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THERMOGRAVIMETRIC ANALYSIS OF INDICATORS OF THE PASTE BASED ON SOUR CREAM

Oksana Kochubei-Lytvynenko

Director Educational and Scientific Institute of Food Technologies National University of Food Technologies 68 Volodymyrska str., Kyiv, Ukraine, 01601 okolit@email.ua

Andrii Marynin

Laboratory of Problem research National University of Food Technologies 68 Volodymyrska str., Kyiv, Ukraine, 01601 andrii_marynin@ukr.net

Natalya Yushchenko

Department of Milk and Dairy Product Technology National University of Food Technologies 68 Volodymyrska str., Kyiv, Ukraine, 01601 YuNM_NUFT@ukr.net

Ulyana Kuzmyk

Department of Milk and Dairy Product Technology National University of Food Technologies 68 Volodymyrska str., Kyiv, Ukraine, 01601 ukuzmik@gmail.com

Maxim Lazarenko

Department of Molecular Physics Kyiv National University Taras Shevchenko 64/13 Volodymyrska str., Kyiv, Ukraine, 01601 maxs@univ.kiev.ua

Abstract

For forming structural-mechanical properties of sour milk pastes and guaranteeing their stability at storage, it is promising to use non-fried buckwheat in their recipes that allows to raise the food value of products additionally.

The aim of the researches was the study of features of the condition of moisture of sour milk pastes, based on sour cream with introducing non-fried buckwheat in the amount 5,0% of the mixture mass. A sample with modified starch E 1410 was taken as a control in the amount 1,3%.

The study of the moisture condition was realized by the thermogravimetric method using a derivatograph Q-1500D (Paulik-Erdey) (Hungry). It was established, that the content of adsorptive moisture of the sour milk paste was 34,0%, whereas in the control – 34,5%, that confirm the effectiveness of using non-fried buckwheat as a moisture-binding component. Such properties of non-fried buckwheat may be explained by the presence of starch compounds and easily accessible protein in its composition, able to hydration in the process of preparation of a component and to keeping moisture at further storage of a product.

Keywords: moisture condition, non-fried buckwheat, thermogravimetric analysis, moisture-binding properties, sour milk pastes, sour cream.

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1. Introduction

For forming structural-mechanical properties of sour milk pastes and guaranteeing their stability at storage, it is promising to introduce cereals in recipe compositions [1]. Buckwheat is remarkable among cereals for rather high content of protein -13,0...15,0 %. The peculiarity of buckwheat proteins comparing with proteins of other cereals is practically complete absence of prolamins, low content of glutelin and high content of albumin and globulins [2]. Buckwheat protein contains 18 amino acids, grains are rich with arginine and lysine, biological value of proteins is 93,1 % [3]. It is one of most full-value vegetable proteins, characterized by the high solubility and assimilability. Buckwheat proteins have a high moisture-keeping ability and emulsifying properties. These characteristics may be used for directed formation of the structure and increase of the food value of products [4].

Buckwheat starch granules [5, 6] are mainly polygonal, less often spherical and oval, and particles surface – uneven that conditions it stabilizing and moisture-keeping properties.

The general content of buckwheat food fibers is 5...11 %, among them – cellulose, nonstarch polysaccharides, lignans. Soluble cellulose prevails in buckwheat.

Food fibers and slime of buckwheat have a moisture-keeping ability. They can form chelate compounds with heavy metals and cholesterols, inhibit tumors formation, favor metabolism normalization [7].

2. Materials and Methods

Model samples of the sour milk base for pastes based on sour cream with fat mass share 20 %, acidity 80 °T were prepared for the study. Previous studies established [8] that non-fried buckwheat is preliminary comminuted to the particles size no more than 2 mm that increases accessibility of components of the internal part of a grain. Comminuted buckwheat in the amount 5,0 % was mixed with milk whey in ratio 1: 4 and thermally processed at the temperature (90±2) °C during 10...15 minutes. The prepared stabilizing component was introduced into the sour milk base at the temperature (20±2) °C in the amount 25,0 % of the mixture mass.

At more value of the hydro module the mixture consistence is liquid, excessive moisture is present. At the hydro module less than 1: 4 – the mixture consistence is dense and loses its fluidity.

The active acidity of buckwheat-whey mixture also changed depending on the buckwheat-milk whey ratio. At the hydromodule 1: 2 and 1: 3 the active acidity was 4,7 pH units, at the hydromodule 1: 4-4,5 pH units, and at the hydromodule 1: 6-4,3 pH units. The active acidity value is within limits, typical for sour milk pastes and the additional correction of buckwheat dose is not needed.

For substantiating technological parameters of buckwheat preparation, there was studied the influence of the temperature and duration of the process of buckwheat-whey mixture preparation on the moisture-keeping indicator. Based on obtained data, there was observed a proportional dependence, the higher temperature of mixture preparation, the better mixture ability to keep moisture is. The highest moisture-keeping indicator was observed at the temperature 85 °C - 73,0 %, at further temperature rise this indicator increased by 1,0 %. In further it was decided to apply the temperature of buckwheat-whey mixture preparation (90±2) °C.

The moisture-keeping ability in a sample with the process duration 15 minutes was 76,0 %, whey mixture preparation (90 \pm 2) °C. The moisture-keeping ability in a sample with the process duration 20 minutes increased only by 0,1 %.

For the control, a sample was prepared using phosphate starch E-1410 as a moisture-keeping component that is characterized by the ability to form rather viscous pasters, tolerant to pH medium changes and mechanical effects, stable at storage. The preparation of the moisture-keeping component was realized as following. Milk whey, heated to the temperature (40 ± 2) °C was added with modified starch in the amount 5,0 % at continuous mixing. The preparation of the starch-whey paster of a higher concentration is not expedient, because such solutions are characterized with a high viscosity and lose fluidity. The mixture was heated to the temperature (82 ± 2) °C and kept during 30 s, after which cooled to (20 ± 2) °C. The whey-starch paster was introduced in the sour milk base in the amount 25,0 % of the mixture mass. The content of modified starch in a ready product was

1,3 %. Such doses of introduction of stabilizing components allow to get sour milk pastes with similar indicators of dynamic viscosity.

For studying the moisture content, the most informative method is dynamic thermogravimetry, because it allows to make measurements of the temperature of the studied sample (T), measurements of its mass (TG), speed of mass change (GTG), measurements of enthalpy (DTA) synchronously.

Thermogravimetry (TG) – it is a method of thermal analysis, at which a mass change depending on a temperature is registered. TG-curve gives information about thermostability and content of a sample in the initial condition, formed at intermediate stages of the process, and about the content of a residual, if it takes place. This method is effective, only if a sample emits volatile matters as a result of different physical and chemical processes [9].

Thermogravimetry by a derivative (GTG) – in this case a derivative of a mass change in time is registered:

$$\frac{\mathrm{d}\mathbf{m}}{\mathrm{d}\mathbf{t}}$$
, (1)

as a function of a temperature or time, that is:

$$\frac{\mathrm{dm}}{\mathrm{dT}} = f(T),\tag{2}$$

or

$$\frac{\mathrm{dm}}{\mathrm{dt}} = f(t). \tag{3}$$

Differential-thermal analysis. The method of differential-thermal analysis DTA, (**Fig. 1**) is based on the comparison of properties of a sample (2) of the studied substance and thermally inert substance, taken as a standard (1). A registering parameter is a difference of their temperatures (3), measured at the cooling of a sample with a constant speed that can be presented as a functional dependence as a function of a temperature of a sample and standard. The change of a standard temperature is caused by physical transitions or chemical reactions, connected with enthalpy changes. They include: phase transitions, melting, reconstruction of the crystal structure, boiling, sublimation and evaporation, reactions of dehydration, dissociation and decomposition, oxidation and restoration, destruction of a crystal lattice and so on. These transformations are accompanied with absorption or emission of heat. In the general case phase transitions, dehydration, restorations and several reactions of decomposition are accompanied with endothermic effects, and crystallization, oxidation and several processes of decomposition – with exothermic effects.

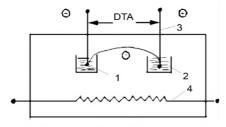


Fig. 1. Scheme of DTA method. 1 – crucible with a standard, 2 – crucible with a sample, 3 – differential thermocouple, 4 – heater

The study of the moisture condition was determined by the thermogravimetric method using a derivatograph Q-1500D (Fig. 2) (Paulik-Erdey), made in Hungry.



Fig. 2. Derivatograph Q-1500 D

The derivatograph is equipped with analytic thermoscales, the ceramic holder for samples and standard is fixed on one yoke of them. Three thermocouples are placed on the holder. Crucibles with samples can be placed on two thermocouples, a crucible with a standard – on the third one.

This device can function in two regimes: the regime of simple thermometry and the regime of differential thermometry. In the first case one simple thermocouple with a crucible with a sample is used in the work. In the second case a differential thermocouple, consisted of two simple thermocouples, connected to each other by homonymous poles, is used. A crucible with a sample is placed on one of them, on the other – with a standard substance. The choice of one of shooting regimes is realized by a switch, placed on the front panel of the device. Two devices, used for measuring a weight loss and a weight loss speed of a sample, are placed on the other yoke of scales. The principle of the work of these devices is based on magnetic induction.

The principal scheme of the derivatograph is presented on Fig. 3.

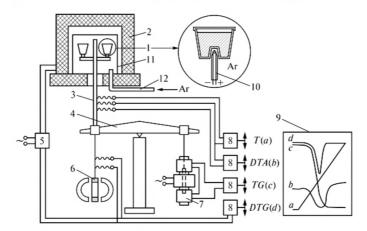


Fig. 3. Principal scheme of the derivatograph Q-1500D: 1 – crucible with the studied sample;
2 – stove; 3 – ceramic tube with thermocouples; 4 – scales; 5 – programmer of heating;
6 – sensor of a mass change speed; 7 – sensor of a mass change; 8 – output signal amplifier;
9 – derivatogram; 10 – thermocouple; 11 – protective quartz glass; 12 – feeder of inert gas;

a – temperature change of a standard (*T*); b – record of differential analysis (*DTA*); c –standard mass change (*TG*); d – standard mass change speed (*DTG*)

For measuring a weight loss, there is used a differential transformer (7), consisted of three coils, placed vertically on the same axis. The transformer is fixed immovably on the device corpus. A metal core, suspended on the scale yoke, is placed inside of the transformer. This core moves when a mass of the studied sample changes. When alternating current is fed on the middle coil (primary winding of the transformer), inductive current appear in neighboring coils (secondary winding of the transformer), connected oppositely (differentially). At the symmetric position of a core, the summary tension on coils of the secondary winding of the transformer is practically equal to null. At the core displacement the summary tension changes proportionally to the displacement value. Thus, the differential transformer reforms the movement of a scale arm in an electric signal, fixed by the registering device. The high sensitivity and measurement distinctness are typical for the differential transformer.

GTG curve is formed by a sensor of a mass change (6), consisted of a permanent magnet and inductive coil. An inductive coil is suspended on scales and placed in the field of a permanent magnet. When a sample mass changes, a coil begins to move in the homogenous magnet field. At this movement inductive current, which value is proportional to a mass change speed, appears in coil loops. Signals from thermocouples, differential transformer and inductive coil are fed through an amplifier. Thus, we synchronously get curves of the simple (T) and differential thermal (DTA) analyzes, mass loss curve (TG) and mass loss speed curve GTG) on a computer monitor [10].

Methods of the calculation of kinetic parameters of dehydration processes, such as activation energy (E) and pre-exponential factor (k_0) , are described in work [11]. The linear law of the temperature change is applied. The kinetic equation of desorption process can be signed as:

$$d\Theta / dt = -k\Theta n; k = (-d\Theta / dt) / \Theta n.$$
 (4)

The water covering degree of biopolymer molecules (Θ) changes from 1 (filling with an initial material) to 0 (after complete evaporation of moisture from a material). The reaction order (n) – integral number from 1 to 3, it is assumed that the covering degree of biopolymer molecules is known from the experiment. The constant of a reaction speed (k), can be signed as:

$$\mathbf{k} = \mathbf{k}_{0} \exp\left(-\mathbf{E} / \mathbf{RT}\right), \tag{5}$$

where R – the universal gas constant (assumed as a constant value).

Substituting equation (4) in equation (5) and finding a logarithm, we get:

$$\ln k = \ln \left[\left(-d\Theta / dt \right) / \Theta n \right] = \ln k_0 - E / RT.$$
(6)

Assuming initial conditions $\Theta t=0=1$, $\Theta t=\infty=0$ and experiment at the constant heating speed (β), that is the linear dependence of a temperature on time

$$T(t) = T_0 + \beta t \tag{7}$$

The following expressions can be signed:

$$\Theta(t) = ST / S_0; -d\Theta / dt = \beta f_3 / S_0, \qquad (8)$$

where S_0 and ST –correspondingly areas on the graph f_3 in the whole peak and the part of the peak from T to ∞ .

$$S_{T} = \int_{T}^{\infty} f_{3} dT; \ S_{0} = \int_{0}^{\infty} f_{3} dT.$$
 (9)

If all assumptions, based in this method, are correct and an order of n reaction is chosen correctly, the dependence $\ln \left[(-d\Theta/dt)/\Theta n \right]$ from the reverse temperature (6) is linear on the whole

temperature interval. Having experimental values of f_3 and β , by expressions (8) and (9), we get Θ and $d\Theta/dt$, parameters of anisothermic kinetics k_0 and E are calculated from equation (6).

The advantage of the aforesaid procedure is the use of the whole massive of experimental data, including the high-temperature part of a thermogram that is especially important at determining n order, establishing the reaction mechanism and model adequacy.

3. Results

Based on the analysis of properties of cereals, there was grounded the choice of non-fried buckwheat as a structure-forming and enriching component [5, 6]. There were established technological parameters of production of sour milk pastes with spices. There was grounded a perspective of using non-fried buckwheat in the composition of recipes of sour milk pastes as a structure stabilizer. There were determined non-fried buckwheat compatibility with a milk base by organoleptic parameters, established a recommended dose of its introduction -5,0...6,0% [8].

The dependences of TG, GTG and DTA for the sour milk paste, stabilized by modified starch and for the sour milk paste, stabilized by the buckwheat-whey mixture, were received during the study. Analyzing the dependences of the relative mass loss for the studied samples, we observe that the mass loss takes place at heating in the temperature interval 30–175 °C. It is accompanied by the peaks on GTG temperature dependences in the same temperature interval.

At heating the mass loss of samples is accompanied by the endothermic peaks on the temperature dependencies of DTA. An endothermic peak is connected with a phase transition of 1 kind – evaporation. The wide temperature interval (30–175 °C) may be connected with the fact that water is in different conditions in samples.

That is why we divided GTG dependence in three peaks with the maximums at the temperatures $T_1=111$ °C, $T_2=116$ °C and $T_3=130$ °C using Gauss distribution.

The first peak (f_1) is connected with evaporation of moisture of the physical-mechanical bond – capillary and butt one that is in rough macropores of a sample. The second and third ones (f_2, f_3) – are connected with evaporation of moisture of the physical-chemical bond and moisture of polymolecular and monomolecular hydrate layers. Water in the hydrate tunic is bound with a biomolecule by hydrogenous bonds, broken at heating.

Table 1 presents the distribution of free and bound moisture in the studied samples. According to the results of the differential-thermal analysis, there were calculated activation energy (E) and pre-exponential factor (k_0) at the temperatures of the maximal removal of adsorptionally bound moisture.

It was established, that the content of adsorptionally bound moisture is at the same level for studied samples. For a studied sample – sour milk base with buckwheat the content of free (capillary bound) moisture is by 1,0 % more comparing with the sour milk base, structured by the traditional stabilizer (modified starch). It proves the expedience of using non-fried buckwheat as a moisture-binding component in the technology of sour milk pastes.

Name of a studied sample	Distribution of values of components, %			Pre-exponential	Activation energy
	\mathbf{f}_{1}	\mathbf{f}_2	\mathbf{f}_3	factor (k ₀)	(E) kJ/mol
Sour milk paste, stabilized by modified starch	52,5	34,5	13,0	110	363
Sour milk paste, stabilized by buckwheat-whey mixture	52,0	34,0	14,0	100	330

Table 1

Summary data of thermogravimetric indicators of sour milk pastes

4. Conclusions

Based on the thermogravimetric analysis, there was realized the comparative analysis of the moisture condition in sour milk pastes with using non-fried buckwheat and modified starch. The

content of adsorptive moisture of the sour milk paste with using non-fried buckwheat is 34,0 %, that is comparable with its content in a sample of the paste using modified starch (34,5 %).

The data prove the effectiveness of using buckwheat as a moisture-binding component in the amount 6,0 % of a mixture mass.

