STUDY OF THE PROPERTIES OF MARSHMALLOW WITH THE SUDANESE ROSE AND BLACK CHOKEBERRY DYES UPON STORAGE

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Abstract

Creation of marshmallow with natural dyes is impossible without investigation of properties of products and estimation of its quality. Our objects of investigation were organoleptic, physico-chemical and antioxidant properties of the products at storage for 30 days. The six of marshmallow samples were the objects of our research. They differed in the type of structuring agent – gelatin or gelatin with solubilized substances and the type of dye – water or water-alcohol extract of cryopowder from Sudanese rose or water-alcohol extract of cryopowder from black chokeberry.

Necessary indexes of quality are supplied for the new types of marshmallow with natural dyes. Moisture content (19.0...21.5 %), total acidity (3.5 degrees), density (0.51...0.67 g/cm^3), reducing substances content (not more than 13.6 %) were determined by standard

methods. Use of natural anthocyanin dyes let us to increase antioxidant properties of the ready product. Value of antioxidant capacity of the new samples, determined with use of galvanostatic coulometry method, is in 2...2.5 times more than the same results for samples, made without the dyes.

It was established that short time storage (up to 2 days) of marshmallow with natural anthocyanin dyes at temperature (15...18) °C and relative air humidity 60...75 % is possible without packing materials. Storage of the products in hermetically polyethylene wrap and cardboard box provides high indexes of quality, stability of colour in long time (up to 30 days). It was shown that antioxidant properties of marshmallow with water-alcohol extracts of cryopowder from Sudanese rose and black chokeberry remain stable.

The new developed types of marshmallow with natural anthocyanin dyes makes wide market of confectionery and can be used for correction of feeding of a man.

Keywords: anthocyanin dye, cryogenic technology, antioxidant capacity, stability of colour, marshmallow.

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1. Introduction

The results of investigations on the influence on human organism of combinations of food supplements in quantities typical for distributed food products for children, show that chemical dyes decrease growth of nerve cells in 4…7 times [1]. Therefore the investigations lead us to the development of new types of products using natural herbal ingredients. Supplements may contain mixture of various saccharides [2]; polysaccharides of herbal and microorganism nature [3]; barley-malt and polymalt extracts, carrot and pumpkin juices, flour of fried wheat seeds [4], isomaltytol, eritrytol, maltytol, its mixtures with fructose [5], hummiarabic [6, 7]. Among herbal dyes special place possess cryopowders, produced by cryogenic milling of raw materials. It let us to save biological active substances and increase quality of the final product. Authors of works [8, 9] used cryopowder from red beetroot in butter technology. Cryopowders from grape and black chokeberry were used in technology of yeast products and shortcakes, what let to improve its organoleptic and physical-chemical indexes also to increase its biological quality [10].

Among powders from berries with high dye effects we can distinguish small dispersed ones, obtained according to cryogenic technology at "Krias Plyus" factory (Kharkiv, Ukraine), especially powders (krias-powder) from Sudanese rose and black chokeberry [11]. Use of these small dispersed herbal supplements let us to obtain food of attractive appearance and bright colour, with high antioxidant potential, high food quality. But, development of the new food technologies with use of krias-powders is impossible without investigation of products properties and quality. Necessary experimental data can be obtained by various physical chemical methods.

The main purpose of our research is to investigate organoleptic, physico-chemical and antioxidant properties of marshmallow with dyes from Sudanese rose and black chokeberry at storage with found out optimal conditions of its storage and type of packing.

2. Materials and Methods

2. 1. Materials and Samples

The following chemicals, used in this study are as follows: potassium bromide (CG Chemikalien GmbH & Co. KG, Germany), sulphic acid, hydrochloric acid (Sumychimprom, Ukraine), sodium hydroxide (Harkivreahim, PrAT, Ukraine), phenolphthalein (Shostka Chemical Reagents Plant, Ukraine), 96 % ethanol-water (w/w) (Galichpharm, Ukraine), toluene (Cherkassy State Plant of Chemical Reagents, Ukraine), glucose (Harkivreahim, PrAT, Ukraine), potassium hexacyanoferrate (III) (Merck, Germany), methylene blue (Merck, Germany). All the chemicals used in this experiment were of analytical grade, except for ethanol, which was of food grade.

