1. Introduction

Marshmallow is a confection of foam-like structure and demand for it is constantly growing on the world market. Due to the presence of gelatin, it possesses good chewing properties. It is used directly for food, undergoes thermal treatment, added to hot chocolate, coffee or cocoa, used as an ingredient in confectionery [1]. Marshmallow is produced by big transnational companies, like Nestle (Switzerland), in the countries different in their level of development (Table 1).

Technologies of marshmallow that is stable to melting with the use of food microcrystalline cellulose [2], a mixture of various saccharides [3], with spirulina [4], based on plant or microbial polysaccharides [5], etc. are widely known. In order to improve the nutritional value of marshmallow, dry bee pollen is included in the receipts of it [6].

To ensure high organoleptic characteristics of marshmallow, dyes and flavoring substances are included in the receipts. The most of them are synthetic, therefore a positive impact does not go beyond a good colour, taste and smell.
But the nutritional value of the main types of marshmallow remains very poor.

<table>
<thead>
<tr>
<th>Geography of marshmallow producers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trademark</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Nestle</td>
</tr>
<tr>
<td>Campfire</td>
</tr>
<tr>
<td>Haribo</td>
</tr>
<tr>
<td>Guandy</td>
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<tr>
<td>Fruna</td>
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<tr>
<td>Sweet snow</td>
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<tr>
<td>Lisova kazka</td>
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</tbody>
</table>

The results of investigations on the influence of combinations of food supplements in the quantities typical for common children foods on the human organism show that chemical dyes inhibit the growth of nerve cells 4–7 times [7]. Therefore, the investigations lead us to the development of new types of products using natural herbal ingredients. Among herbal supplements, we can distinguish cryopowders, obtained by cryogenic grinding of raw materials, which allows saving biologically active substances and improving the quality of the final product. The authors of works [8, 9] used red beetroot cryopowder in butter technology. Cryopowders made of grape and black chokeberry were used in the technology of yeast products and shortcakes, which helped to improve their organoleptic and physicochemical characteristics, and also to increase the biological value [10].

Among the fruit and berry powders with high dye effects, we can distinguish fine ones, obtained according to the cryogenic technology at the “Krias Plyus” factory (Kharkiv, Ukraine), especially Sudanese rose and black chokeberry cryopowders [11].

Thus, it is important to study natural anthocyanin dyes to produce high-quality marshmallow with improved food value and natural colour. Realization of the idea will let us to expand the marshmallow range and create competitive products on the confectionery market.

2. Literature review and problem statement

Scientists are actively developing new marshmallow technologies for special purposes with the use of herbal raw materials or products of their treatment. So, marshmallow for functional purposes may include barley-malt and polymalt extracts, carrot and pumpkin juices, flour of fried wheat germ flakes, etc. [12, 13]. The use of new-generation sweeteners (isomaltitol, erythritol, maltitol) and mixtures thereof with fructose in marshmallow production [14, 15] allows obtaining dietary products [16]. Introduction of carrot and pumpkin juices to the dietary marshmallow increases its nutritional value and provides the “functional-dietary” status of the product [17]. To increase the nutritional value of marshmallow, the priority of using non-traditional raw materials – topinambur powder and fruit juices has been proved [18, 19]. But the task to give an attractive stable colour to the products due to natural dyes has not been solved in these works. The antioxidant capacity of the dietary, functional-dietary products has not been determined too.

There are also no references dealing with determination of the antioxidant capacity of the developed fortified products – marshmallow with inverted sugar syrup and phyto-extracts, vitamins C, B [20]. At the same time, the issue of improving the colour and taste of marshmallow due to the introduction of black chokeberry phyto-extract is discussed in the work. More recent investigations of 2014–2016 are dedicated to the development of marshmallow for functional purposes and expansion of its range [21–24]. The technology of marshmallow for functional purposes with the use of natural functional ingredient – “Instantgum” gum arabic has been developed. This ingredient is a source of natural food fiber, improving digestion, reducing blood glucose levels, which is especially important for diabetics [21, 22].