Such properties of non-fried buckwheat may be explained by the presence of starch compounds and easily accessible protein in its composition, able to hydration in the process of preparation of a component and to keeping moisture at further storage of a product.

The obtained results will be a base for elaborating sour milk recipes on the base of sour cream using non-fried buckwheat as a structure-forming and moisture-keeping component.

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INVESTIGATION OF THE RESPIRATION RATE DURING STORAGE OF FRUIT VEGETABLES UNDER THE INFLUENCE OF ABIOTIC FACTORS

Olesia Priss

Department of technology of processing and storage of agricultural products Tavria State Agrotechnological University 18 B. Khmelnitskiy ave., Melitopol, Zaporizhia region, Ukraine, 72312 olesyapriss@gmail.com

Viktoria Yevlash

Department of Chemistry, Microbiology and Nutritional Hygiene Kharkiv State University of Food Technology and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051 evlashvv@gmail.com

Valentina Zhukova

Department of Technology of Processing and Storage of Agricultural Products Tavria State Agrotechnological University 18 B. Khmelnitskiy ave., Melitopol, Zaporizhia region, Ukraine, 72312 zhuzhuvf@gmail.com

Sergey Kiurchev

Department of structural materials technology Tavria State Agrotechnological University 18 B. Khmelnitskiy ave., Melitopol, Zaporizhia region, Ukraine, 72312 dec.tgatu@ukr.net

Valentyna Verkholantseva

Department of Processing and Food Production Equipment named after professor F. Yalpachik Tavria State Agrotechnological University 18 B. Khmelnitskiy ave., Melitopol, Zaporizhia region, Ukraine, 72312 wer.valentina@gmail.com

Iryna Kalugina

Department of restaurant and health promoting catering Odessa National Academy of Food Technologies 112 Kanatna str., Odessa, Ukraine, 65039 ik101273@gmail.com

Svetlana Kolesnichenko

Department of restaurant and health promoting catering Odessa National Academy of Food Technologies 112 Kanatna str., Odessa, Ukraine, 65039 svetlanalk@ukr.net

Alla Salavelis

Department of restaurant and health promoting catering Odessa National Academy of Food Technologies 112 Kanatna str., Odessa, Ukraine, 65039 onapta@ukr.net

Olena Zolovska

Department of restaurant and health promoting catering Odessa National Academy of Food Technologies 112 Kanatna str., Odessa, Ukraine, 65039 zolovska.lena@gmail.com

Halyna Bandurenko

Department of food technology Kyiv Cooperative Institute of Business and Law 18 Lomonosova str., Kyiv, Ukraine, 03022 gbandurenko@ukr.net

Abstract

The aim of the work was to establish the influence of most important abiotic planting factors (temperature, precipitation quantity) on the respiratory rate of fruit vegetables at storage and also a possibility of correction of respiratory metabolism by post-harvest thermal processing by antioxidant compositions. Fruits of cucumbers of the hybrids Masha and Afina, bush pumpkins Kavili and Tamino, sweet pepper of the hybrids Nikita and Hercules, tomato of the varieties Novachok and Rio Grande Original were used for the studies. It was established, that the respiratory rate of pumpkin fruit vegetables is importantly influenced by the variety specificity. The respiratory level of pumpkin vegetables directly correlates with the sum of active temperatures of the period of fruits formation and reversibly – with precipitation and hydrothermal coefficient.

The influence of the variety specificity for nightshade vegetables is leveled, and among meteorological planting conditions the important intense influence on the respiratory rate is realized by the sum of active temperatures of the period of fruits formation and ripening. Precipitation and hydrothermal coefficient have the important influence only on pepper fruits.

It was established, that the use of post-harvest thermal processing by antioxidant compositions results in inhibition of respiratory processes in fruit vegetables at storage.

Keywords: respiratory rate, storage, fruit vegetables, post-harvest thermal processing by antioxidants, abiotic factors.

© Olesia Priss, Viktoria Yevlash, Valentina Zhukova, Sergey Kiurchev, Valentyna Verkholantseva, DOI: 10.21303/2504-5695.2017.00494 Iryna Kalugina, Svetlana Kolesnichenko, Alla Salavelis, Olena Zolovska, Halyna Bandurenko

1. Introduction

Quality characteristics of fruit vegetables vary widely by years. Even at planting fruits or vegetables of the same variety, their biomechanical composition, storage life and other technological properties change under the influence of changeable abiotic factors [1]. The problem of the influence of abiotic factors on the post-harvest quality of fruit and vegetable products, connected with climate global changes becomes more serious [2]. The most important physiological process in the post-harvest period for fruits and vegetables is respiratory metabolism [3]. Just the respiratory rate reflects a reaction of fruit tissues to stress abiotic factors at planting and storage. The speed of spoilage of fruit vegetable products at storage depends on the level of respiratory processes [3]. For shortening the respiratory activity in the post-harvest period, there were elaborated the series of arrangements: decrease of the storage temperature, preliminary thermal processing, use of ethylene inhibitors and other biologically active substances [4–6]. But the influence of abiotic factors of planting of fruit and vegetable products on physiological processes in the post-harvest period was not taken into account in these researches. So, for prognosticating and correcting storage life of fruit vegetables by the post-harvest thermal processing by antioxidant compositions, their respiratory rate depending on abiotic factors was studied.

2. Materials and Methods

The observations were realized during 2005...2012 years. 2 varieties of pumpkin vegetables and 2 varieties of nightshade vegetables were used in the researches. The subject of the research was fruits of cucumbers of the hybrids Masha F1 and Afina F1, bush pumpkins Kavili F1 and Tamino F1 (**Fig. 1**), sweet pepper Nikita F1 and Hercules F1, tomato Novachok and Rio Grande Original. Vegetables were planted at Southern Zaporizhia region, Ukraine. The region of planting is charac-

terized by the high heat supply: annual sum of temperatures higher than 10 °C is 3400...3600. And humidity is the least in Ukraine: the annual hydrothermal coefficient (HTC) is 0,5...0,7 units) [7]. So, at planting all fruit vegetables, drop irrigation was used. The spray norm within $30-90 \text{ m}^3/\text{ha}$, in separate cases $-110-130 \text{ m}^3/\text{ha}$ was observed.



Fig. 1. Refrigeratory storage of bush pumpkins: *a* – Kavili F1; *b* – Tamino F1

Healthy fruits with a pedicle were laid for storage. The maturity degree of pumpkin fruits was determined by size characteristics and the one of nightshade fruits – by coloration. The size of cucumbers – 11-14 cm and of bush pumpkins – 16-21 cm. Tomatoes of the red maturity degree were selected, sweet pepper – at main coloration of no less than 80 % of the surface.

Cucumbers and bush pumpkins were submerged in solutions of antioxidant compositions with the temperature 42 °C for 10 min. They were stored at 8 ± 0.5 °C and relative humidity 95 ± 1 %.

Peppers and tomatoes were submerged in solutions of antioxidant compositions with the temperature 45 °C for 15 min. Tomatoes were stored at 2 ± 1 °C, relative humidity of air 90 ± 3 %. Peppers – at 7,0±0,5 °C at the relative humidity 95 ± 1 % (**Fig. 2**).



Fig. 2. Refrigeratory storage of sweet pepper Nikita F1 and Hercules F1

Compositions included the following components: chlorophyllipt (Chl), water extract of horseradish (Hr), ionol (I) and lecithin (L) [8, 9]. The composition Chl+I+L that differed by concentrations of separate cases was used for cucumbers and bush pumpkins: for cucumbers 0.38 % Chl, 0.036 % I, 4 % L; for bush pumpkins – 0.75 % Chl, 0.048 % I, 4% L. The composition Chr+I+L was used for tomatoes and pepper. The water extract of horseradish was prepared in ratio of raw material and extractant 1:2. The composition included 4 % of L and 0.30 % of I for tomatoes and 0,024 % of I for pepper.

Non-processed fruits were used in control variants.

4.2. Research methods

According to annual data of the meteorological station of Melitopol city, there were calculated:

- the sum of active temperatures (SAT) higher than 10 °C of the vegetation period,

- SAT of the period of fruits formation (10 days before harvesting for pumpkins [10], 30 days for pepper [11] and 40 days for tomatoes [12]);

- Selyaninov hydrothermal coefficient (HTC).

According to the same data, there was determined the number of days of the vegetation period that didn't correspond to the biological minimum and maximum for fruit vegetables.

The respiratory rate (RR) in mg of $CO_2/kg \times hour$ was determined by Tolmachev's method [13] (Fig. 3).



Fig. 3. Determination of vegetables respiratory rate by Tolmachev's method

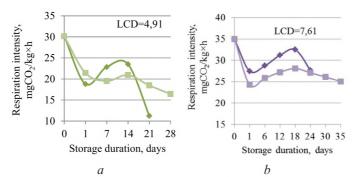
This method was concluded in absorption of CO_2 , emitted at fruits respiration, by the alkali solution. The level of CO_2 was determined by titration by the solution of hydrochloric acid.

3. Results

The veritable variety specification in the respiratory activity of pumpkin fruits was established during the researches (**Table 1**). Nightshade vegetables are characterized by specific differences of respiratory rate, but variety peculiarities are not expressed.

There were established essential fluctuations of levels of CO_2 , emitted by fruits, depending on a year of the research. Despite the variety specificity, such regularities were revealed between the respiratory rate and abiotic factors during vegetation. Most close dependencies are typical for SAT of the period of formation of fruits of both botanic families.

The thermal processing by antioxidants had the important inhibiting influence on respiratory activity in fruits of both pumpkin and nightshade vegetables (**Fig. 4**).



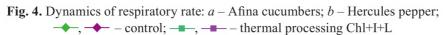


Table 1

Respiratory rate of nightshade vegetables before storage, mg of CO₂/kg×hour, n=3

Туре	Variety	Respiratory rate, mg of CO ₂ /kg×hour, n=3	HIP _{0,95}	V, %	Sx, %
Cucumber	Afina	31,73	2,35	27,51	2,44
Cucumber	Masha	16,75	0,75	10,67	1,48
Duch numelie	Kavili	38,68	1,72	36,40	1,46
Bush pumpkin	Tamino	58,38	1,78	16,59	1,00
Dermon	Hercules	41,49	3,03	37,64	2,40
Pepper	Nikita	46,21	3,90	37,11	2,78
Tomata	Rio Grande	10,73	13,29	10,70	1,22
Tomato	Novachok	9,09	8,32	9,79	1,29

4. Conclusions

The obtained results allow to state that the respiratory rate of pumpkin fruit vegetables is importantly influenced by the variety specificity. The respiratory level of pumpkin vegetables directly correlates with the sum of active temperatures of the period of fruits formation and reversibly – with precipitation and hydrothermal coefficient.

The influence of the variety specificity for nightshade vegetables is leveled, and among meteorological planting conditions the important intense influence on the respiratory rate is realized by the sum of active temperatures of the period of fruits formation and ripening. Precipitation and HTC have the important influence only on pepper fruits.

It was established, that the use of post-harvest thermal processing by antioxidant compositions results in inhibition of respiratory processes in fruit vegetables at storage.

The research results may be useful at making adequate decisions as to planning of arrangements on storage and post-harvest processing of products for decelerating respiratory metabolism. For the deeper understanding of the dependency of respiratory processes in the post-harvest period on abiotic factors, it is necessary to investigate the influence of such stressors as sun radiation, illumination intensity level and other.

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DEVELOPMENT AND RESEARCH CANDIES WITH INCREASED BIOLOGICAL VALUE WITH PROTEIN-FAT COMPOSITE

Sergiy Bochkarev

Department of Physical Education National Technical University «Kharkiv Polytechnic Institute» 2 Kyrpychova str., Kharkiv, Ukraine, 61002 bochkarev.s.v@gmail.com

Nataliya Cherevichna

Department of Commodity and examination of foods Kharkiv State University of Food Technology and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051 cherevichna@gmail.com

Igor Petik

Ukrainian Scientific Research Institute of Oils and Fats of the National Academy of Agricultural Sciences of Ukraine 2A Dziuba ave., Kharkiv, Ukraine, 61019 igor171984@gmail.com

Anna Belinska

Department of Organic Synthesis and Nanotechnology National Technical University «Kharkiv Polytechnic Institute» 2 Kyrpychova str., Kharkiv, Ukraine, 61002 belinskaja.a.p@gmail.com

Oleksandra Varankina

Department of Biotechnology, Biophysics and Analytical Chemistry National Technical University «Kharkiv Polytechnic Institute» 2 Kyrpychova str., Kharkiv, Ukraine, 61002 avarankina@gmail.com

Oleksandra Zakhozhyi

Department of Biotechnology, Biophysics and Analytical Chemistry National Technical University «Kharkiv Polytechnic Institute» 2 Kyrpychova str., Kharkiv, Ukraine, 61002 zahozhyy@mail.ru

Oleksandra Ilina

Department of Biotechnology, Biophysics and Analytical Chemistry National Technical University «Kharkiv Polytechnic Institute» 2 Kyrpychova str., Kharkiv, Ukraine, 61002 sasha.ilina.05.97@gmail.com

Olena Shyrokova

Department of Fat Technologies and Fermentation Products National Technical University «Kharkiv Polytechnic Institute» 2 Kyrpychova str., Kharkiv, Ukraine, 61002 lena.shirokova1234@gmail.com

Abstract

The composition of "truffle" cream candies enriched with polyunsaturated fatty acids of ω -3 group, sesamol and tocopherols antioxidants and plant proteins in the digestible form was developed. Cream candies contain a protein-fat composite based on flax,

sesame and sunflower seeds. These products can be used both in everyday and in special nutrition of athletes, soldiers, heavy manual workers, children and young people. It was determined that the oxidative stability of the model creamy candy mass increased with the concentration of protein-fat composite in it. The positive effect of the plant supplement on taste, aroma and "mouth-feeling" sensation parameters was proved by the obtained profilogram of organoleptic quality control parameters of experimental samples of candy masses with different content of protein-fat composite. Thus, it was established that the protein-fat composite in the composition of sweets improved its organoleptic and physicochemical quality control parameters, and also increased shelf life. The development allows to increase the consumer evaluation of the quality of "truffle" cream candies and, accordingly, their competitiveness.

Keywords: candy mass, protein-fat composite, flax, sesame, sunflower seeds, oxidation, biological value.

	© Sergiy Bochkarev, Nataliya Cherevichna, Igor Petik, Anna Belinska,
DOI: 10.21303/2504-5695.2017.00504	Oleksandra Varankina, Oleksandra Zakhozhyi, Oleksandra Ilina, Olena Shyrokova

1. Introduction

Recently, the confectionery industry produces a variety of products for the general public. Sugar confections characterized by a high content of caloric, carbohydrate, fat and low protein content are sufficiently popular [1]. They have a steady demand among consumers, especially children and youth. But usually modern confectionery products, in particular, sugary, have two significant drawbacks – a low shelf life and an unbalanced composition [2]. And, if the first problem can be effectively solved by the use of preservatives and antioxidants in most cases of synthetic origin [3], but the problem of unbalanced fatty acid composition is almost always left unaddressed [4, 5].

It should be noted that in recent years, manufacturers have sought to increase the attractiveness of their products by increasing their biological value [6-8]. Most often this is expressed in the application of semi-finished products from natural raw materials. Indeed, the complexes of vitamins, minerals and antioxidants are contained in their composition. But the number of such confectionery products, reasonably enriched with ingredients for health purposes, is less than 1 % of the total world production [9].

The composition of a protein-fat composite based on crushed seeds of flax, sunflower and sesame was substantiated in [10-12], its antioxidant properties were investigated, and processing parameters ensuring the maximum biological value of the composite were determined.

The aim of the work is the development of Ukrainian competitive confectionery products enriched with such biologically valuable substances as polyunsaturated fatty acids, antioxidants and proteins. These products can be used both in everyday and in special meals for athletes, heavy manual workers and military personnel.

2. Materials and Methods

The following materials were used for research:

- sunflower seeds according to DSTU 7011;
- flax seeds according to DSTU 4967;
- sesame seeds according to DSTU 7012;
- cocoa butter according to DSTU 5004;
- cocoa powder according to DSTU 4391;
- sugar powder according to DSTU 4623;
- skimmed milk powder according to DSTU 4273.

The preparation of the protein-fat composite includes the following stages: mixing of the oil seeds, their grinding to 0.2–0.4 mm, moisture-thermal treatment using a microwave source according to [12]. This protein-fat composite has a high content of irreplaceable branched amino acids – leucine, isoleucine, valine, and also minimal content of tryptophan. With regard to its fatty acid composition, the ratio of essential polyunsaturated fatty acids (PUFA) of ω -6 and ω -3 groups is about 1.4:1. This composition is justified for enriching food intended for athletes during physical exertion, military personnel, heavy manual workers in changing climatic conditions and other segments of the population [8].