For preparation of the solutions distilled water with electric conductivity no more 0.55 mS/m was used. The electric conductivity was measured by device CEL-1M2 (Analitpribor, Georgia).

Organoleptic, physicochemical, antioxidant properties of the product during 30 days store was investigated in our work. The object of our investigation is marshmallow with dyes from Sudanese rose and black chokeberry (**Fig. 1**), made on gelatin or on gelatin with solubilized substances (**Table 1**). As a control we used marshmallow, made on gelatin without natural anthocyanin dyes.

a *b*

Fig. 1. Samples of the new marshmallow types with natural anthocyanin dyes:
a – extract of krias-powder from Sudanese rose; *b* – extract of krias-powder from black chokeberry

Table 1
The test samples of marshmallow

Abbreviation of marshmallow sample	Component of marshmallow	
	Dye	Structuring agent
MSR-1	Water extract of krias-powder from Sudanese rose	Gelatin
MSR-2		Gelatin with solubilized substances
MSR-3	Water-alcohol extract of krias-powder from Sudanese rose	Gelatin
MSR-4		Gelatin with solubilized substances
MBC-5	Water-alcohol extract of krias-powder from black chokeberry	Gelatin
MBC-6		Gelatin with solubilized substances

Technological process of marshmallow with natural anthocyanin dyes manufacturing included next operations: preparation of the receipt ingredients, preparation of sugar-treacle syrup, swelling of structuring agent, mixing of ingredients, scuffling, mixing with dye, formation of products, cutting, staying.

Like dyes small dispersed powders of Sudanese rose (*Hibiscus Sabdariffa*) and black chokeberry (*Aronia melanocarpa*), obtained by the cryogenic technology (NPP Krias Plyus, Ltd., Ukraine), was used (**Fig. 2**).

a *b*

Fig. 2. Krias-powders from: *a* – Sudanese rose; *b* – black chokeberry

Water and water-alcohol extracts of krias-powder from Sudanese rose (SR) was put of quantity 3–5 % from the total mass of marshmallow, water-alcohol extract of krias-powder from black chokeberry (BC) – 8,5–9,5 %. Like structuring agent gelatin of food mark P-11 (Ukraine) or gelatin with solubilized substances [12] was used.

2. 2. Experimental procedures

2. 2. 1. Method of estimation of organoleptic characteristics

Organoleptic characteristics of marshmallow were determined by sensory evaluation of the products by the method of expert estimation on a five points scale [13, 14]. Complex index of quality (K_0) of the all types of marshmallow according to organoleptic indexes was calculated by expression:

$$K_0 = M_1 \frac{P_1}{P_1^b} + M_2 \frac{P_2}{P_2^b} + M_3 \frac{P_3}{P_3^b} + M_4 \frac{P_4}{P_4^b} + M_5 \frac{P_5}{P_5^b}, \quad (1)$$

where M_1, M_2, M_3, M_4, M_5 – are coefficients of weight, and were determined by the method of expert estimation at conditions that $M_1+M_2+M_3+M_4+M_5=1{,}0$; P_1^b, P_2^b, P_3^b, P_4^b, P_5^b – are organoleptic indexes of quality of the basic sample at the condition that maximal value of $P_1^b = P_2^b = P_3^b = P_4^b = P_5^b$ is 5 points; p_1, p_2, p_3, p_4, p_5 – are organoleptic indexes: form, surface, consistence, taste and smell, colour of the investigated marshmallow samples. The intensity of the complex index assessed on a scale as follows: 0.90–1.0 is "excellent"; 0.75–0.89 – "good"; 0.50–0.74 – "satisfactory"; 0.00–0.49 – "failed".

2. 2. 2. Methods of investigation of physicochemical indexes of quality

Quantitative characteristic of quality of the marshmallow samples and its investigation during the term of storage in various types of packing was done according to the main physical-chemical properties – moisture content, reducing substances content, total acidity, density. These indexes were determined using standard methods [15, 16].

Moisture content in marshmallow was determined by drying 5 g of the sample in weighting bottle in stove for 50 minutes at (130±2) °C temperature.