The use of gum arabic together with xanthan and agar as a structure former in the production of colored and flavored marshmallow has been proposed. This has allowed expanding the range of confectionery in the absence of animal ingredients [23, 24].

The problems of preserving the organoleptic, physicochemical properties, colour stability, antioxidant capacity of the developed marshmallow over time have also not been solved in the works [21–24].

The solution of these problems has been considered by the authors of the present publication. New types of marshmallow with natural anthocyanin dyes – Sudanese rose (SR) and black chokeberry (BC) cryopowders have been developed [25]. These are fine dyes. They are obtained by the low-temperature technology, which allows saving all biologically active substances of raw materials. It has been shown that the use of these dyes in marshmallow technology gives antioxidant properties to the product [26]. Investigations of the properties of new types of marshmallow with natural anthocyanin dyes during the storage period have not been done. A study of organoleptic, physicochemical and antioxidant properties of these products is necessary to justify their storage conditions and type of packaging.

So, to solve the problem of preserving the quality, colour stability, antioxidant capacity of marshmallow with natural anthocyanin dyes, it is important to investigate its properties within the storage period.

3. The purpose and tasks of the investigation

The purpose of the work was to investigate the organoleptic, physicochemical and antioxidant properties of marshmallow with natural anthocyanin dyes within the storage period, to justify its storage conditions and type of packaging.

To achieve the purpose, it is necessary to accomplish the following objectives:

- to determine the organoleptic, physicochemical quality characteristics and antioxidant capacity of marshmallow with Sudanese rose and black chokeberry cryopowder extracts;
- to justify the storage conditions and type of packaging for marshmallow with natural anthocyanin dyes;
- to investigate changes in the physicochemical characteristics and antioxidant capacity of marshmallow during storage in different types of packaging;
- to investigate the colour stability of marshmallow with natural anthocyanin dyes during storage in different types of packaging.
4. Materials and methods of investigation of the properties of marshmallow with natural anthocyanin dyes within the storage period

The object of the investigation are the organoleptic, physicochemical, antioxidant properties of the products during storage for 30 days. The subject of the investigation are marshmallows with natural anthocyanin dyes. They differed in the type of a structuring agent – gelatin or gelatin with solubilized substances and the type of a dye – Sudanese rose or black chokeberry cryopowder (Table 2). As a control sample, we used gelatin-based marshmallow without natural anthocyanin dyes.

Table 2

<table>
<thead>
<tr>
<th>Marshmallow sample abbreviation</th>
<th>Variable ingredients of the marshmallow recipe</th>
<th>Dye</th>
<th>Structuring agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSR-1</td>
<td>Water extract of Sudanese rose cryopowder</td>
<td>Gelatin</td>
<td>Gelatin with solubilized substances</td>
</tr>
<tr>
<td>MSR-2</td>
<td>Water-alcohol extract of Sudanese rose cryopowder</td>
<td>Gelatin</td>
<td>Gelatin with solubilized substances</td>
</tr>
<tr>
<td>MSR-3</td>
<td>Water-alcohol extract of black chokeberry cryopowder</td>
<td>Gelatin</td>
<td>Gelatin with solubilized substances</td>
</tr>
<tr>
<td>MSR-4</td>
<td>Water extract of black chokeberry cryopowder</td>
<td>Gelatin</td>
<td>Gelatin with solubilized substances</td>
</tr>
<tr>
<td>MBC-5</td>
<td>Water-alcohol extract of black chokeberry cryopowder</td>
<td>Gelatin</td>
<td>Gelatin with solubilized substances</td>
</tr>
<tr>
<td>MBC-6</td>
<td>Water extract of Sudanese rose cryopowder</td>
<td>Gelatin</td>
<td>Gelatin with solubilized substances</td>
</tr>
</tbody>
</table>

More details about the investigated materials and equipment, used in the experiment, as well as the methods of determination of quality indices of the samples are given in [27].