A cream candy mass as an object of enrichment with a protein-fat composite for the "truffle" type candies production was chosen. The choice is based on the fact that the classic recipe for these candies is quite simple, and the ingredient composition is represented by natural products. This candy mass (according to DSTU 4135) is a finely ground sugar and fat base with or without addition of cereals or other crops, food additives and other raw materials, with a fat mass fraction of 18 % at least.

The preparation of cream candy mass includes such stages as formulation components preparation (powdered sugar, cocoa powder, skimmed milk powder, protein-fat composite), their mixing and homogenizing, candy mass spreading (melted cocoa butter adding), candy mass warming up (mixing after spreading to transfer the mass to a plastic state), candy mass tempering (heating to 38 ± 1 °C with following cooling to 28 ± 1 °C for the required polymorphic cocoa butter form forming), candy mass churning and its shaping.

Oxidative stability of candy masses is determined by the accelerated method of "active oxygen". The method is based on the oxidation of candy masses at a temperature of 85 ± 2 °C in a reactor with free light and air access and with mixing. The dependence of changing of the oil peroxide value from the time is built by measuring the time in hours and the peroxide value in ½O mmol per kg. And then the induction period can be graphically determined using this dependence. The induction period of the samples oxidation is the time indicating to the significant increasing of oxidation products concentration. An antioxidant activity is the total oxidation inhibition effect caused by a combination of elementary initiation reactions, lengthening and chains termination.

Sensory evaluation is carried out by testers according to ISO 8586-1 and ISO 8586-2. The olfactory, taste and tactile sensitivity of experts is determined according to ISO 5496, ISO 3972 and ISO 11036. The special score system quantitatively expressing a number of quality control parameters of candy samples is used for the sensory evaluation.

The organoleptic evaluation of candy masses is determined according to GOST 5897. The moisture mass fraction in candy masses is determined according to GOST 5900, the fat mass fraction – according to GOST 5899, the total sugar mass fraction – according to GOST 5903.

Mathematical methods with *Microsoft Excel 2016* and *Statistica Advanced 8* software packages are used for experiment planning and data processing (plotting diagrams, graphs, and regression and variance analysis).

3. Experimental procedures

The model candy mass was obtained in the laboratory conditions according to the formulation presented in **Table 1**. It should be noted that the rate of crystallization of the fat phase allows the filling not to freeze during the deposition and crystallize after the formation of the body.

Table	1
-------	---

Model creamy mass formulation			
Quantity of dry substances (DS), %	Quantity of raw materials, kg		
	actually	in DS	
99,90	330	329,67	
99,85	480	479,28	
95,00	125	118,75	
96,00	80	76,80	
_	1015	1004,50	
97,69	1000	976,66	
	Quantity of dry substances (DS), % 99,90 99,85 95,00 96,00	Quantity of dry substances (DS), % Quantity of rave actually 99,90 330 99,85 480 95,00 125 96,00 80 – 1015	

The oxidation induction periods of the investigated candy mass samples without and with the protein-fat composite addition in an amount of 5, 10 and 20 % at a temperature of 85 ± 2 °C are shown in **Fig. 1**.

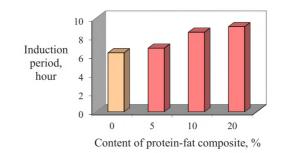


Fig. 1. The oxidation induction periods of investigated creamy candy masses at a temperature of 85 ± 2 °C

The sensory evaluation of the experimental candy samples was carried out for determining the effect of the protein-fat composite on the consumer properties of cream candies. The form, consistency, sweetness, color, taste and aroma of candy samples were assessed during the sensory evaluation. The results of the sensory evaluation are reflected in the profilogram, which is shown in **Fig. 2**.

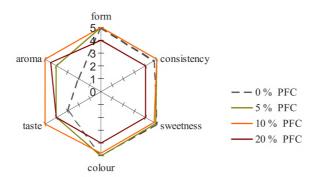


Fig. 2. Profilogram of organoleptic quality control parameters of candy masses samples with different content of protein-fat composite (PFC)

The study of physicochemical quality control parameters of candy mass with a justified content of protein-fat composite was the next stage of the work. The results of this study are presented in **Table 2**.

Table 2

Physicochemical quality control parameters of candy masses

Distantes		Candy masses	The norm according to DSTU 4135
Physicochemical quality control parameters	Control sample (0 % PFC)	Sample with 10 % PFC	
Moisture mass fraction, %	2,31	3,40	not more than 7 %
Fat mass fraction, %	34,06	35,15	not less than 27 %
Total sugar mass fraction in terms of sucrose, %	47,30	42,54	not standardized

The model candy mass with the composition presented in **Table 1** was used as a control sample.

4. Discussion

The oxidative stability of the model cream candy mass with the addition of a different amount of the protein-fat composite, which was described in [10], in comparison with the control sample (the model candy mass) was investigated. It can be seen in **Fig. 1** that the stability to oxidation, and, consequently, the predicted storage times of the investigated creamy candy masses depend on the content of the protein-fat composite in them. The induction period of candy mass with 5 % protein-fat composite exceeds that of the control sample by only 8 %, but the induction periods of candy masses containing 10 % and 20 % of the additive exceed the benchmark by 35 % and 44 %, respectively.

From the profilogram of the organoleptic quality control parameters of the experimental samples of candy masses with different contents of the protein-fat composite (**Fig. 2**), it is evident that the use of the protein-fat composite in the cream candy masses affects on such organoleptic parameters as taste and aroma, which in experimental samples better than in the control one. In particular, a characteristic piquant nutty aroma and taste and longer "mouth-feeling" sensation appear in the experimental samples of candy masses. Further increase in the dosage of the additive – over then 10 % – leads to the appearance of a mealy aftertaste and a harsh flavor of flaxseed. Thus, the effective concentration of protein-fat composite in the candy mass at the level of 10 % was chosen based on the results of sensory evaluation.

The results of the physicochemical quality control parameters of candy masses determining (**Table 2**) indicate that the change in the moisture mass fraction and the fat mass fraction takes place within the limits of the standardized values with the adding of 10 % of protein-fat composite to the cream candy mass. A slight decrease in the total sugar content does not affect for organoleptic characteristics of candy mass, but reduces the cost of production.

5. Conclusions

It is determined that the protein-fat composite based on flax, sesame and sunflower seeds promotes to increase of the oxidative stability of creamy candy masses, and also has a positive effect on their organoleptic parameters such as taste, aroma and "mouth-feeling" sensation. It is determined that the protein-fat composite adding to these candy masses in an amount of 10 % allows keeping the normalized physicochemical quality control parameters within the framework acording to the requirements of the DSTU 4135.

The possibility of using of protein-fat composite based on flax, sesame and sunflower seeds in the production of "truffle" cream candies as an additive increasing the biological value of the product and improving its organoleptic characteristics, and, accordingly, raising the consumer's assessment of the quality of sweets is determined. The developed products can be used in everyday nutrition of athletes, heavy manual workers, military personnel, as well as children and adolescents. It will reduce the deficit of a number of essential amino acids, polyunsaturated fatty acids, antioxidants and, as a result, improve the prevention of diseases caused by unbalanced nutrition: metabolic disorders proteins and lipids, atherosclerosis and premature aging of the body.

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STUDY OF INFLUENCE OF CALCIUM CONTENT IN MILK ON QUALITY INDICATORS OF COTTAGE CHEESE

Nataliya Grynchenko

Department of Meat Processing Technologies Kharkiv State University of Food Technologies and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051 tatagrin1201@gmail.com

Daria Tyutyukova

Department of Meat Processing Technologies Kharkiv State University of Food Technologies and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051 tutukova.d.o.hduht@gmail.com

Pavlo Pyvovarov

Department of Meat Processing Technologies Kharkiv State University of Food Technologies and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051 pcub@ukr.net

Abstract

The analysis was realized, and the dependence between the calcium content and organoleptic and functional-technological properties of milk as a raw material for producing sour milk cheese was determined. It was demonstrated, that alongside with other factors, the important role in milk clotting belongs to calcium, which role is in binding of free OH-groups of phosphoric acid of casein micelles. As a result of the aforesaid, their negative charge and colloid stability decrease with further hydrophilicity decrease with further aggregation of casein molecules. It was established, that the excessive content of calcium in milk is negative that is manifested in formation of the dry and brittle consistence of sour milk cheese. There was offered the way of calcium content regulation in milk by its decalcification using the natural sorbent of sodium alginate. Regulation of the milk salt system, especially, the calcium content as an initial raw material for producing sour milk cheese by the change of the content and condition of calcium allowed to correct parameters of the process of sour milk cheese making and its functional-technological properties, especially, moisture-keeping ability, form stability and other. It was established, that the decrease of the calcium content in milk provides getting sour milk cheese with the soft, easily smearing consistence, without whey separation. The obtained data on the characteristic of organoleptic indicators fully correlate with studies of the microstructure and dispersity of sour milk cheese. It was determined, that milk decalcification results in raising dispersity of sour milk cheese at the synchronous increase of the percent content of protein particles with minimal size characteristics in the system. It was elucidated, that the microstructure of studied samples consists of protein grains of the same form, evenly distributed by the whole volume. Based on the obtained experimental data, there were corrected parameters of the technological process of sour milk cheese production. There were elaborated ways of formation of the culinary products assortment on the base of sour milk cheese, produced of decalcified milk.

Keywords: skim milk, regulated content of calcium, decalcification, sodium alginate, sour milk cheese, casein micelles, moisture-keeping ability, textural characteristics.

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© Nataliya Grynchenko, Daria Tyutyukova, Pavlo Pyvovarov

1. Introduction

Coagulation of milk proteins (mainly casein) is the one of important physical-chemical processes that is in the base of industrial technologies of sour milk cheese, cheese desserts, sour milk beverages and is determined by functional-technological properties of a raw material. Technological properties of milk are considered in the modern literature as [1, 2], which realization provides getting milk products with given consumption properties. The technological process of sour milk cheese production provides using the raw material with the high ability to the acid or rennet clotting, conditioned by casein properties to coagulate under conditions of the medium pH decrease [3, 4]. Calcium plays the important role in this process. Its quantitative content in the raw material considerably influences the process of a protein clot formation in the process of milk pickling, and also the quality of sour milk cheese that is a reflection of its organoleptic, structural-mechanical and functional-technological properties [5–7].

Fundamentalization of existent ideas about the role of calcium and regularity of milk proteins coagulation, understanding of the interconnection between the content, structure and functional-technological properties of casein allow to prognosticate a possibility of its structural modifications. Such modifications induce the increase of hydrophilicity, ability to dissociation, evenness of distribution of the surface charge and, correspondingly, correction of functional-technological properties [8, 9].

Modification of casein properties by milk decalcification using the natural ion-exchanger – sodium anginate considerably influences its technological properties [10, 11]. So, the question of determining a dependence between the calcium content in milk and the quality of sour milk cheese, produced on its base, becomes urgent. Based on it, the aim of this research is the determination of the influence of the calcium content in milk on the quality of sour milk cheese, produced on its base. The established regularities between the aforesaid indicators allow to receive final products with stable quality indicators and to determine its proper use in technologies of culinary and confectionary products.

2. Materials and Methods

The subjects of the research were:

- skim milk, received by separating milk of the raw material zone of SE "SF "Kutuzyvka", NAAS of Ukraine;

- a complex-creator - sodium alginate (AlgNa) FD-157 (made by "Danisco", Denmark), allowed for use by the Central body of executive power in the sphere of health protection of Ukraine;

- skim milk with different content of calcium, achieved by sorption of ionized calcium by AlgNa solution;

- sour milk cheese, received from skim milk at the different content of calcium.

AlgNa solutions were received by dispersing of AlgNa batch in de-aired and demineralized drinking water at the temperature 18-20 °C during (3–4)×60 s with further keeping during 24×60^2 s. These parameters are recommended by the firm-producer of AlgNa, their observance allows to create all conditions for realizing functional-technological parameters of the used food additive.

Sorption of ionic calcium was realized by the drop introduction of AlgNa solution to skim cow milk with further keeping during 1 hour with formation of gel as sphere-like granules, eliminated by decantation.

Samples of sour milk cheese of skim milk (control) and decalcified milk were received by the traditional technology by the acid method of milk of one line [12]. Milk was pasteurized at the temperature 78–80 °C during 20–30 s and cooled to the temperature 32–34 °C. Prepared milk was added with pickling culture of the direct introduction and thermostated at the temperature 32-34 °C to pH 4,5–4,6. The created clot was cut in bricks with the size 2×2×2 cm for better whey separation. For accelerating whey separation, the ready clot was thermally processed to the temperature 40-42 °C during (15–30)·60 s. The boiled clot was separated from whey and self-pressed at the temperature 16-20 °C. The received clot was cooled to the temperature 4-6 °C.

The following research methods were used at experimental works.

2. 1. Methods of milk study

The mass share of fat, protein, lactose, dry substance in milk with the different Ca²⁺ content was determined on the device BENTLEY SOMACOUNT-150 (Bentley Instruments Inc., USA) (**Fig. 1**).

The mass share of general mineral substances and mineral content of skim milk was determined on the roentgen-fluorescent analyzer ElvaX Light SDD (Elvatex, Ukraine) (**Fig. 2**).

The content of calcium in skim cow milk, decalcified cow milk was realized by the method of complex-sonometric titration. This method is based on the interaction between calcium and trilon b in the alkaline medium. This reaction results in the transfer of calcium from compounds

with proteins and phosphorus in a solution. A residue of trilon b was titrated by the calcium chloride solution [13].



Fig. 1. Milk analyzer BENTLEY SOMACOUNT-150



Fig. 2. Roentgen-fluorescent analyzer ElvaX Light SDD

The active acidity of skim milk was determined using pH-meter pH-150 MI (Measuring technique, Russia) with the electrode system for measuring pH (**Fig. 3**).



Fig. 3. pH-meter pH-150 MI

The titrated acidity of milk and sour-milk cheese – by titration of samples by 0,1 n solution of sodium hydroxide. Titration was realized at presence of phenolphthalein up to faint pink coloration that doesn't disappear during 60 s.

2. 2. Methods of studying acid clots and whey

The moisture-extracting ability of protein clots (MEA) is determined by centrifuging at the division factor 1000. At the amount of separated whey, we judged about the clot's ability to moisture output. The results were expressed in the number of ml of whey, received of 10 cm^3 of an acid clot.

The mass share of protein and dry substance in whey was determined on the device BENT-LEY SOMACOUNT-150 (Bentley Instruments Inc., USA).

2. 3. Methods of studying sour milk cheese

The studies of the content of general protein in sour milk cheese at the different calcium content were realized by Kjeldahl method [14].

The moisture-keeping ability of sour milk cheese was determined by the gravimetric method. This method is based on determining the amount of water, separated from a product at light pressing, absorbed by filtering paper. Ash-free, slowly absorbing filters $\emptyset(9-11)$ mm, kept in the dessicator with chlorine calcium for establishing the constant moisture, were used in the work. A filter was placed on a glass plate with the size $11\times11\times0,5$ cm. The cheese batch 0,3 g was placed on a disk of polyethylene film with the diameter 40 mm, weighed on analytic scales with exactness up to 0,5 mg and transferred on a filter in such a way that the batch is under the polyethylene disk. The batch was covered by the glass plate of the same size and a load with the mass 0,5 kg was set on it. The content was pressed for (5–7)·60 s. After that the filter with the batch was taken of the filtering paper and weighed. The difference in the mass of the product with the disk before and after pressing demonstrates the mass of moisture, extracted from the sample. The moisture-keeping ability (MKA) was determined by formula (1).

$$MKA = 100 \cdot \frac{a-b}{a},$$
 (1)

where MKA – moisture-keeping ability of sour milk cheese, %; a – amount of moisture in a cheese batch, g; b – amount of moisture, extracted from a cheese batch, g.

The amount of moisture in a cheese batch was determined by formula (2):

$$a = \frac{300 \cdot B_{sc}}{100}, \qquad (2)$$

where 300 – cheese batch, mg; B_{sc} – mass share of moisture in sour milk cheese, %.

The mass share of moisture in the studied systems was determined using the moisture analyzer "Kett Electric Laboratory", made by "Infrared Moisture Meter. Model F-IA" (Japan) (Fig. 4).