Total acidity (X_a) of the investigated samples in degrees was determined by results of titration of water extract of the 5 g of the sample from microburette (2 ml) 0,1 M sodium hydroxide solution with phenolphthalein and calculated by the expression:

$$X_a = \frac{V \cdot C \cdot 100}{m \cdot 10}, \quad (2)$$

where V – volume of sodium hydroxide solution for titration, ml; C – molarity of sodium hydroxide solution for titration, M; m – mass of the marshmallow sample for analysis, g; 100 – coefficient of recalculation on 100 g of the product; 10 – coefficient of recalculation of 0,1 M sodium hydroxide solution into 1 M.

Determination of density of the products was done on device, that consists of glass cylinder of height about 400 mm, diameter about 75 mm with burette of 25 ml volume, welded to its upper part ,and plastic lid, and plunger with screw for fixation it on the perfect height in the center of the lid. Density was determined by the volume of toluene, replaced at plunging in it marshmallow sample.

Mass fraction of the reducing substances was determined by ferricyanide method.

2. 2. 3. Method of determination of sorption moisture of marshmallow

Determination of the sorption moisture of the marshmallow samples was carried out by keeping 9 g samples to the state of equilibria artificially created in vapor-air medias with relative humidity of air 40, 60, 80, 90, 97 % at temperature 20 °C followed by determination of moisture content of the samples by weighting it.

2. 2. 4. Method to determine stability of marshmallow colour

Stability of colour of the samples, due to presence of anthocyanic substances, was investigated by spectrophotometry method. Intensity of colour of the products was measured by the value of optical density of fresh marshmallow solution. For the purpose the sample of 5 g of marshmallow was dissolved in water heated up to (40–50) °C. Solution was replaced in 100 ml volumetric flask, added 2 ml of saturated hydrochloric acid and brought up to the mark by distilled water. Optical density of the obtained solution was measured on spectrophotometer SF-2000 (LOMO) on 510 nm wave length, use quartz cuvette with 10 mm layer. Initial and the next (in 15, 30 days) determinations of optical density of the solutions of investigated marshmallow samples were carried out in the same conditions like initial measurement. Change of optical density was measured in percent, and initial optical density was considered to be 100 %.

2. 2. 5. Methods of research of antioxidant properties

Total oxidant capacity (TAC) of marshmallow with natural anthocyanin dyes was determined by the method of galvanostatic coulometry with electrogenerated bromine according to methodic [17]. The experimental data of coulometric titration were used to calculate the TAC values (Kl/100 g) of the investigated samples by formula:

$$TAC = \frac{100 \cdot I \cdot t \cdot m_s}{m_a \cdot m}, \quad (3)$$

where I – current strength, A; t is the time of reaching the titration end-point, s; m – mass of the test sample used for analysis, g; m_s – mass of marshmallow solution, g; m_a – mass of aliquot, used for analysis, g.

Obtained values of TAC were recalculated on the values of total antioxidant capacity with use of nominal scale of concentrations with referent substance-well known antioxidant ascorbic acid (AAE). Values of TAC in ascorbic acid equivalent (mg AAE/100 g sample) were calculated by expression:

$$TAC = \frac{Q}{Q_{AA}}, \quad (4)$$

where Q and Q_{AA} – are quantity of electricity needed for oxidation of the unit of mass of the sample and ascorbic acid respectively.

For correct comparison of TAC value, the data obtained by experiment, at perfect content of moisture in the sample, were recalculated on the mass of dry substances of marshmallow. Value of present mass of moisture was considered at the beginning and at the end of the term of storage. To do it we considered linear dependence of change of antioxidant capacity with the change of humidity content in the sample. According to this assumption, the value of antioxidant capacity of dry substances of the sample marshmallow $TAC_{d.s.}$ (mg AAE/100 g of dry substances of marshmallow) was calculated according to the equation (5):

$$TAC_{d.s.} = TAC\frac{100}{100 - W}, \quad (5)$$

where TAC – antioxidant capacity of the sample at corresponded contain of moisture W (%).