5. The results of investigations of organoleptic, physicochemical, antioxidant properties of marshmallow with natural anthocyanin dyes

5.1. Organoleptic quality characteristics and sensory evaluation of marshmallow with natural anthocyanin dyes

The results of determination of organoleptic characteristics and sensory evaluation of marshmallow with natural anthocyanin dyes are given in Table 3, 4.

We can see from Table 4 that the quality of marshmallow samples corresponds to the following estimates: control – excellent, marshmallow with natural anthocyanin dyes – excellent (\(K_r=1.0–0.9\)).

5.2. Physicochemical properties and antioxidant capacity of marshmallow with natural anthocyanin dyes

The results of determination of physicochemical quality characteristics and antioxidant capacity of the new types of marshmallow are given in Table 5.

Table 3

<table>
<thead>
<tr>
<th>Organoleptic quality characteristics of marshmallow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Index</td>
</tr>
<tr>
<td>Shape</td>
</tr>
<tr>
<td>Surface</td>
</tr>
<tr>
<td>Consistency</td>
</tr>
<tr>
<td>Taste and smell</td>
</tr>
<tr>
<td>Colour</td>
</tr>
</tbody>
</table>

We can see from Table 5 that moisture content for marshmallow with natural anthocyanin dyes is within 19.0...21.5 %, density is 0.51...0.67 g/cm³, reducing substances content does not exceed 13.6 %, total acidity is 3.5 degrees.

The data from Table 5 proved that the use of natural anthocyanin dyes in marshmallow technology has allowed increasing the TAC of the products up to 24.7...34.6 mg AAE/100 g of the sample.

Storage period is one of the main characteristics, which determines the competitiveness of any product on the market. During storage, quality characteristics of marshmallow may change due to physicochemical and microbiological processes. Decrease of the properties can be explained by moisture diffusion and various chemical transformations. Their chemical mechanism is connected with hydrolysis of hydrocarbons, redox reactions of marshmallow compo-
ments, condensation, polymerization of reversion products. Also, their intensity depends on composition, production technology, storage conditions and packaging method.

5.3. Justification of storage conditions of marshmallow with natural anthocyanin dyes

With the purpose to justify the storage conditions of the new marshmallow types, the mass dynamics (Δm) of marshmallow samples at different values of relative air humidity during storage at a temperature of (15...18) °C for 30 days was investigated. The results obtained in 2 days are given in Table 6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass variation index of marshmallow samples at a relative humidity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Control</td>
<td>-5.90</td>
</tr>
<tr>
<td>MSR-1</td>
<td>-5.80</td>
</tr>
<tr>
<td>MSR-2</td>
<td>-5.90</td>
</tr>
<tr>
<td>MSR-3</td>
<td>-5.80</td>
</tr>
<tr>
<td>MSR-4</td>
<td>-6.00</td>
</tr>
<tr>
<td>MBC-5</td>
<td>-2.78</td>
</tr>
<tr>
<td>MBC-6</td>
<td>-7.00</td>
</tr>
</tbody>
</table>

Table 6
Marshmallow mass variation in 2 days of storage at different relative air humidity

During storage of the samples at a relative humidity of 60...80 %, after 2 days the mass variation of marshmallow samples without additives and with additives did not exceed 4.80±0.20 %. After 30 days of storage, the mass variation of marshmallow without additives amounted to 7.15...+62.97 %, mass variation of marshmallow with cryopowder extracts amounted to 15.50...+50.84 %, depending on relative humidity.

According to regulatory documents, this type of products should be stored at a temperature of (15...18) °C and relative humidity not more than 75 %. Thus, short-term storage (up to 2 days) of marshmallow with natural anthocyanin dyes at a temperature of (15...18) °C and relative humidity of 60...75 % is possible without packaging. Storage of new products during long periods (up to 30 days) is possible only in polymer packaging materials that prevent moisture diffusion.

5.4. Variation of quality, antioxidant capacity of marshmallow samples during storage

The influence of storage methods and periods on the quality of new types of marshmallow was determined based on the variation of the main physicochemical and organoleptic characteristics. The investigation was carried out during the entire storage period – 30 days from the manufacturing date. Marshmallow with natural anthocyanin dyes was stored at 15...18 °C and relative humidity not more than 75 %. In accordance with current requirements, the samples were packed in polyethylene wrap or polyethylene wrap and a corrugated cardboard box, designed for confectionery products, 150 g in each. The results of the research of changes in physicochemical properties during the storage period are shown in Fig. 1, 2.