Fig. 4. Moisture analyzer "Kett Electric Laboratory", made by "Infrared Moisture Meter Model F-IA"

The action of this device is based on the thermogravimetric principle: moisture of the studied sample is determined by its mass decrease as a result of drying at heating. Infrared lamps are used as a heating element. The estimation of the sour milk cheese microstructure was realized using the light microscope with a photo header at 40-multiple magnification. For preparing samples, an average sample of sour milk cheese was rubbed in a mortar to the homogenous mass. Then 0,005 of the preparation were evenly brought by a loop on the slide glass, occasionally choosing vision fields at the whole preparation surface for obtaining objective, statistically reliable results and photographed.

The determination of dispersity of sour milk cheese was realized using the microscope with the digital photo camera ScopeTek DCM310 and personal computer with ScopePhoto software for processing obtained photos. A sample of the studied systems was photographed using the microscope and digital photo camera. The obtained photos were processed using ImageJ 1.47 software, calculating the number of particles and determining their diameter by formula (3):

$$d = 2\sqrt{\frac{S}{\pi}},$$
(3)

where S - particle area.

The optic density of sour milk cheese samples was measured on the concentrating photoelectronic colorimeter CPC-2 (Russia) (Fig. 5).



Fig. 5. Concentrative photoelectronic colorimeter CPC-2

Based on the obtained data, there was determined the sedimentation stability of selected samples. For preparing samples, a batch of sour milk cheese was rubbed in a mortar to the homogenous mass and mixed with distilled water in ratio sample:water 1:500. Dishes with the studied sample and distilled water were set in a dish-keeper. The wave length at measuring was 540 nm.

The organoleptic estimation of samples was realized by the sensor analysis [15].

The experimental studies were realized in the following scientific-research laboratories:

- the laboratory of rheological studies of Kharkiv state university of food and trade (Ukraine);

- the laboratory of the estimation of forages and animal husbandry products, NAAS of Ukraine;

- the scientific-research laboratory of the chair of organic synthesis and nanotechnologies of Kharkiv national university "Kharkiv polytechnic institute" (Ukraine).

3. Results

The decrease of the calcium level in skim milk was realized by using the natural ion-exchanger – sodium alginate. It was determined, that the step-by-step introduction of sodium alginate in milk as a sequestrant allows to decrease the calcium level in it from 10 % to 50 %. At that there is fixed the change of organoleptic properties of milk, especially its appearance that is manifested in glass-likeness and transparency increase.

The rational level of milk decalcification that is 20-25 % was determined by the condition of a protein clot, whey, received after pressing a clot, and the sour milk cheese quality. It was

established, that the dense clot with the satisfactory moisture-extracting ability forms in the rational interval of decalcification level. At that the mass share of soluble protein in whey is within legitimate values. The increase of the decalcification level up to 50 % results in the increase of the soluble protein level in whey. It is conditioned by the transfer of low molecular casein fractions in the soluble condition. At the same time there is fixed the decrease of the output of sour milk cheese that is inadmissible from the point of view of the rational technological process realization.

There were studied organoleptic and physical-chemical indicators, output of sour milk cheese, received of skim milk at the different calcium content. The estimation of organoleptic properties was realized at the gustatory council with participation of 27 leading specialists of the university, included in the expert gustatory commission. The generalization on the research results allows to reveal the following regularities: the decrease of calcium content in skim milk essentially influences the consistence and appearance of sour milk cheese. At that the consistence of the control sample may be characterized as crumbly, brittle, grain-like with insufficient whey extraction. Samples, which calcium content was regulated by milk decalcification, are characterized by the homogenous, soft, plastic consistence. Whey in these samples is not separated, grain-likeness is absent. It must be also taken into account, that taste, smell and color of all samples are unchangeable, not depending of the amount of calcium, extracted from milk.

The obtained research data of organoleptic properties of sour milk cheese fully correlate with its indices of moisture-keeping ability, dispersity and sedimentation stability.

It was proved, that formation of easily smearing, plastic consistence is a result of the increased level of protein particles with the size characteristics ≤ 20 mcm. At the same time the increase of dispersity level results in formation of the stable hydrate tunic around protein particles. It is correspondingly reflected on the index of the moisture-keeping ability of sour milk cheese that regularly grows with increasing the milk decalcification level within rational values.

Thus, the regulation of calcium content in milk as an initial raw material for producing sour milk cheese by its decalcification allows to correct parameters of the technological process of sour milk cheese making. The result of such modification is also the increase of technological properties of sour milk cheese, especially, its moisture-keeping ability, form stability, texture change that is important from the point of view of its use in the technology of the wide assortment of culinary products (**Fig. 6**).

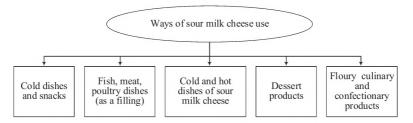


Fig. 6. Ways of formation of the assortment of culinary products based on sour milk cheese, made from decalcified milk

From the practical point of view, this mechanism of the calcium content regulation in milk allows to receive sour milk cheese with the high dispersity, moisture-keeping ability, homogenous structure and to increase the output of products that is economically grounded. Thus, the applied aspect of the offered technological solutions realization is the increase of the resource potential of milk as a raw material, increase of the technological process effectiveness, elaboration of the wide assortment of competitive products with high consumption properties for different population layers.

4. Conclusions

Within the realized studies the expedience of casein micelles modification by milk decalcification by sodium alginate was proved. The offered method allows to decrease the calcium level in milk to the certain level that allows to produce sour milk cheese with the homogenous structure, easily

smearing, plastic consistence, without whey separation. The further use of sour milk cheese with determined characteristics in the technologies of culinary and confectionary products allows to avoid such additional operations as rubbing, homogenization, plastification at the expanse of introducing fat components. It essentially widens a possibility of the technological use of defatted sour milk cheese and allows to elaborate the wide assortment of semi-products and ready products on its base.

At the same time it is determined that the exceeding of the rational milk decalcification level results in decreasing the sour milk cheese quality. Alongside with it the obtained results open prospects of using the decalcification process for receiving concentrated products of milk proteins with new functional-technological properties – dispersity, solubility, ability to emulsification and other ones.

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RESEARCH OF CRANBERRY MAIN INDICATORS OF CHEMICAL COMPOSITION AND ITS PROCESSING PRODUCTS

Galyna Khomych

Departament of Food industry technologies and restaurant industry Poltava University of Economy and trade 3 Kovalay str., Poltava, Ukraine, 36014 homichgp27@ukr.net

Yuliia Matsuk

Department of Food Technologies Oles Honchar Dnipro National University 72 Gagarina ave., Dnipro, Ukraine, 49010 lyly2006@ukr.net

Julia Nakonechnaya

Departament of Food industry technologies and restaurant industry Poltava University of Economy and trade 3 Kovalay str., Poltava, Ukraine, 36014 nakonechna4554@gmail.com

Natalia Oliynyk

Departament of Food industry technologies and restaurant industry Poltava University of Economy and trade 3 Kovalay str., Poltava, Ukraine, 36014 nataliy_oleinik1963@ukr.net

Lolita Medved

Departament of Food industry technologies and restaurant industry Poltava University of Economy and trade 3 Kovalay str., Poltava, Ukraine, 36014 lolita.medved@ukr.net

Abstract

It is well-known that cranberry is an especially rich and heterogenic source of phytochemical substances. Modern technologies allow to produce food products of wild fruits and berries, but they use their diverse and useful chemical composition insufficiently. The aim of the work was in studying features of the chemical composition and content of biologically active substances in cranberries, harvested at the territory of Ukraine, and the influence of processing technologies of cranberry on main indicators of its chemical composition at producing juices.

It was established, that the maximal extraction of biologically active substances is possible at juices production using biocatalysis method, because the essential part of functional elements in the raw material is in the bound condition and is a base of cellular walls that is why it is expedient to disturb nativity and integrity of these natural biopolymers.

There was experimentally grounded the influence of a processing technology on the quality of cranberry juice. There was studied the phenol composition of cranberry composition and influence of different ways of fermentolysis on PS extraction.

It was confirmed by results of the study of the fraction composition of phenol substances, that their maximal extraction is achieved after the enzymatic processing of pulp and momentary heating to inactivate the effect of enzymatic preparations.

It was proved, that enzymatic biocatalysis of cranberry pulp also favors the essential increase of the output of organic acids (lemon, apple, amber), sugars (fructose, glucose), sorbite polyalcohol and also phenol substances of cranberries. The mechanism of the enzymatic complex influence on cranberry pulp at fermentolysis was demonstrated.

The use of products of cranberries processing at food products manufacturing will allow: to enrich the chemical composition, to compensate deviations of functional-technical properties of the raw material and to introduce resource-saving technologies.

Based on the researches there were substantiated perspectives of using juices and marc of cranberry in different branches of the food industry: non-alcoholic, meat processing and at manufacturing products of the restaurant industry.

Keywords: enzymatic preparations, phenol substances, anthocyans, cranberries, cranberry juice.

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1. Introduction

The one of main conditions of the human organism functioning corresponding to the theory of rational and balanced nutrition, accepted in the international practice, is the compulsory presence of biologically active substances (BAS), such as vitamins, phenol compounds, carotenoids and other in the food ration [1]. The main source of BAS is fruits, vegetables, processing products and functional products with their use.

The important place among vegetable raw materials, contained the essential amount of BAS, belongs to wild berries – natural vitamin-carriers that different treating-prophylactic properties are typical to [2, 3].

Modern technologies allow to produce food products of wild fruits and berries, but they use their diverse and useful chemical composition insufficiently. At processing wild berries it must be taken into account that they have more dense morphological structure, lowered ability to juice extraction. At traditional ways of processing berries, both cultivated and wild ones, there are observed essential losses of BAS that results in the decrease of the quality of received products (BAS losses are 20...80 %) [4–8].

In this connection studies, connected with the use of promising ways of berries preliminary processing for enriching a ready product with the biologically active raw material complex, are urgent.

2. Review of the problem

The development of industrial manufacturing of food products advances on the first place the necessity to create resource-saving technologies that allow to use the food raw material potential more effectively [9].

Wild berries are the high-technological raw material, processed by diverse ways that allow to get semi-products that can be used as food products, ready for consumption [3, 6-8]. Cranberry is an especially rich and heterogenic source of phytochemical substances. More than 150 individual phytochemical substances that demonstrate the high biological activity, functional properties and treating–prophylactic effect, are revealed in it [10–11].

Cranberries are remarkable not only for the high content of dyeing substances of anthocyan origin but also for their stable and durable dyeing properties [12–14]. The one of most progressive ways of the raw material processing is juices production [15]. But a defect at their production is existent regimes of the raw material technical processing that have rather rigid parameters that result in the decrease of the quality of a ready product because of the essential loss of valuable biologically active and dyeing substances.

The use of enzymatic preparations is the most effective way of the preliminary processing of the dark-colored fruit-berry raw material in the world and Ukrainian practice. Their use allows to accelerate the speed of technological processes, to raise the food value at the expanse of enriching with phenol compounds and dyeing substances [16].

The crucial value in the mechanism of stability of the wild berries complex belongs to the fraction composition of polyphenols of the raw material, which change is influenced by the cultivation region and technological methods of the raw material processing [17]. But the influence of enzymatic processing methods on phenol substances (PS) extraction is not studied.

The aim of the work is in the study of the influence of the processing technology of cranberries on main indicators of the raw material chemical composition at juices production that allows to get food products of the high biological value by the maximal PS extraction from the raw material and its enrichment with BAS. The following tasks were set for attaining this aim:

- to study features of the chemical composition and BAS content in cranberries, harvested at the territory of Ukraine;

- to determine the expedience of using biocatalytic methods of cranberries processing at juices production for the maximal extraction of BAS;

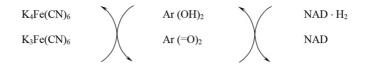
– to study the fraction composition of PS and influence of different methods of enzymatic catalysis on their extraction.

3. Materials and methods

3. 1. Standard methods of studies of physical-chemical indicators of cranberry and products of its processing

The biological activity indicator in juices was determined by the method of control of the electron-transport activity of juices, beverages, extracts in the system of renewed nicotinamide adenine nucleotide (NAD \times H₂) – potassium ferrocyanide in the phosphate buffer (pH 7,5) [18].

 $NAD \times H_2$ is a co-enzyme with the universal biological role and presents the first link in the chain of transferring an electron and proton from an oxidizing substrate. At the interaction of renewed nicotinamide adenine nucleotide with potassium ferrocyanide, phenol compounds that have electron-transport properties are catalyzed in the phosphate buffer of the electrons transfer. The transfer speed depends on their nature and concentration:



The value of the biological activity indicator was determined by the colorimetric method at the wave length 325 nm and thickness of the absorbing layer of a dish 10 mm [18].

Biological activity was calculated by the ratio of $NAD \times H_2/NAD$ oxidation speed change in the control experiment and experimental sample taking into account the dilution by the formula:

$$\mathbf{E}.\mathbf{a} = \frac{\left(\mathbf{A}_{0}^{\pi} - \mathbf{A}_{120}^{\pi}\right) \cdot \mathbf{V} \cdot \mathbf{K}}{\left(\mathbf{A}_{0}^{\kappa} - \mathbf{A}_{120}^{\kappa}\right) \cdot \mathbf{m}}, \text{ con., un. act., Ba}$$

where A_0^{π} – initial optic density of the experimental system; A_{120}^{π} – optic density of the experimental system in 120 s; A_0^{κ} – initial optic density of the control system; A_{120}^{κ} – optic density of the control system in 120 s; V – volume of a volumetric flask, cm³; K – degree of the extraction dilution in distilled water; m – raw material batch, g.

3. 2. Method of chromatographic studies at identification of PS, organic acids and sugars

The identification of PS of berries and cranberry juices was realized by the method of high effective liquid chromatography. For realizing the analysis, there was used a chromatographic column with the size $2,1\times150$ mm, filled with octadecylsilyl sorbent, grains – 3,5 mcm, "ZOR-BAX-SB C-18" (USA).

The parameters of the spectrum survey – each peak 190...600 nm, measurement scale 1,0, scanning duration 2 s, wave length: 313 nm (phenol and derivative acids), 350 nm (flavon glycosides), 371 nm (flavons), 525 nm (anthocyans); for the fluorescent detector – extinction 280 nm, emission 320 nm (catechins and epicatechins).

The identification of phenol compounds was realized by the time of keeping standards and spectral characteristics compared with literary data of the high-effective liquid chromatography of studying berries and juices [19–21].

The content of organic acids and sugars was determined by the method of the high-effective liquid chromatography on a chromatograph Agilent Technologies (model 1100) (USA). A carbohy-

drate chromatographic column with the size 7,8×300 mm, "Supelcogel-C610H" (USA) was used for the analysis.

The following chromatographing regime was set for the analysis: the speed of a movable phase feed 0,5 ml/min; water eluent 0,1 % solution of H_3PO_4 ; working pressure of the eluent 33...36 kPa; temperature of the column thermostat 30 °C; sample volume 5 mcl.

The following parameters of the spectrophotometric detecting were set: wave length 210 nm; fissure width 8 nm; scanning time 0,5...1,0 s. The identification of organic acids and sugars was realized by the time of keeping correspondent standards.

Sample-preparation for the analysis of sugars and organic acids in the raw material. Approximately 5 g of fruit pulp was weighted in a volumetric flask of 10 cm³ with distinctness up to 0,1 mg and added with water to a mark. After 30 min of keeping in the ultrasound bath, the solution was filtered through a membrane Teflon filter with the pores size 0,45 mcm in a vial for the analysis.

Sample-preparation for the analysis of sugars and organic acids in juices. The studied sample was centrifuged and filtered through a membrane filter with the pores sizes 0,45 mcm in a vial for the analysis.

For indentifying components there was use a library of mass-spectrums associated with programs for AMDIS and NIST identification. The internal standard method is used for quantitative calculations [19].

4. Experiments

Marshy cranberry in the stage of consumption ripeness, harvested in Western and Northern regions of Ukraine, was studied by organoleptic and physical-chemical indicators. Cranberry juice was received by pressing of comminuted cranberry (control sample) and after processing by different ways of enzymatic catalysis (F1, F2, F3) [22].

The studies determined the effectiveness of using the multi-enzyme composition (MEC) of enzymatic preparations, based on enzymes of pectofoetidine and celoterin for the preliminary processing of cranberries.

The regimes of the preliminary processing of cranberry pulp by the multi-enzyme complex of enzymatic preparations of pectolytic and cellulolytic effect: ratio of enzymatic preparations in MEC-1: 7 (Pectofoetidine P20x:Celoterin G3X), temperature 50 °C, duration 60 min.