For comparison analysis of the TAC marshmallow samples was considered to be 100 %. Relative change of δTAC samples (%) in 30 days of store was calculated according to the equation (6):

$$\delta TAC_{d.s.} = \frac{TAC^{30}_{d.s.}}{TAC^{0}_{d.s.}} \cdot 100\ \%, \quad (6)$$

where $TAC^{30}_{d.s.}$ – antioxidant capacity of dry substances of the sample in 30 days of store, mg AAE/100 g; $TAC^{0}_{d.s.}$ – antioxidant capacity of dry substances of the sample after preparation, mg AAE/100 g.

2. 3. Statistical analysis

Determination of the experimental values of variable *x* was done in a number of parallel determinations (n=4 or 5). The difference of parameters were tested by Student's t-test with P=0,95. The values of the experimental data obtained by this way or calculated from it are presented in tables like $\bar{x} \pm \Delta x$ where $\bar{x}$ is mean value, Δx – the mean mistake. Statistical treatment of the data was done using Excel, Microsoft Office 2010 Software.

3. Results

3. 1. Quality characteristics, antioxidant capacity of the marshmallow samples

Using a sensor the estimation organoleptic characteristics of marshmallow was determined and complex indexes of quality were calculated: control K_0=0,92, marshmallow with natural anthocyanin dyes – K_0=0,96–0,97.

The results of determination of physicochemical characteristics and antioxidant capacity proved quality of the new marshmallow types. Present mass of moisture for marshmallow with natural anthocyanin dyes is in values from 19.0 to 21.5 %, density – in 0.51…0.67 g/sm^3, reducing substances content not more than 13.6 %. Total acidity – 3.5. Use of natural anthocyanin dyes in marshmallow technology let us to increase of TAC of the samples up to 24,7...34,6 mg AAE/100 g sample.

3. 2. Prove of conditions of marshmallow samples storage with anthocyanin dyes

With the purpose to prove the storage conditions of the new marshmallow types the dynamics of change of mass of marshmallow samples at various values of relative humidity of air at storage at temperature (15…18) °C during 30 days was investigated.

It was determined that during the storage of the samples at a relative humidity of 60...80 % after 2 days the mass change of marshmallow samples without additives and with additives had not exceed 4.80±0.20 %. After 30 days of storage the mass change of marshmallow without additives amounted to 7.15...+62.97 %, mass change of marshmallow with extracts of krias-powder amounted to 15.50...+50.84 %, depending on a relative humidity.

According to regulatory documents, this type of products should be stored at the temperature (15...18) °C and relative humidity no more than 75 %. Thus, short-term storage (up to 2 days) of marshmallow with natural anthocyanin dyes at the temperature (15...18) °C and relative humidity of 60...75 % is possible without packing. Storage of new products during the long term (30 days) is possible only when packaging materials that prevent moisture diffusion is being used.

3. 3. Changes of quality characteristics, antioxidant capacity of the marshmallow samples during its storage

An influence of ways and terms of storage on the quality of new types of marshmallow was determined on the base of change of physicochemical and organoleptic characteristics throughout 30 days from manufacturing date. Marshmallow with natural anthocyanin dyes was stored at 15...18 °C and at relative humidity not more than 75 %. The samples were packed in accordance with current requirements in polyethylene wrap or polyethylene wrap and box of corrugated cardboard, designed for confectionary products with mass of 150 g. Received results of research of changes in physico-chemical properties during storage period are shown in **Table 2**.

The results of $\delta TAC_{d.s.}$ determination of the marshmallow samples in various types of package were obtained after storage for 30 days. The most stable from the point of view of antioxidant properties are marshmallow samples with water-alcohol extracts of krias-powders (MSR-3, MSR-4, MBC-5, MBC-6). An increase of TAC shows us redox reactions between chemical substances of complete food matrix. An analysis of literature sources show us that analogous dependencies were obtained for fruit and vegetable juices [18–20], extracts [21].

3. 4. An investigation of colour stability of marshmallow with natural anthocyanin dyes at storage in various types of package

It was determined that within 1–14 days of storage in polyethylene wrap organoleptic quality characteristics of the marshmallow had matched just manufactured products. Within 15–30 days the intensity of the products' colour was reduced, other organoleptic characteristics remained without changes. For products with additional cardboard package visual perception of colour after 30 days of storage remained without changes. Thus, further researches were related to the study of the products' colour stability during storage for 30 days with different types of packaging (**Table 3**).

