg/100 g (n=3, p<0.05)

Sample name	Organic acids			Sugars		Polyalcohol
	citric acid	malic acid	succinic acid	glucose	fructose	sorbitol
Control	1,282.10	493.13	202.00	1,280.00	1,020.00	360.00
MES processing	1,859.00	661.00	250.00	1,516.00	1,283.00	693.00

Table 7

Quality indicators for nonalcohol beverages (n=3, p<0.05)

Mass fraction, %		Mass concentration, mg/dm <sup>3</sup>			pH, pH un.
dry matter	titrated acids	vitamin C	coloring agents	phenolic substances	
Beverages with the use of water-alcohol extracts					
9.00	0.27	3.56	17.50	45.00	3.06
Beverages with a use if water-alcohol extracts and flavors identical to natural produced by Doehler GmbH					
9.20	0.27	5.30	25.30	65.00	3.15
Beverages that contain PARS water-alcohol extracts and flavors					
8.90	0.27	7.04	28.20	70.00	3.20

Table 6

Indicators of quality of fruit sauces (n=3, p<0.05)

Product name	Mass fraction, %		Content, mg/100 g	
	titrated acids	mono- and di-saccharides	L-ascorbic acid	phenolic compounds
«BanZhur» banana-cranberry sauce	0.54	18.80	12.20	20.40

The results of experimental studies confirm that samples of nonalcohol beverages have not high organoleptic characteristics only but are characterized by appropriate quality indicators (Table 7), they have adipose and refreshing effects.

There is a method of production of meat pastes [19] with the addition of cranberries in quantities of 2.5–7.5 % to the mass of main raw material. It is established that such quantity is optimal for obtaining a product with high organoleptic,

functional and technological, structural and mechanical indicators and it increases an output of a finished product.

Meat pastes made with the addition of cranberries have high nutritional and taste properties. They are balanced by chemical composition with definite stable functional and technological, structural and mechanical characteristics.

### 6. Discussion of results of study of the content of biologically active substances in cranberry and cranberry juices

Investigation of the chemical composition of cranberries (Table 1, 2) confirmed that this raw material is a natural source of BAS, which are extremely important for the human body.

It was established that the use of biocatalytic methods in juice production contributes to the maximum removal of BAS, as a significant proportion of functional ingredients in raw material is in a bound state and is a basis of cell walls. The destruction of nativeness and integrity of protein-carbohydrate-phenolic complexes of plant raw material walls can increase production of juice and extraction of organic matter from a cell wall matrix.

We investigated the ingredient composition of fractions of phenolic compounds of cranberries collected on the territory of Ukraine and its change depending on methods of fermentolysis in the production of juice. We established the influence on the extraction of phenolic substances by combining endo- and exoenzyme activity with enzymatic squash maceration. To maximize the removal of phenolic substances, it is recommended to carry out an instantaneous warming of squash after its enzymatic treatment in order to inactivate the action of enzyme preparations.

Introduction of the proposed technological solution (method F3) to the production will give opportunity to extract the content of phenolic substances from berries to juice at most (up to 97 %), while their extraction is 88 % at mechanical grinding. The use of traditional enzymatic treatment of squash (method F1) in the production makes it possible to extract phenolic substances up to 90 %, which is only 2 % higher compared to mechanical grinding (Table 4).

It is confirmed that the treatment of cranberry squash with enzymatic preparations of complex action increases the produce of organic acids and sugars in a soluble part of juices (Table 6). A significant amount of BAS remains in cranberry (Table 4).

Based on the results of present research, we propose using complex processing of cranberry with the use of juice and vinegar in a formulation of food products, such as fruit sauces, nonalcohol beverages and meat pastes.

One of the ways to use cranberry juice is to use it as a formulation component in the production of banana mashed fruit sauces. Cranberry juice provides product with a pleasant color, prevents darkening of bananas in processing. Bananas give necessary structural and mechanical properties to the finished product.

The study proves the prospect of processing of waste of juice production and its use in the production of nonalcohol carbonated beverages and paste products.

The use of a cranberry water-alcohol extract will expand a range of nonalcohol carbonated beverages, will make

it possible to avoid a use of artificial coloring agents, to increase the quality of finished products and to apply resource-saving technologies in production.

In the course of research into paste products, we found that the addition of cranberry squashes can increase moisture binding capacity of meat by 5...8% and the yield of finished product, which is 112...116%. Paste products made according to the developed formulations have properties characteristic of traditional assortment of pastes and low-calorie content.

Thus, the use of complex processing of cranberries will make it possible to maximize the natural potential of cranberry and technological reserves of their phenolic substances.

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## 7. Conclusions

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1. We determined the chemical composition of berries of European cranberries (moor berries) gathered in Ukraine. We found the high content of titrated acids – 2.94%, pectic substances – 0.77%, the content of phenolic and colorants – 90.0 mg/100 g and 48.70 mg/100 g, biological activity is 2,840.0 cond. unit act. The use of fermentolysis

increases the quality of juice. The content of organic acids, sugars, sorbitol, phenol and colorants increases.

2. We identified the composition of phenolic substances in berries, juices and cranberry squash according to the results of chromatographic studies. They contain oxyric acids, flavones and anthocyanins. The predominant representatives are caffeic acid, quercetin-3-O-galactoside, peonidin-3-O-galactoside and cyanidin-3-O-galactoside. Among the organic acids are citric acid, malic acid and succinic acid, the citric acid is predominant. Sugars are predominantly fructose and glucose, and polypyridine is sorbitol. We determined 54 compounds among the volatile compounds that characterize the aroma of cranberry juice, and identified 53.

3. Experiments confirmed the positive effect of enzymatic catalysis on the extraction of phenolic substances and the quality of cranberry juice. To maximize the removal of phenolic substances, it is recommended to carry out an instantaneous warming of squash after its enzymatic treatment in order to inactivate the action of enzyme preparations.

4. We offered the complex processing of cranberries with the use of cranberry juice in the technology of fruit sauces, and squashes obtained during the production of juice, – in the technology of nonalcohol beverages and meat pastes as a result of the conducted researches.

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