There were studied different ways of fermentolysis of pulp for phenol and anthocyan substances extraction from the raw material for determining the influence of a combining way at fermentolysis on activity of endo- and exoenzymes. Cranberry pulp was processed by MEC, based on enzymes of pectofoetidine and celoterin (variants F1, F, F3) and obtained results were compared with a control sample (C1). Enzymatic samples: F1 – the complex of enzymes was introduced in prepared pulp and kept during 60 min at the fermenting temperature 50 °C; F2 – pulp was preliminary heated to the temperature 85 ± 5 °C, cooled to the fermenting temperature and the complex of enzymes was introduced; F3 – pulp was heated after fermenting at the temperature 50 °C to the temperature 85 ± 5 °C, cooled and pressed. Preliminary studies established parameters of enzymatic catalysis and their influence on the juice extraction [22, 23].

5. Results

The organoleptic indicators of cranberries were: the round form, red color, specific taste and smell, typical for the raw material.

The analysis of the chemical composition of cranberries (**Table 1**) demonstrated that cranberry is a rich source of biologically active compounds.

Table 1

 Physical-chemical indicators of cranberries (n=3, p≤0,05)

 Mass share, %
 Mass share, %

 Dry substances
 sugars
 pectin
 protopectin
 cellulose

 13,20
 3,65
 0,77
 0,35
 1,80

Cranberries has 86...87 % of water in their composition and have rather high titrated acidity. Carbohydrates are the important component of organic compounds in the composition of cranberry. Polysaccharides of cranberry consist mainly of pectin substances, cellulose.

At the studies it was established, that lemon acid and also apple and amber ones dominate in cranberries that raise antioxidant properties of berries.

According to the results of the experimental studies, cranberries are characterized by the rather high index of biological activity (2840,00 con. un. of act). L-ascorbic acid was revealed in analyzed samples (16,60 mg/100 g), dyeing (48,70 mg/100 g) and phenol (90,00 mg/100 g) substances.

It was established, that PS fraction composition in cranberries is presented by oxycoric acids and their derivatives (19,46 mg/100 g), flavons and their derivatives (24,44 mg/100 g), anthocyans (43,40 mg/100 g).

But the essential part of physiological-functional ingredients in berries is in the bound condition. Main chemical components of the cellular wall are organic substances, unessential part are mineral substances. Pectin substances in vegetable cells are in two main forms: soluble pectin (hydropectin) and insoluble (protopectin) that is a strong compound of pectin with cellulose.

For disturbing integrity of natural biopolymers, it is most effective to use enzymes of the complex effect with pectolytic and cellulolytic activity for the preliminary processing.

There was studied the fraction composition and influence of different ways of fermentolysis on phenol compounds extraction at receiving juice (Fig. 1).

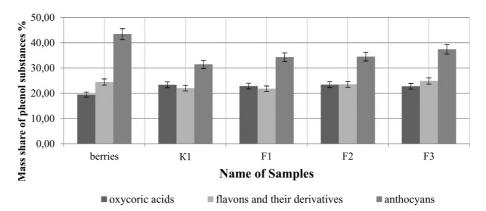


Fig. 1. Influence of preliminary processing of cranberry on PS extraction at receiving juices

It was determined, that the composition of phenol compounds is presented by oxycoric acids, flavons and their derivatives and anthocians.

Myricetin-3-o-arabinoside, quercetin-3-o-galactoside, quercetin-3-o-arabinoside, quercetin-3-o-rhamnoside, camppherol-3-o-glycoside and camppherol derivatives were identified in the group of flavons and their derivatives by the fraction composition. Coffee and vanillin acids were identified in the group of oxycoric acids.

Anthocyans prevail in cranberries among flavonoids, their content is 64 % of the content of phenol compounds. Anthocyans of cranberry are presented by glycosides of cyanidin and glycosides of peonidin with three carbohydrates – glucose, galactose and arabinose. Peonidin glycosides dominate in cranberries, their share is 61,0 % of the total content of anthocyans, peonidin-3-o-galactoside prevails. The share of cyanidin glycosides is 39 % of the total content of anthocyans, cyandinin-3-o-galactoside prevails.

It was established, that best results for the maximal PS extraction are achieved by the fermenting method F3. PS transition in juice at such processing method is 97,4 % of their content in the raw material. Method F3 gives best results for flavons and their derivatives and anthocyans, and in the case of oxycoric acids the maximal extraction is achieved at method F2.

At the enzymatic processing of cranberry pulp the content of organic acids increases comparing with the control: lemon acid – from 1,2 to 1,9 %; apple – from 0,5 to 0,7 %; amber – from 0,2 to 0,3 %. The use of the preliminary enzymatic processing results in the destruction of the organic matrix of the cellular wall of the vegetable raw material, and the part of organic acids transforms from the bound condition into the free form. The presence of amber acid in juices and its content increase in the process of fermentolysis raises antioxidant properties of a ready product.

The quality of juices is greatly influenced by sugars, which presence together with organic acids conditions a taste and energetic value of beverages. The enzymatic processing use increases the sugars content in juice: fructose – by 25,8 %; glucose – by 18,4 % comparing with the control sample. The sorbite extraction from the raw material in juice is also increased almost in 2,0 times comparing with the control. It undoubtedly plays a positive role and gives juices prophylactic properties.

6. Discussion of results

The study of the cranberry chemical composition (**Table 1**) proved that this raw material is a natural source of BAS, extremely important for the human organism.

It was established, that the maximal BAS extraction is possible at producing juices by biocatalysis methods, because the important share of functional ingredients in the raw material is in the bound condition and is a base of cellular walls that is why it is expedient to destruct nativity and integrity of these natural biopolymers. The introduction of method F3 in production allows to extract the PS content of cranberries in juice maximally (up to 97 %).

The mechanism of the influence of enzymes complex on cranberry pulp at fermentolysis is following: as a result of the effect of pectolytic enzymes there takes place the disintegration of tissues to separate cells, splitting of the cellular wall. Pectolytic enzymes split cross bridges that combine D-galacturonans with hemicelluloses that cover microfibrils of cellulose and make them accessible for cellulolytic enzymes that favor insoluble protopectin transformation into the soluble form. Without the modification of the cellular wall by pectolytic enzymes, other enzymes that affect polysaccharides cannot attack their substrates.

The enzymatic biocatalysis of cranberry pulp also favors the essential increase of the output of organic acids and sugars in the soluble part of juices, allows to extract phenol compounds (anthocyans) of cranberries maximally, so it is expedient to use the offered processing type in technologies of products of health–improving destination. But it was established, that the essential amount of BAS remains in cranberry marc and is wasted.

Based on the research results, it was offered to use the complex processing of cranberries and there were separated fields of using received cranberry juices in recipes of fruit juices for establishments of the restaurant industry, and the high content of dyeing substances in marc allows to use them at producing non-alcoholic gas beverages as natural coloring agents; in the meat processing industry – at pastes production.

7. Conclusion

As a result of the studies:

- the chemical composition of cranberries, harvested at the territory of Ukraine, was determined; the high PS content was revealed in it;

- it was proved, that the preliminary processing of cranberry pulp by the complex of enzyme preparations of pectolytic and cellulolytic effect increases the total content of compounds that form the juices quality: organic acids (lemon, apple, amber), sugars (fructose, glucose), sorbite polyalcohol and also PS;

- the results of the study of the PS fraction analysis proved that PS maximal extraction is achieved after the enzymatic processing of pulp and its momentary heating to inactivate the effect of enzymatic preparations (sample F3).

Based on the researches there were substantiated perspectives of using juices and marc of cranberry in different branches of the food industry: non-alcoholic, meat processing and at manufacturing products of the restaurant industry.

The perspective of further studies in this direction is a test of the improved technology of juices production in industrial conditions.

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EFFECT OF COMPONENT COMPOSITION OF PIGMENT COMPLEX ON THE FORMATION OF COLOR OF RHUBARB AND GOOSEBERRY

Antonina Dubinina

Department of Merchandising and Goods' Examination Kharkiv State University of Food Technology and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051 tovaroved206@ukr.net

Galina Selyutina

Department of Merchandising and Goods' Examination Kharkiv State University of Food Technology and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051

Tetiana Letuta

Department of Merchandising and Goods' Examination Kharkiv State University of Food Technology and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051

Tetiana Shcherbakova

Department of Merchandising and Goods' Examination Kharkiv State University of Food Technology and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051

Vita Afanasieva

Department of Marketing and Trade Entrepreneurship Kharkiv Trade and Economic Institute of Kyiv National Trade and Economic University 8 O. Yarosha lane, Kharkiv, Ukraine, 61045 vitaaf@ukr.net

Abstract

The objective of present study is to determine the influence of component composition of pigment complex on the formation of color of rhubarb and gooseberry that defines consumer properties of these plant products. We report comparative study of rhubarb of the botanical varieties Monarch, Linney, Krupnochereshkovyy, Ogrski, and of gooseberry of the varieties Malachite, Pavlovsky green, Green urozhainyy, Green butylochnyy, zoned in the eastern regions of Ukraine. To determine the content of pigment complex substances of rhubarb and gooseberry, we used methodology by V. F. Gavrilenko and L. M. Khandobina. The method of the International Commission on Illumination (ICI) was applied for quantitative characteristic of color.

Results of research into qualitative and quantitative composition of pigment complex of berries of gooseberry and rhubarb stalks revealed that the main components are the chlorophylls whose overall content for different varieties of rhubarb is $(3.7...4.5)\cdot10^{-3}$ %, for berries of gooseberry is $(3.5...4.7)\cdot10^{-3}$ %. The color characteristics of the examined samples of gooseberry and rhubarb are correlated with the quantitative content of pigments in the raw materials and make it possible to determine the dominant tone (λ_d , nm) – green, color purity – green with shades of blue, brightness – green, light green, dark green, which coincide with the visual estimation of color.

We show expediency of the application of the ICI XYZ method to characterize the color, which considerably facilitates the estimation of color when assessing the quality of food products.

Keywords: dominant wavelength, color purity, brightness, the International Commission on Illumination method.

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1. Introduction

Among the chlorophyll-containing fruits and vegetables that grow in Ukraine and which are used for processing in order to extend assortment of food products rich in natural functional ingredients (chlorophylls, carotenoids, vitamins, mineral elements, dietary fibers), quite common are rhubarb and gooseberry. They are characterized by early ripening times and high annual yield. Products from rhubarb and berries of gooseberry are distinguished by high consumer properties and are in great demand among the population [1, 2]. At the same time, thermal treatment leads to the deterioration of physical appearance, especially color, compared with the raw materials. In this case, natural green color transforms into yellow or yellow-brown [3, 4].

It should be noted that the papers on the processing of rhubarb and gooseberry [1, 2, 5–7] fail to adequately address issues related to the pigment complex and its relationship with varietal differences, as well as to questions of maximal preservation of these components; not enough attention is paid to chromaticity problems.

In some cases, color becomes a decisive indicator of quality, which, in line with the requirements of the standard or other normative documentation, defines the technical advantages of the examined product. Such a relationship between quality and color is especially pronounced for the products of plant origin since this is predetermined by a close correlation between the color and the degree of ripeness of fresh fruits and vegetables. Most often, coloration is regulated as the attribute representative of a given vegetable variety or the property typical for a given fruit. A specific color is rarely specified, for example, red, pink for tomato; red-violet, blue-red for red cabbage.

The coloration of raw plant materials is predetermined by the presence of natural dyes – chlorophylls, carotenoids and flavonoids. The first two relate to lipoids because they are insoluble in water, but only in fats and organic solvents. Flavonoids belong to water-soluble substances. This classification is based on the properties of these compounds and is rather widely applied. The data accumulated up to now indicate that chlorophyll not only exerts the effect of its color on consumer properties of food products, but also improves nutritional value [3, 8].

The objective of present study is to determine the impact of component composition of pigment complex on the formation of the color of rhubarb and gooseberry, which characterizes consumer properties of these plant products.

2. Materials and Methods

We selected, for conducting the experiment, the berries of gooseberry of the varieties Malachite, Pavlovsky green, Green urozhainyy, Green butylochnyy, and the stalks of rhubarb of the varieties Monarch, Linney, Krupnochereshkovyy, Ogrski, from the Institute of Vegetable and Melon Cultivation of the Ukrainian Academy of Agrarian Sciences, the city of Merefa, Kharkiv oblast (**Fig. 1, 2**).

We used methodology by V.F. Gavrilenko and L.M. Khandobina to determine the content of pigment complex substances for rhubarb and gooseberry [9]. According to this method, a batch of fresh plant material (0.3...0.5 g) is thoroughly ground in a porcelain mortar with a small amount of organic solvent (2...3 cm³), pure quartz sand and magnesium carbonate. After holding for (2...3) min, the extract is taken on a glass filter and is filtered into a Bunsen flask using a waterjet pump. The extraction of pigments with small portions of pure solvent is repeated on the filter 3...4 times till full removal of the pigments. The last portions of the filtrate must be colorless. The extracts are quantitatively taken to a measuring flask of 50 cm³; the volume of the extraction is brought by pure organic solvent to the mark. The obtained extraction contains the sum of green and yellow pigments of the plant raw material.

Using the spectrophotometer SF-103 (NPKF Aquilon, Russia) (**Fig. 3**), we determined the intensity of light absorption by the resulting extraction of pigments at wavelengths corresponding to the maxima of absorption of pigments in a given solvent – 662 nm, 644 nm, 440.5 nm. Pigment concentration was calculated from formulae [10].

We used the International Commission on Illumination (ICI) method to quantitatively characterize the color [11]. The purpose of the method is determining the process for measuring and estimating color characteristics (**Fig. 3**). а

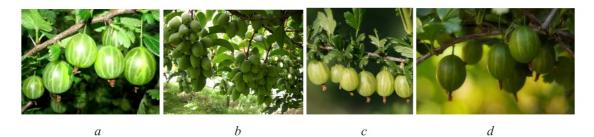


Fig. 1. Gooseberry of the varieties: (a) Malachite; (b) Pavlovsky green; (c) Green urozhainyy; (d) Green butylochnyy

С



Fig. 2. Rhubarb of the varieties: (a) Monarch; (b) Linney; (c) Krupnochereshkovyy; (d) Ogrski



Fig. 3. Spectrophotometer SF-103

This model is the closest to the perception of an actual observer. We measured spectra of the diffuse reflection of experimental samples using the spectrophotometer Techkon SP-810 (Techkon, Germany) in the range of 400...700 nm in a step of 10 nm and the number of cycles of accumulation of 20 (Fig. 4).



Fig. 4. Spectrophotometer Techkon SP-810

Using the embedded software SFScan, we determined integral color coordinates X, Y, Z, conditionally expressed in relative units of the ICE system; they are dimensionless. Applying the obtained coordinates of color, we estimated specific coordinates (x, y), which enable determining of the following parameters – purity of the color (P, %), brightness (T, %), dominant wavelength (λ_d , nm).

Experiments were repeated five times in the course of research. Statistical processing of research results was carried out using a correlation-regression analysis. Experimental data were processed by the method of Fisher-Student at confidence level of 0.95. Results of the experiment were processed in the environment Microsoft Excel of the MathCad software package.

3. Experimental procedures. Exploring the composition of pigments and the color of rhubarb and gooseberry depending on the type of botanical and pomological varieties

We conducted comparative study of the botanical varieties of rhubarb, which are zoned in the eastern regions of Ukraine. To that end, we obtained extracts that contained coloring substances, from the stalks of rhubarb of the varieties Monarch, Linney, Krupnochereshkovyy, Ogrski, and acquired absorption spectra that characterize the presence of chlorophylls. Basic substances of the pigment complex of the examined varieties of rhubarb are given in **Table 1**.

Table 1

Basic components of the pigment complex of rhubarb

Content of nigment complex substances 10-3 0/	Botanical varieties of rhubarb							
Content of pigment complex substances, 10 ⁻³ , %	Krupnochereshkovyy	Linney	Monarch	Ogrski				
Chlorophylls:	3.8±0.3	4.1±0.3	4.5±0.4	3.7±0.3				
chlorophyll a	2.7±0.2	2.9±0.2	3.3±0.3	2.7±0.2				
chlorophyll b	1.08 ± 0.09	1.17±0.09	1.3±0.1	1.08 ± 0.9				

An analysis of the obtained results showed that the main pigments that determine green coloration of rhubarb samples are the chlorophylls. Their total content is within $(3.7...4.5) \cdot 10^{-3}$ %; in this case, the content of blue-green chlorophyll *a* is larger in the stalks of rhubarb of the variety Monarch – $3.3 \cdot 10^{-3}$ %, which are distinguished by dark green color, the lowest content of this pigment is in rhubarb of the variety Ogrski, $2.7 \cdot 10^{-3}$ %.

Similar study was carried out for different varieties of gooseberry. Characteristic of the pigment complex of berries of gooseberry for different pomological varieties is given in **Table 2**.