Table 2

Physicochemical properties of marshmallow in 30 days storage

Marsmallow sample	Moisture content, %	Reducing substances content, %	Density, g/cm^3	Total acidity, °degree
		Package – polyethylene wrap		
Control	17,0±0,5	14,0±0,6	0,50±0,02	3,8±0,1
MSR-1	14,6±0,5	16,0±0,6	0,49±0,02	4,2±0,2
MSR-2	14,2±0,5	16,0±0,5	0,50±0,02	4,3±0,2
MSR-3	12,5±0,5	15,0±0,6	0,49±0,02	3,7±0,1
MSR-4	11,9±0,5	15,0±0,5	0,48±0,02	3,8±0,1
MBC-5	13,8±0,3	18,2±0,6	0,58±0,02	3,7±0,1
MBC-6	13,2±0,3	18,2±0,5	0,59±0,02	3,8±0,1
		Package – polyethylene wrap and cardboard box		
Control	17,8±0,5	12,5±0,6	0,52±0,02	3,9±0,1
MSR-1	17,5±0,5	15,6±0,6	0,53±0,02	4,3±0,2
MSR-2	17,2±0,5	15,6±0,5	0,54±0,02	4,4±0,2
MSR-3	14,8±0,5	14,0±0,6	0,50±0,02	3,7±0,1
MSR-4	14,0±0,5	14,0±0,5	0,48±0,02	3,8±0,1
MBC-5	17,0±0,5	15,1±0,6	0,59±0,02	3,8±0,1
MBC-6	16,7±0,5	15,1±0,5	0,59±0,02	3,9±0,1

Table 3

The colour intensity of the marshmallow samples at store it in various types of package

Marsmallow sample	Day of storage	The colour intensity of the marshmallow samples (%) at store in package	
		polyethylene wrap	polyethylene wrap and cardboard
MSR-1	15	62.9 ± 1.8	67.8 ± 2.0
	30	42.0 ± 1.2	45.0 ± 1.3
MSR-2	15	64.0 ± 1.8	66.0 ± 1.9
	30	46.0 ± 1.3	48.5 ± 1.4
MSR-3	15	84.0 ± 2.5	89.0 ± 2.6
	30	**60.0 ± 1.7**	**65.0 ± 1.9**
MSR-4	15	80.0 ± 2.4	83.0 ± 2.4
	30	**67.0 ± 2.0**	**72.1 ± 2.1**
MBC-5	15	87.0 ± 2.5	95.0 ± 2.7
	30	**78.0 ± 2.3**	**82.0 ± 2.5**
MBC-6	15	85.0 ± 2.5	89.0 ± 2.6
	30	**80.1 ± 2.4**	**80.1 ± 2.4**

Data from **Table 3** show us, that in 15 days intensity of colour of the products decrease on 5−38 %. At the end of storage changes are 18−58 %.

4. Conclusions

Complex index of new types of marshmallow was determined with the use of sensor estimation. It is 0.96−0.97 and higher than the control result (0.92).

Investigation of new types of marshmallow with natural dyes from Sudanese rose and black chokeberry by standard methods show us that moisture content in it 19.0...21.5 %, density − 0.51...0.67 g/cm^3. Reducing substances content not more than 13.6 %, total acidity − 3.5 degrees).

The results of investigation of marshmallow with natural dyes from Sudanese rose and black chokeberry by galvanostatic coulometry method with electrogenerated bromine prove an increase of its antioxidant properties in 2...2.5 times more than the same results for samples, made without the dyes.

The results of determination of moisture content, density, total acidity, intensity of colour, antioxidant properties on the new types of marshmallow show us the possibility of its storage without packing within 2 days. At the storage temperature of air should be not more than 15...18 °C, relative humidity − 75 %. The use of hermetic package (for example − polyethylene wrap and cardboard box) let us to save marshmallow properties at prolonged storage at these conditions up to 30 days.

Our future investigations will be devoted to carry out differential-thermic and thermogravimetric analysis of marshmallow with dyes from Sudanese rose and black chokeberry to determine quantity of free and bound water in products, what let us to control changes that take place at storage. Conformation of safety of the products for human organism during the term of storage, considered by normative documentation, assumed also investigation of microbiological indexes of marsmallow quality.

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