Table 2

Comparative characteristic of the pigment complex of berries of gooseberry for different pomological varieties

Content of pigment complex substances, 10 ⁻³ %	Pomological varieties of gooseberry								
Content of pigment complex substances, 10 76	Green butylochnyy	Green urozhainyy	Pavlovsky green	Malachite					
Chlorophylls:	4.3±0.3	3.5±0.3	3.6±0.3	3.9±0.3					
chlorophyll a	3.1±0.3	2.5±0.2	2.6±0.2	2.8±0.2					
chlorophyll b	$1.2{\pm}0.1$	$1.04{\pm}0.08$	$1.05 {\pm} 0.08$	1.11±0.09					

As evidenced by the obtained data (**Table 2**), basic components of the chlorophyll complex of berries of gooseberry for different varieties are the chlorophylls *a* and *b*: their content in different varieties of gooseberry ranges within $(3.5...4.3) \cdot 10^{-3}$ %. It should be noted that the minimum content of chlorophyll *a* was found in berries of the variety Green urozhainyy – 2.49 \cdot 10⁻³%; the maximum content is in the variety Green butylochnyy – 3.1 $\cdot 10^{-3}$ %. These very pigments mainly determine green coloration of the berries of gooseberry.

4. Results

The color of the examined samples is determined mainly by the presence of such colorants such as chlorophyll *a* and chlorophyll *b*. Other components do not significantly affect the coloring of stalks since their content is considerably less in comparison with the amount of chlorophyll.

The content of chlorophyll (a+b) makes it possible to characterize the nutritional value of the product, but does not make it possible to fully assess its color, which is an important indicator of commercial estimation of food quality. In order to obtain a more objective assessment, we determined spectral reflection coefficients R_f for different varieties of rhubarb in the visible wavelength range 400...700 nm, which allowed us to establish characteristics of color in a three-color ICI XYZ coordinate system. Reflection spectra are shown in **Fig. 5** for all botanical varieties of rhubarb (**Fig. 5**).

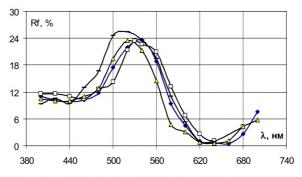


Fig. 5. Reflection spectra of rhubarb samples: (1) variety Ogrski, (2) variety Linney, (3) variety Krupnochereshkovyy, (4) variety Monarch

In a given method, color is characterized by such parameters as brightness, color purity (of the basic tone), dominant wavelength (dominating tone) (**Table 3**). The dominant wavelength (λ_d , nm) for all samples is in the range 495...511 nm, that is, in the green spectral region of visible light. Brightness (R) varies from 40.7 % for rhubarb of the variety Monarch, to 52.6 % for rhubarb of the variety Ogrski. Color purity of the sample of rhubarb of the variety Monarch, which is characterized by darker stalks, is 52.25 %. For other samples, 49.37...52.60 %. Organoleptic evaluation of the color of all samples of rhubarb, conducted in line with the standard, allows us to characterize it as green of different intensity [12].

Table 3

Color characteristics of rhubarb samples (Sr=0.05, n=5, p=0.95)

Botanical varieties	Dominant wavelength	Brightness	Color purity	Visual assessment of
	λ_d , nm	Т, %	P, %	samples' color
Krupnochereshkovyy	508.9	50.6	50.23	green
Linney	510.5	51.7	49.37	green
Monarch	494.7	40.7	52.25	saturated green
Ogrski	510.7	52.6	52.60	light green

Similarly, we acquired spectral reflection coefficients R_f for the samples of different varieties of gooseberry in the specified range. The calculated color parameters are given in **Table 4**.

Color purity of the sample of gooseberry of the variety Green butylochnyy whose berries are characterized by dark green color is 47.0 9 %. For other samples, color purity is from 47.7 % to 52.6 %. Minimum brightness is demonstrated by gooseberry of the variety Green butylochnyy - 38.8 %; for other samples, it is 50...53.6 %. Organoleptic evaluation of the color of all samples of gooseberry also allows us to characterize it as green of different intensity.

Pomological varieties	Dominant wavelength	Brightness	Color purity	Visual assessment of
romological varieties	$\lambda_{d}^{}, nm$	Т, %	P, %	samples' color
Green butylochnyy	493.2	38.8	47.09	dark green
Green urozhainyy	511.6	52.6	50.04	green
Pavlovsky green	510.3	51.0	47.70	green
Malachite	511.8	53.6	52.59	green

Table 4

Color characteristics of the examined samples of gooseberry (Sr=0.05, n=5, p=0.95)

The results of pigment content in rhubarb and gooseberry make it possible to evaluate their biological significance, as well as select required technological operations for maximum preservation of biologically active substances and natural coloration of raw materials. The obtained color characteristics allow us to predict, with a high probability, the character of changes of pigments during technological processing of raw materials and their quantitative composition. Since the reflection spectra measurement does not require lengthy preparation of samples, the color characterization by color indicators can be considered an express-method, which considerably facilitates the work of specialists when selecting technological operations during processing of fruits and vegetables in order to preserve their quality.

5. Conclusions

1. Results of research into qualitative and quantitative composition of pigment complex of gooseberry and rhubarb stalks showed that the main components are the chlorophylls whose overall content for different varieties of rhubarb is $(3.7...4.5) \cdot 10^{-3}$ %, for berries of gooseberry – $(3.5...4.7) \cdot 10^{-3}$ %.

2. The color characteristics of the examined samples of gooseberry and rhubarb correlate to the quantitative content of pigments in the raw materials and make it possible to determine the dominant tone (λ_d , nm), which is green; color purity, which is green with shades of blue; brightness, which is light green, dark green, which coincide with the visual assessment of color.

An important criterion of quality is the color, which for food, in most cases, is determined in accordance with the organoleptic standard, in other words, by a subjective method. Modern consumer requirements to quality and safe products necessitates the use of new and the improvement of existing methods for evaluating color.

The obtained characteristics are in good agreement with the visual assessment of color, which is why the specified spectral method could be employed in future when selecting formulation components, selecting the conditions for technological processing of fruits and vegetables, which would significantly facilitate the work of specialists.

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RESEARCH INTO TECHNOLOGICAL INDICATORS OF A RYE-WHEAT DOUGH SEMI-FINISHED PRODUCT WITH THE ADDITION OF THE POLYFUNCTIONAL FOOD SUPPLEMENT "MAGNETOFOOD"

Iryna Tsykhanovska

Department of food and chemical technologies Ukrainian Engineering-Pedagogics Academy 16 Universitetska str., Kharkiv, Ukraine, 61003 cikhanovskaja@rambler.ru

Victoria Evlash

Department of Chemistry, Microbiology and Food Hygiene Kharkiv State University of Nutrition and Trade 333 Klochkivska str., Kharkiv, Ukraine, 61051 evlashvv@gmail.com

Alexandr Alexandrov

Department of food and chemical technologies Ukrainian Engineering-Pedagogics Academy 16 Universitetska str., Kharkiv, Ukraine, 61003 alexandrov.a.v.a.v@gmail.com

Tetiana Lazareva

Department of food and chemical technologies Ukrainian Engineering-Pedagogics Academy 16 Universitetska str., Kharkiv, Ukraine, 61003 Lazareva_T.A@ukr.net

Karina Svidlo

Department of Technology and Restaurant Business Organization Kharkiv Trade and Economic Institute of Kiev National Trade and Economic University of Ukraine 8 O. Yarosha lane, Kharkiv, Ukraine, 61045 karinasvidlo@rambler.ru

Tatyana Gontar

Department of food and chemical technologies Ukrainian Engineering-Pedagogics Academy 16 Universitetska str., Kharkiv, Ukraine, 61003 taty-gontar@ukr.net

Abstract

We studied influence of the polyfunctional food supplement "Magnetofood" on the technological parameters of rye-wheat dough semi-finished product and the finished product. A positive effect of the supplement "Magnetofood" on the technological

parameters of dough and the bread baked using it, is shown. It was established that adding the food supplement "Magnetofood" in the amount of 0.15 % of the weight of flour reduces dough fermentation time by 13.0 on average %. The introduction of the food supplement "Magnetofood" also increases the yield of a dough semi-finished product by 2.9 % on average and improves the yield of the finished product by 3.45 % on average. It was revealed that the multifunctional food supplement "Magnetofood" enhances the quality of rye-wheat dough semi-finished product and the finished product due to its capacity of moisture retention and the inhibition of hydrolysis processes of the basic ingredients of dough.

The obtained experimental data could be used to develop a technology of rye-wheat bread, enriched with the polyfunctional food supplement "Magnetofood".

Keywords: magnetofood, food supplement, technological indicators of rye-wheat dough semi-finished product.

	© Iryna Tsykhanovska, Victoria Evlash, Alexandr Alexandrov,
DOI: 10.21303/2504-5695.2017.00511	Tetiana Lazareva, Karina Svidlo, Tatyana Gontar

1. Introduction

Bread baking technologies involve various technological techniques that are applied to create the required functional-technological properties of bread (increasing nutritional value and resistance to microbial spoilage; improving quality of the finished products; lengthening of the storage period, extending assortment, etc.) [1–5].

To enhance quality and improve the composition of rye-wheat bread, technologists in the baking industry widely employ various additives-improvers [6–10].

Information sources [1–13] reveal a lack of data about technologies of bread baking that utilize polyfunctional food supplements with a comprehensive effect, and, specifically, nano-powders, which improves technological indicators of dough semi-finished products and the products made from them.

The identified properties of the polyfunctional food supplement "Magnetofood" allow us to recommend it for the introduction to rye-wheat bread. The purpose of adding "Magnetofood" is the formation of new functional-technological properties of rye-wheat bread. "Magnetofood" is the nanopowder with a large specific and active surface [4–6].

2. Materials and Methods

2. 1. The examined materials and equipment used in the experiment

The object of present study is the technology of rye-wheat bread.

To study the effect of polyfunctional food supplement "Magnetofood" on rye-wheat bread, we used model systems. Hence follows the description of the experimental samples of rye-wheat dough and the bread made from it; as well as the equipment and techniques employed in the research.

Fig. 1 shows experimental samples of the dough semi-finished products.

Fig. 1, a – sample 1, control, – rye-wheat dough semi-finished product, baked using flour of grade 1 and pressed yeast; Fig. 1, b - sample 2, rye-wheat dough semi-finished product, baked using flour of grade 1, pressed yeast, and the polyfunctional food supplement "Magnetofood" in the amount of 0.15 % by weight of flour, in the form of a powder; Fig. 1, c – sample 3, rye-wheat dough semi-finished product, baked using flour of grade 1, pressed yeast, and the polyfunctional food supplement "Magnetofood" in the form of oil-magnetofood suspension (OMS), in this case, OMS is introduced in the amount of 0.35 % by weight of flour; Fig. 1, d sample 4, control, rye-wheat dough semi-finished product baked using flour of grade 2 (with short-tearing gluten), pressed yeast with reduced amylolytic activity; Fig. 1, e - sample 5, ryewheat dough semi-finished product, baked using flour of grade 2 (with short-tearing gluten), pressed yeast with reduced amylolytic activity, and the polyfunctional food supplement "Magnetofood" in the amount of 0.15 % by weight of flour in the form of a powder; Fig. 1, f – sample 6, rye-wheat dough semi-finished product, baked using flour of grade 2 (with short-tearing gluten), pressed yeast with reduced amylolytic activity, and the polyfunctional food supplement "Magnetofood" in the form of an oil-magnetofood suspension (OMS), in this case, OMS is introduced in the amount of 0.35 % by mass of flour, Fig. 1.

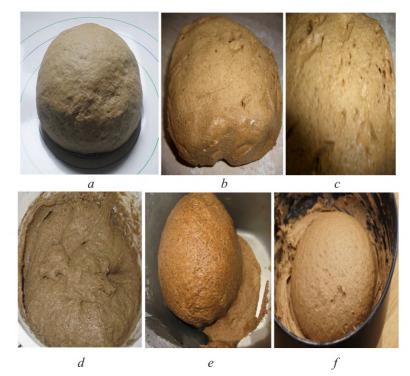


Fig. 1. Experimental samples of wheat-rye dough: a –sample 1, control; b – sample 2; c – sample 3; d – sample 4, control; e – sample 5; f – sample 6

Fig. 2 shows experimental samples of rye-wheat bread.

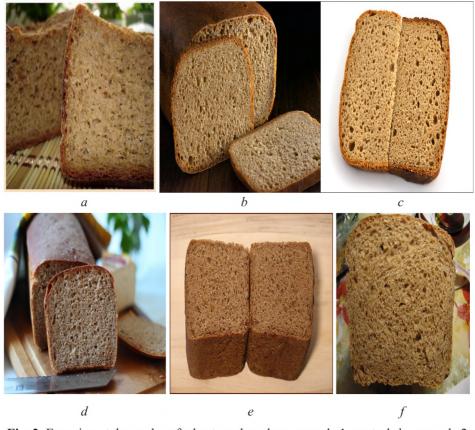
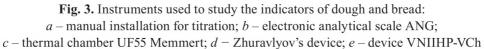


Fig. 2. Experimental samples of wheat-rye bread: a – sample 1, control; b – sample 2; c – sample 3; d – sample 4, control; e – sample 5; f – sample 6



Fig. 3 shows instruments used in the study of dough and bread indicators.



The yield of dough and bread was determined using the electronic analytical scale of the series ANG (Ukraine); humidity of bread was determined in the thermal chamber UF55 Memmert (Germany), humidity of dough – using the device VNIIHP-VCh (Ukraine). Titrated acidity was determined using a manual installation for titration. Crumb porosity was determined using the Zhuravlyov's device.

2. 2. Procedures for determining organoleptic, physical-chemical, structural-mechanical and technological indicators

We employed standard research methods to conduct the experiment, which are described below [10-15].

The quality of rye-wheat bread was assessed by the organoleptic method [GOST 52961-2008, and DSTU-P 4583:2006]. Tasting board assessed it using a five-point scale, taking into consideration a significance factor for each indicator: physical appearance: shape, surface condition, color; condition of crumb: baking quality, mixture, porosity; taste; smell.

The tasting assessment was conducted using compiled tables in which each quality indicator is matched to its characteristic [10-12].

According to the requirements of normative and technical documents, the main physical-chemical quality indicators of bakery products are crumb humidity, acidity, porosity, bread yield determination [10].

We determined humidity by the standard accelerated method in line with GOST 21094-75. The essence of the method is the drying of the batch of shredded crumb at a certain temperature and humidity determination [10, 11]. We determined acidity of the bakery products by a titrimetric method in line with GOST 5670-96 [10, 11]. Porosity was determined by the standard method in accordance with GOST 5669-96 using the Zhuravlyov's device [10, 11].

The yield of bread (OFP, %) was determined as the difference in weight of the starting half-finished product and the finished product using a procedure developed by G. Yu. Botasheva [15]. One of the main stages in breadmaking is the kneading of dough. The kneading of dough is carried out in the dough mixing machines in order to obtain a formulation from the components that ensures the dough that is homogeneous in mass and structure.

Following the kneading, dough undergoes *fermentation*. Fermentation is performed to obtain dough with optimal organoleptic and rheological properties. Dough acquires these properties as a result of alcohol and lactic acid fermentation caused by yeast cells and lactic acid bacteria.

Dough fermentation. The kneaded dough is placed in a fermentation container, which is taken to the thermostat. The thermostat maintains a temperature of 35 °C while relative air humidity is 80-85 %. If the fermentation proceeds without humidification of air, then the dough is covered with a wet cloth so that there is no crust formation. Duration of holding-fermentation, a piece of dough is formed manually on the table, thereby giving it the shape. The dough piece is placed into a metallic mold greased with oil. The mold with the dough is taken to the thermostat (temperature 35 °C, $W_{rel} = 80$ %). The duration of holding depends on many factors and is not regulated. Thus, its duration is affected by the moisture content and temperature of dough; the weight of dough pieces; the presence of sugar and fat in the formulation, as well as improvers with oxidation effect; the grade of flour; the strength of flour; the temperature in the defreezer. The end of holding is determined by the organoleptic method – by the condition and physical appearance of dough pieces, not allowing them to fall. The mass and resulting acidity is determined; the losses during fermentation are derived from formula (1):

$$\mathbf{B}_{\text{fer}} = (\mathbf{M}_{\text{t. b. before fer.}} - \mathbf{M}_{\text{t. b. after fer.}}) / \mathbf{M}_{\text{t. b. before fer}}$$
(1)

where B_{fer} are the losses during fermentation, arbitrary units; $M_{t. b. before fer}$ is the mass of a dough piece prior to fermentation, g; $M_{t. b. after fer}$ is the mass of a dough piece after fermentation, g.

Control over dough fermentation is carried out by the organoleptic parameters (flavor, structure, volume rise, taste), moisture content, and acidity. Quality of the prepared bread depends on the quality of dough [3, 13].

Organoleptic assessment of the dough semi-finished product.

To assess a semi-finished product for organoleptic indicators, its entire mass is examined. The quality of a liquid semi-finished product and dough is assessed by the organoleptic method for the following indicators:

- condition of the surface (convex, flat, settled, crusted, with a fine grid etc.);

- degree of rise and looseness; consistency (weak, strong, normal) and mixing;

– degree of "dryness" (wet, dry, smear, sticky, slimy);

- taste, color, flavor.

The readiness of thick dough is judged by its surface setting. Under normal fermentation, dough would have a convex surface, under abnormal – flat.

Tangible, visible to the eye (in the form of small droplets) moisture content of dough testifies to its defects. Under normal course of fermentation dough should be well loosened and have a net-ted structure (observed when it is rolled out manually), smell of dough – strong alcohol.

We calculated the *yield of dough* from formula (2) [13]:

$$B_{dough} = (M_{dough}/M_{flour}) \cdot 100\%, \qquad (2)$$

where B_{dough} is the yield of dough, %; M_{dough} is the weight of dough after kneading, g; M_{flour} is the weight of flour, taken to knead the dough, g.

Determination of dough moisture content. Moisture content of dough W_{dough} was determined immediately after the kneading by express method of drying at a temperature of 160 °C in the device VNIIHP-VCh using the following technique [3]: two batches of dough 5 g each are weighed on analytical scale to accuracy 0.001 g. These batches are dried in the device VNIIHP-VCh for 5 minutes and cooled in desiccator for 1–2 minutes. Next, they are weighed again on analytical scale to accuracy 0.001 g. W_{dough} is calculated by a difference in the mass of dough before and after its drying (by dry residual) from formula (3):

$$W_{dough} = (M_1 - M_2)/M_1 \cdot 100 \%, \tag{3}$$

where W $_{dough}$ is the dough moisture content, %; M₁ is the mass of the batch of dough prior to drying, g; M₂ is the mass of the batche of dough after drying, g.

Determination of titrated acidity of dough. Titrated acidity is an important indicator that characterizes dough quality. The rise in titrated acidity indicates the way the process occurred in a given phase (concerning temperature conditions and duration), which is important to establish dough readiness. Titrated acidity is the objective indicator of dough readiness to processing.

The magnitude of titrated acidity of the prepared dough indicates the acidity of bread baked from this dough (formula (4)):

$$\mathbf{K}_{\text{bread}} = \mathbf{K}_{\text{dough}} + (0, 5 - 1) \tag{4}$$

Procedure for determining titrated acidity implies the following. 5 g of dough is weighed on a technical balance. The batch is placed in a porcelain mortar and ground with 50 ml of distilled water. First, by adding water by drops, the batch of dough is brought to the state of suspension, then the remaining water is added. Three-five drops of 1 % alcohol solution of phenolphthalein are added. The resulting nutrient mixture is titrated with 0.1 n solution of NaON until pale pink coloration that persists for a minute. The acidity is calculated from formula (5):

$$X_{dough} = 2\alpha K, \tag{5}$$

 X_{dough} – where α is the amount of NaOH solution consumed for titration, ml; K is the correction factor to alkali titer.

Upon completion of the procedure, the mold with dough is put into oven. The baking of rye-wheat bread was carried out at a temperature of 200–240 °C for 55–57 minutes [SOU 15.8-37-00032744-004:2005; 16].

Cooling and storing bread after baking was carried out under conditions of a bread-storer at a relative air humidity of 70–75 % [16–19].

3. Results

The methods of research considered in chapter 2 might have practical application when studying functional-technological characteristics of dough semi-finished products and the products made from them.

It was established that the introduction of the polyfunctional food supplement "Magnetofood" contributes to the reduction of time of rye-wheat dough fermentation by 13.0 % on average [20, 21]. This is related to the activating properties of the food supplement "Magnetofood", which leads to a reduction in the duration of dough fermentation, as well as decreases temperature and brings down losses during fermentation process.

The introduction of the polyfunctional food supplement "Magnetofood" contributes to an increase in the yield of rye-wheat dough semi-finished product and the finished product all experimental samples by 2.9 % and 3.45 % on average, respectively [21]. It is associated with the moisture-retaining capacity and complex-formation properties of the food supplement "Magnetofood", which contributes to maintaining the required humidity of dough.

The obtained experimental data could be used in the development of technology of ryewheat bread, enriched with the food supplement "Magnetofood".

4. Conclusions

1. The techniques for studying dough semi-finished product and bread, reported in the present paper, could be used for examining the effect of different supplements, improvers, technological methods, etc., on the functional-technological characteristics of the rye-wheat dough semi-finished product and the bread baked from it.

Applying the considered techniques, scientists in the future will be able to better explore the impact of various dietary supplements with a comprehensive effect on the yield of dough semi-finished and finished products; to examine in more detail the duration of fermentation of various dough semi-finished products.

The shortcoming of present work is that the action of the proposed techniques was considered only for one kind of a dough semi-finished product, the rye-wheat, with the effect of only one food supplement, the polyfunctional food supplement "Magnetofood" on a given semi-finished product. It also remains unknown in what way this supplement would affect technological indicators of dough semi-finished products with other formulation composition (from other kinds and varieties of flour).

The positive side is that the research methods proposed in the present study could be employed to investigate functional-technological characteristics of not only of the rye-wheat dough semi-finished and finished products, but rye, wheat, etc. as well.

Moreover, research results could be proposed for using in the technological process of ryewheat bread baking with the addition of the polyfunctional food supplement "Magnetofood".

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INVESTIGATION OF THE INFLUENCE OF NANOPARTICLES OF METALS ON FERMENTTATION OF WORT OF HIGH CONCENTRATIONS

Svetlana Kovalchuk

Department of Biotechnology of fermentation and winemaking products National University of Food Technology 68 Volodymyrska str., Kyiv, Ukraine, 01601 sofi55508@ukr.net

Peter Shiyan

Department of Biotechnology of fermentation and winemaking products National University of Food Technology 68 Volodymyrska str., Kyiv, Ukraine, 01601 chiyan@nuft.edu.ua

Tatiana Mudrak

Department of Biotechnology of fermentation and winemaking products National University of Food Technology 68 Volodymyrska str., Kyiv, Ukraine, 01601 mudrak t o@ukr.net

Anatoly Kuts

Department of Biotechnology of fermentation and winemaking products National University of Food Technology 68 Volodymyrska str., Kyiv, Ukraine, 01601 anatolykuts@ukr.net

Roman Kyrylenko

Department of Biotechnology of fermentation and winemaking products National University of Food Technology 68 Volodymyrska str., Kyiv, Ukraine, 01601 nuftkrg@ukr.net

Abstract

There was theoretically grounded and experimentally proved the expedience of enriching high-concentrated wort of the starch-containing raw material with such additional source of mineral nutrition for yeast cells as nanoparticles of metals.

There was studied the influence of nanoparticles of metals on hydrolysis of biopolymers of the raw material and biosynthesis of organic compounds at wort fermentation. It was experimentally established, that the most positive influence of biosynthetic properties of yeast cells is realized by zinc and magnesium. At using zinc and magnesium, yeast biomass and alcohol content in mashes increase.

Best chemical-technological indices of mashes were received at adding nanoparticles of zinc and magnesium at the stage of batch dilution.

There was experimentally studied the synthesis of volatile organic admixtures in marsh distillates depending on point of adding nanoparticles of metals.

Keywords: yeast, wort, alcohol marsh, nanoparticles of metals, marsh distillate.

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1. Introduction

Fermentation of wort of high concentrations is a promising and attractive research direction and has the important practical value. However, fermentation of wort of high concentrations conditions the increase of the specific output of alcohol, decrease of energy consumption, decrease production wastes. But the increase of fermentation temperature and also increase of ethanol concentration in marshes results in extreme conditions for yeast life activity. It is known, that yeast cells are demanding to the cultivation environment and need essentially more mineral substances under stress conditions. Zinc, in its turn, positively influences stress-tolerance of cells, activate enzymes of a yeast cell, fermentation activity [1]. Magnesium positively influences budding of yeast cells [2]. The microelement of iron is necessary for the synthesis of a series of respiration enzymes. In little amounts it stimulates budding of cells [3]. Cuprum, necessary for respiration enzymes, increases fermentation activity of yeast cells. For improving physiological condition of industrial strains of Saccharomyces cerevisiae yeast, mineral nutrition is important. It can essentially influence the process of alcohol wort bioconversion. Not only the qualitative and quantitative composition, but "bioaccessibility" of metals in fermented substrates is important. It is known, that many metals influence yeast productivity that is why more attention must be paid to mineral components in wort. At the same time physiologically adapted yeast cultures are able to increase general indices of alcohol marsh [4–7].

The influence of macro- and microelements of physiological processes is explained by the fact that they are included in accessory substances: respiratory pigments, vitamins, hormones, enzymes that take part in regulation of life activity processes [8–10]. The great importance in alcohol production is inherent to yeast biological activity. Their physiological condition influences the speed of processes and composition of fermentation products. For today the study of the influence of nanomaterials and their use in food industry, especially in alcohol one, is a promising scientific direction [11–13].

The idea of using nanoparticles for fermentation of wort of high concentrations is based on the fact that substances in the nanoform have properties, different from ones of substances in the macrodispersed form. From the microbiological point of view, approaches, based on nanotechnologies, may be used for increasing the quality and safety of food products [14].

Especially, the high specific surface of nanomaterials leads to the fact that surface phenomena begin to prevail in processes of their interaction with macromolecules and biological objects [15–19]. It is resulted in the fact that even small concentrations of nanoparticles can essentially influence yeast cells.

The aim of the work was to study the influence of nanoparticles of metals on hydrolysis of biopolymers of the raw material and biosynthesis of organic compounds at high-concentrated wort fermentation. And also their influence on the synthesis of volatile organic admixtures in marsh distillates depending on point of metal nanoparticles introduction. It allows to improve chemo-technological indices of alcohol marshes at fermentation of wort of high concentrations.

2. Materials and Methods

The grist of corn grains with dispersity 100 % of pass through the sieve with the orifices diameter 1mm was used for the study. For producing and fermenting industrial yeast, wort with the concentration 28 % of DS was used. Wort was fermented by the osmophilic, thermo-tolerant strain of Saccharomyces cerevisiae yeast Y - 16.

Amyloidity of output grain was determined by Evers' method [20]. Grain humidity – by Chizhova's method and drying to the constant mass [20].

The granulometric composition of the grist of grain was determined by the method of sowing on metal and kapron sieves [20]. The concentration of dry substances – using the sugar meter and on the refractometer [20].

Wort from corn with the concentration 28 % of DS was used for cultivating industrial yeast in laboratory conditions.

Wort preparation was realized by the low-temperature scheme of soft boiling at the temperature 85–92 °C using concentrated enzyme preparations of α -amylase with the duration 3 hours. The diluted mass was cooled to the temperature 50–55 °C and sugared by glucoamylase during 0,5 hours. After sugaring, wort was pasteurized at the temperature 80 °C during 20 min., cooled to 50 °C and acidulated by sulphuric acid to the acidity 0,5–0,6 degrees. Yeast cultivation was realized at the temperature 30–32 °C. For diluting and sugaring of batches, there were used enzymatic preparations, made by "Danisko", Belgium: as α -amylase – Amilex 4T, glucoamylase – Diazim TGA (**Fig. 1**).

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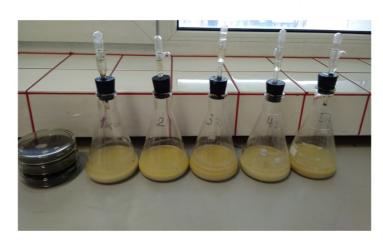


Fig. 1. Preparation of samples for wort fermentation in laboratory condition

The physiological condition of yeast cells was determined by coloration of a yeast cell by Lugol's solution, the content of dead cells – by blue methylene, the amount of budding yeast and their accumulation – in Goryav's chamber.

In laboratory conditions pure cultures of studied yeast from the shoal were resown in a testtube with sterile wort with the concentration 9-10 % of DS and fermented during 24 hours at the temperature 30 °C. After that the content of the test-tube was sterilely transferred in a flask that contains 200 ml of sterile wort, and fermented during 24 hours, marsh was centrifuged, residual was washed by the physiological solution and used for fermenting wort.

The total number of yeast cells in 1 cm³ was determined by the method of direct calculation in Goryav's chamber.

Nanoparticles of aqueous dispersions were transferred from the Problem scientific-research laboratory of the National university of food technologies (Ukraine), kept by the method of volumetric electric-spark dispersion of current-conductive metals in liquid.

The studies of electrophoretic mobility and distribution of particles by sizes in the colloid system were realized by the method of photocorrelation spectroscopy LCS on the laser spectrometer Zeta Sizer Nano (Malvern, Great Britain) (**Fig. 2**, *c*) with the electric system of measurement of ζ -potential Universal Dipcell (ZEN1002) and cell – Disposable polystyrene (DTS0012).

In laboratory conditions wort was fermented by the method of "fermenting sample" in conic tubes with sulphuric acid locks in the thermostat at different temperatures 30-35 °C Fig. 1. The dynamics of the carbon dioxide emission was controlled by the weight method [20].

pH in mature marsh was determined by the electrometric method, ethanol content – by the pycnometric method, soluble and alcohol-soluble carbohydrates, insoluble starch and dextrins – by the photoelectrocolorimetric method with the antrhron reagent [20] Fig. 2, b.

The composition of volatile admixtures in marsh distillates was determined by the gas chromatographic method on the gas chromatograph Crystal-2000M CSC SCB "Chromatech", Joshkar-Ola, Russia, **Fig. 2**, *a*.



Fig. 2. Equipment: *a* – Crystal-2000M, *b* – Photocolorimeter CPC-2MP, *c* – Laser spectrometer Zeta Sizer Nano

3. Results and Discussion

The studies of the influence of Mg, Fe, Cu, Zn nanoparticles on the process of fermentation of wort of high concentrations of the starch raw material were realized in the work.

Wort was prepared of corn, the grist dispersity was 100 % of pass through the sieve with the orifices diameter 1mm. The wort concentration was 28 % of DR. The concentration of sowing yeast -30 mln/cm^3 . Carbamide in the calculation of 800 g/m³ was added as nitrogen nutrition. The concentration of nanoparticles of metals was 1,2 mcg/cm³.

Nanoparticles of metals were introduced at the stage of batch dilution and wort fermentation.

As it was shown by research results, samples with Mg, despite the stage of its introduction, demonstrated better chemo-technological indices of marsh compared with the control. The content of alcohol in marshes increased by 1,2-1,5 % (**Table 1**).

Table 1

Influence of nanoparticles of metals on fermentation of sources of high concentrations

	Point of nanoparti- cles intro- duction	Metal name	$\frac{\sum CO_{2,}}{g/200 \text{ cm}^3}$		Content of non-fermented carbohydrates, g /100 cm ³				Alcohol	Number of	0/ 6
No.				рН	Soluble carbohy- dratess	Insoluble carbohy- drates	Dextrins	Alcohol- soluble car- bohydrates	content, % об.	yeast cells, mln/cm ³	% of dead cells
1		Mg	21,74	4,58	0,46	0,04	0,17	0,25	13,46	221	9
2		Fe	21,30	4,55	0,58	0,08	0,28	0,30	13,32	214	8
3	Before dilution	Cu	21,34	4,60	0,52	0,09	0,24	0,28	13,38	218	10
4	ununun	Zn	21,20	4,50	0,63	0,08	0,31	0,32	13,30	230	7
5		All metals	21,67	4,53	0,49	0,05	0,23	0,26	13,40	219	8
6		Mg	21,54	4,53	0,50	0,09	0,24	0,26	13,41	225	9
7		Fe	21,32	4,52	0,58	0,10	0,26	0,32	13,31	218	10
8	Before fermentation	Cu	21,29	4,54	0,63	0,10	0,34	0,29	13,30	220	10
9	Termentation	Zn	21,30	4,52	0,57	0,09	0,25	0,32	13,30	258	8
10		All metals	21,41	4,54	0,55	0,09	0,28	0,27	13,39	232	9
11	Cont	rol	20,93	4,51	0,68	0,2	0,34	0,32	13,27	218	13

But despite a zone of introduction of nanoparticles of metals and their mixture, marsh indices were better compared with the control sample.

Introduction of nanoparticles of metals at the stage of dilution favored not only the increase of fermenting activity of yeast, but had a positive influence of dilution and sugaring of a batch that may be connected with activation and stabilization of enzymatic preparations. It is proved by the decrease of the content of insoluble starch in marshes by 10-35 % compared with the control.

Thus, the use of nanoparticles of metals has a positive influence of the process of yeast fermentation. There were realized the studies of the synthesis of volatile organic admixtures in marsh distillates depending on point of metal nanoparticles introduction (at the stage of batch dilution and wort fermentation). According to the data (**Table 2**), it was established, that at adding metal nanoparticles, acetaldehyde concentration decreases comparing with the control sample.

Metal nanoparticles introduction was most effective at the stage of batch dilution, and the concentration of this component depended on a metal. The least amount of acetaldehyde was accumulated at introducing all studied components and was 110,9 mg/dm³. The same concentration was observed in the synthesis of complex asters.

The analysis of the synthesis of fusel alcohols in samples with adding nanoparticles demonstrated that the amount of N-propanol increases by 53,4–80 % depending on type of metal nanoparticles and zone of their introduction. Their concentration was practically close to the control by the sum of high alcohols. Only in samples, where metal nanoparticles were introduced at the dilution stage, their concentration decreased by 17,5–18 %. The content of methanol in all studied samples was at the level of the control sample.

Table 2

Synthesis of volatile organic admixtures in mature marshes depending on metal nanoparticles introduction

	Components of marsh distillates,					Point of	nanopar	rticles introduction					
No.		Control	ontrol Dilution					Fermentation					
	mg/dm ³		Mg	Cu	Fe	Zn	All metals	Mg	Cu	Fe	Zn	All metals	
1	Acetaldehyde	150,87	130,2	129,1	131,3	125,2	110,9	134,2	135,1	134,7	132,34	159,9	
2	Methyacetate	1,925	6,478	5,840	7,39	6,95	8,280	8,914	8,520	9,19	8,95	8,31	
3	Ethylacetate	222,4	212,8	243,9	216,7	217,8	198,6	237,0	241,5	259,5	248,32	239,4	
4	Sum of complex esters	224,63	233,6	249,74	224,09	224,75	216,88	245,91	250,02	268,69	257,27	247,5	
5	N-butanol	12,534	13,48	13,25	15,38	14,18	13,38	15,63	15,45	16,44	15,98	15,84	
6	N-propanol	513,542	787,0	820,3	910,1	859,0	804,7	944,0	928,14	910,5	912,13	939,1	
7	Isobutyl alcohol	397,328	338,4	340,4	350,8	348,14	423,6	404,7	425,7	456,0	465,11	385,1	
8	Isoamyl alcohol	1737,8	1209,0	1190,1	916,82	1253,0	1373,0	1397,0	1328,0	1563,0	1483,3	1332,0	
9	Sum of fusel alcohols	2660,23	2347,88	2364,0	2193,1	2474,3	2614,6	2761,3	2697,3	2945,9	2876,5	2672,0	
10	Acids	37,63	36,63	35,81	33,444	31,85	35,26	36,11	35,24	32,34	33,42	35,71	
11	Methyl alcohol, об. %	0,002	0,003	0,0028	0,0029	0,003	0,003	0,0031	0,0031	0,0027	0,0028	0,003	

The studies on determination of concentrations of volatile organic compounds in marsh distillates allow to make a conclusion that their synthesis depends on type of metal nanoparticles and also on zone of their introduction into the technological process.

4. Conclusions

There was studied the influence of metal nanoparticles on bioconversion of wort and synthesis of organic compounds. It was established, that the most positive influence on wort fermentation was realized by zinc and magnesium. At their use the concentration of yeast cells in marshes increased in 1,3–2,0 times compared with the control, at that the alcohol content in marshes increased by 1,2–1,5 %.

Best chemical-technological indices of mashes were received at adding nanoparticles of zinc and magnesium at the stage of batch dilution.

Introduction of nanoparticles of metals at the stage of dilution favored not only the increase of fermenting activity of yeast, but had a positive influence of dilution and sugaring of a batch that may be connected with activation and stabilization of enzymatic preparations. It is proved by the decrease of the content of insoluble starch in marshes by 10-35 % compared with the control.

Thus, metal nanoparticles introduction has the positive influence on the process of yeast-generation and fermentation of high wort concentrations.

The shortcoming of the studies is a difficultness of using nanoparticles of aqueous dispersions in industrial conditions, because these systems are unstable during a long time. The further development of this study may be in elaborating the technology of fermentation of wort with DS concentration higher than 28 %, and also using other forms of nutrition for yeast cells.

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DEVELOPMENT OF THE EXTRACTION METHOD OF INACTIVE FORMS OF PECTIN SUBSTANCES FROM FRUITS TO EASY-DIGESTIBLE ACTIVE FORM DURING THE OBTAINING OF NANOFOOD

Viktoriya Pogarska

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

Raisa Pavlyuk

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

Roman David Tauber

Department of Academy of hospitality and catering Academy of hotel management and catering industry in Poznań 19 Nieszawska str., Poznan, Poland, 61-022 wshigua@i.ua.

Aleksey Pogarskiy

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

Adelina Berestova

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

Tetyana Kravchuk

Department of health resort business National Academy of food technologies 112 Kanatna str., Odessa, Ukraine, 65039 krytan@ukr.net

Tetyana Stukonozhenko

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

Iuliia Kakadii

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

Abstract

The aim of the work is development of a unique method for deep processing of fruits and vegetables with a high content of sparingly soluble pectin substances, which makes it possible to remove pectic substances from inactive form and transform them into an easily digestible active form when obtaining natural semi-finished products and food products in nanosized form. To achieve

the aim, a complex effect on the raw material of steam-thermal treatment or cryogenic shock freezing and fine-dispersed grinding is used as an innovation.

A new method for obtaining finely dispersed additives and health products from fruits and vegetables with a high content of biologically active substances (BAS) and prebiotic substances is developed, which is based on a complex effect on raw materials of processes of steam-thermal or cryogenic treatment of raw materials and fine-dispersed grinding, which is accompanied by destruction, mechanochemistry, non-enzymatic catalysis. It is found that when these processes are activated, pectic substances are activated, more complete extraction from raw materials (4.5 ... 7.3 times) from a latent form and transformation into a soluble form. The mechanism of these processes is disclosed, recommendations for the creation of recreational nanoproducts are developed. It is shown that, in parallel, non-enzymatic catalysis (up to 70 %) of hardly soluble pectic substances in individual monomers takes place, that is, transformation into a soluble, easily digestible form.

The increase and seizures of latent forms of biologically active substances in finely dispersed frozen and heat-treated purees from fruit compared with fresh raw materials is established. The increase is respectively 1.5...4.0 times and 1.5...3.0 times. The quality of the obtained new types of fine mashed potatoes exceeds the known analogs for BAS content and technological characteristics. New types of purees are in a nanoscale, easily digestible form.

With the use of new types of finely dispersed additives, a wide range of products for health-improving nutrition has been developed with a record content of natural BASs (new types of nano-lipids, nanosorb products, milk-vegetable cocktails, fillings for confectionery and extruded products, curd desserts, bakery products, snacks - falafel, creams, etc.).

Keywords: non-enzymatic catalysis 1, mechanolysis 2, heat treatment 3, cryotreatment 4, nanocomplex 5, heteropolysaccharides 6, pectin substances 7, fruits 8, vegetables 9, health products 10.

	${\mathbb C}$ Viktoriya Pogarska, Raisa Pavlyuk, Roman David Tauber, Aleksey Pogarskiy,
DOI: 10.21303/2504-5695.2017.00520	Adelina Berestova, Tetyana Kravchu, Tetyana Stukonozhenko, Iuliia Kakadii

1. Introduction

Today in Ukraine and other countries of the world, there is a shortage of high-quality natural supplements from fruit and vegetable pectin-rich raw materials, which are also carriers of curative biologically active substances (BAS). Deficiency is associated with inadequate supply of dietary supplements, such as vitamins, carotenoids, minerals, proteins, etc., as well as indigestible food components, in particular pectin substances, cellulose, etc. They are responsible for immunity. The population's need for these substances in the world is only 50 % satisfied. [1–3]. It is also known that pectin substances, cellulose, inulin and other refer to prebiotics that support the gastrointestinal tract in a healthy state. It is known that the health status of the population, as well as its immune system, is 80 % dependent on maintaining the intestines in a healthy state. Such supplements are now needed to create products for healthy nutrition [4–8].

In the most developed countries, the problem of immunodeficiency is solved by introducing in the diets of food products and additives, especially from fruit and vegetable raw materials, which is characterized by a large number of BAS and prebiotics.

The aim of the work is development of a unique method for deep processing of fruits and vegetables with a high content of sparingly soluble pectin substances, which makes it possible to remove pectic substances from inactive form and transform them into an easily digestible active form when obtaining natural semi-finished products and food products in nanosized form.

2. Materials and methods of research for the content of pectin substances and other BASs and biopolymers

To achieve the aim, it is suggested to use a complex effect on the raw material of steam-thermal treatment as an innovation (in a modern apparatus – a convection oven) or cryogenic "shock" freezing and finely divided grinding to activate and remove hardly soluble inactive pectin substances and low molecular weight biologically active substances in a free soluble form .

Kharkiv State University of Food Technology and Trade (Kharkov, Ukraine) in cooperation with the Academy of Hotel Management and Catering Industry in Poznan (Poland) and Odessa National Academy of Food Technologies (Odessa, Ukraine) develop a fundamentally new unique method for deep processing of pectin mills fruits and vegetables. The method allows not only to maximally preserve, but also more fully utilize the biological potential inherent in plant raw materials and to transform BASs and pectin substances from the bound state into a nanostructure. The method is based on the process of steam-thermal mechanodestruction and cryomechanical degradation – non-enzymatic catalysis-mechanolysis (destruction of nanocomplexes in which biologically active substances and pectin are in a latent form) in cryoids or thermal decompositions of plant raw materials, which leads to the production of a nanosized product.

Steam thermal treatment of samples of apples, apricots and pumpkins was carried out in a steam convection oven ("Unox", Italy) at 105 °C in a furnace, in the product – 70...75 °C. Fine chopping was carried out in a cutter (Robot Coupe, France) (Fig. 1).



С

Fig. 1. Equipment used during research: a – cutter for finely divided grinding; b – low-temperature cutter; c – steam convection oven

In researches, fresh fruit and vegetable raw materials (blackcurrant, apricots, lemons with zest, apples, pumpkin, spinach) containing hardly soluble heteropolysaccharide nanocomplex were used as the objects (Fig. 2).



Fig. 2. Objects of research: a – fresh black currant, b – frozen black currant, c – black currant nanopuree; d – fresh apricots, e – frozen apricots, f – nanopuree from apricots; g – fresh lemons, h – frozen lemons,
i – nanopuree from lemons and zedra; j – fresh apples, k – frozen apples, l – nanopuree with apples; m – fresh pumpkin, n – frozen pumpkin, o – nanopuree from pumpkin; p – fresh spinach, r – frozen spinach, q – nanopuree from spinach

In addition, finely dispersed additives in the form of heat-treated or cryopreserved nano-fruits from fruits and vegetables and products for health-improving nutrition (nanobeverages, nano ice cream, fillings for confectionery products, etc.) are studied (Fig. 3).

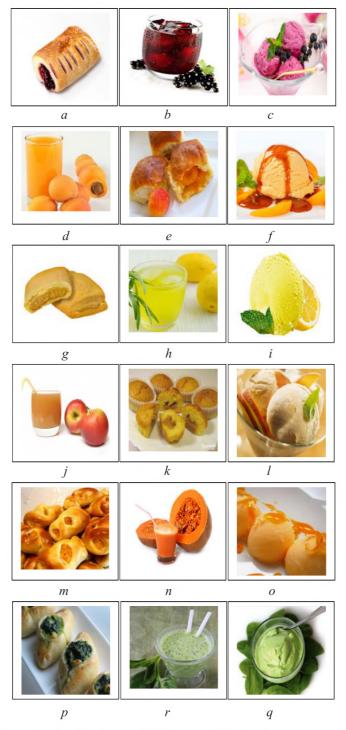


Fig. 3. New developed products for healthy nutrition using nanopuree from fruits and vegetables: a, e, g, k, m, p – confectionery products with filling; b, d, h, j, n, r – nanobeverages; c, f, i, n, m – nano ice cream; a, b, c – products from black currant; d, e, f – products from apricots;

g, h, i – products from lemons; j, k, l – products from apples; m, n, o – products from the pumpkin; p, r, q – products from spinach

3. Experimental procedures

Steam thermal treatment of samples of apples, apricots and pumpkins was carried out in a steam convection oven ("Unox", Italy) at 105 °C in a furnace, in the product – 70...75 °C. Fine pulverization was carried out in a cutter ("Robot Coupe", France) and a low-temperature cutter ("SIRMAN", Italy).

In fresh fruits, berries and vegetables (black currant, apricots, lemons with zest, apples, pumpkin, spinach), heat-treated and frozen to the freezing temperature of the product (-32...-35 C), as well as in finely-dispersed puree (storage temperature – 18 °C for 12 months without loss of vitamins and other BASs) from the fruit and vegetable raw materials the quality of the content of the basic BASs and prebiotic substances is determined.

The control is carried out according to the content of biologically active substances

- Low-molecular phenolic compounds (according to routine and for chlorogenic acids separately), determined by the Folin-Denis colorimetric method in terms of chlorogenic acid [4, 5].

- Tanning substances (by tannin), determined by the titrimetric method in terms of tannin. The method is based on the property of tannins to be oxidized in the presence of an indigo carmine indicator [4, 5].

- L-ascorbic acid, determined by visual and potentiometric titration with a solution of 2,6-dichlorophenolindophenolate Na [4, 5].

 $-\beta$ -carotene, monitored by the Moure colorimetric method after extracting carotene from the product with an organic solvent and purifying the carotene from the accompanying coloring substances by column chromatography [4, 5].

In addition, the prebiotic substances are identified such as pectin (in particular, common pectin substances, soluble pectin and protopectin – insoluble pectin), cellulose, protein.

Chemical, physical-chemical and spectroscopic methods of research are used for BASs control in the research objects, which are reflected in [4, 5, 9, 10].

4. Results

On the basis of experimental studies, nanotechnology of frozen or steam thermal treated fine-dispersed additives from fruits, berries and vegetables (black currant, apricots, lemons with zest, apples, pumpkin, spinach), which differs from the traditional using high freezing rates using liquid or gaseous nitrogen, as well as fine-dispersed grinding.

It is shown that when these processes are activated, pectic substances are activated, more complete extraction from raw materials (4.5...7.3 times) from a latent form, and transformation into a soluble form. The mechanism of these processes is disclosed and recommendations for the creation of recreational nanoproducts are developed. It is shown that, in parallel, non-enzymatic catalysis (up to 70 %) of hardly soluble pectic substances in individual monomers takes place, that is, transformation into a soluble, easily digestible form.

The increase and seizures of latent forms of biologically active substances in finely dispersed frozen and heat-treated purees from fruit compared with fresh raw materials is established. The increase is respectively 1.5...4.0 times and 1.5...3.0 times. The quality of the obtained new types of finely dispersed puree exceeds the known analogs for BASs content and technological characteristics. New types of purees are in a nanoscale, easily digestible form.

5. Conclusions

A new method for obtaining finely dispersed additives and health products from fruits and vegetables with a high content of BASs and prebiotic substances is developed. This method is based on a complex effect of processes of steam thermal or cryogenic treatment of raw materials and fine-dispersed grinding on raw materials, which is accompanied by destruction, mechanochemistry, and non-enzymatic catalysis.

It is found that when these processes are activated, pectic substances are activated, more complete extraction from raw materials (4.5...7.3 times) from a latent form, and transformation into a soluble form. In parallel, non-enzymatic catalysis of sparingly soluble pectic substances in individual monomers (up to 70 %) occurs, i. e., transformation into a soluble, easily digestible form.

The increase and seizures of latent forms of biologically active substances in finely dispersed frozen and heat-treated purees from fruit compared with fresh raw materials is established. The increase is respectively 1.5...4.0 times and 1.5...3.0 times. The quality of the obtained new types of finely dispersed puree exceeds the known analogs for BASs content and technological characteristics. New types of purees are in nanoscale, easily digestible form.

With the use of new types of finely dispersed additives, a wide range of products for health-improving nutrition has been developed with a record content of natural BASs (new types of nano-lipids, nanosorb products, milk-vegetable cocktails, fillings for confectionery and extruded products, curd desserts, bakery products, snacks - falafel, creams, etc.), in particular, fillings for confectionery products "pankake" and extruded products, which, within the framework of 2 economic contracts, were introduced into production (Confectionery firm "Lisova Kazka ", Kharkiv, Ukraine). Also, vitaminized health-improving nanobeverages and nanosorbents have been developed, which were made in production conditions in the SPE "KRIAS" and SPE "KhPK" (Kharkiv, Ukraine).

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