After 30 days of storage in polyethylene wrap, moisture content in marshmallow without additives was 17.0 %, and with the addition of cryopowder extracts was 12.0–14.7 %. For MSR-1 and MSR-2 samples, moisture loss during the first 15 days of storage was similar to marshmallow without additives; moisture loss during 16–30 days increased.

During storage in polyethylene and cardboard, humidity is 17.8 % for marshmallow without additives and 14.0–17.5 % for marshmallow with additives. It was found that after 30 days of storage, the total acidity of marshmallow with water extracts of cryopowders was 4.2–4.3 degrees, of marshmallow with water-alcohol extracts of cryopowders was 3.7–3.9 degrees.

The variation of the reducing substances content in marshmallow is interrelated with the variation of total acidity during storage. It was found that during storage, the accumulation of reducing substances in all experimental samples took place, but it occurred more intensely provided that marshmallow was stored in polyethylene wrap (by 2–4 %).

The data for determining the density of new types of marshmallow throughout the storage period are given in Fig. 2.

At the end of shelf-life, the density of the products with the Sudanese rose and black chokeberry cryopowder extracts was within acceptable limits.
The TAC value gives information about the antioxidant potential of chemical substances of a complex food system regarding its possibility to inhibit oxidation processes. The latter are important in the quality testing of the developed foods during storage under different conditions. For a correct comparison, the values of TAC, obtained by experiment at a certain moisture content in the sample were recalculated into the dry weight of marshmallow. The value of moisture content was recorded at the beginning and at the end of the storage period. To do this, we made an assumption about the linear variation of antioxidant capacity with the variation of moisture content in the sample. TAC<sub>dw</sub> (mg AAE/100 g dry weight of the marshmallow sample was calculated by the formula (1):

\[
TAC_{dw} = TAC_{w} \times \frac{100}{100 - W},
\]

where TAC is the antioxidant capacity at the corresponding moisture content, W (%). To calculate the values of moisture content in the samples, we took the data from Table 5.

For comparative analysis, the TAC of marshmallow samples was considered to be 100%. Relative variation of δTAC of the samples (%) in 30 days of storage was calculated by the formula (2):

\[
\delta TAC_{dw} = \frac{TAC_{dw}^{30} - TAC_{dw}^{0}}{TAC_{dw}^{0}} \times 100\%,
\]

where TAC<sub>dw</sub><sup>0</sup> is the antioxidant capacity of the dry weight of the sample after 30 days of storage, mg AAE/100 g; TAC<sub>dw</sub><sup>30</sup> is the antioxidant capacity of the dry weight of the sample after preparation, mg AAE/100 g.

The results of determination of δTAC<sub>dw</sub> of marshmallow samples after 30 days of storage in different types of packaging are shown in Fig. 3.

According to the obtained data (Fig. 3), relative variations of δTAC<sub>dw</sub> of MSR-3, MBC-5 samples did not exceed 10% regardless of the type of packaging. For gelatin-based marshmallow with solubilized substances (MSR-4, MBC-6 samples), variations of δTAC<sub>dw</sub> were greater – about 50%.

5. 5. An investigation of the colour stability of marshmallow with natural anthocyanin dyes during storage in different types of packaging

It was determined that within 1–14 days of storage in polyethylene wrap, organoleptic quality characteristics of marshmallow matched just manufactured products. Within 15–30 days, the colour intensity of the products reduced, other organoleptic characteristics remained unchanged. For the products with additional cardboard packaging, visual colour perception after 30 days of storage remained the same. Thus, further researches were related to the study of the products’ colour stability during storage for 30 days in different types of packaging (Fig. 4).

![Fig. 4. The colour intensity I of the marshmallow samples during storage depending on the type of packaging: a – polyethylene wrap; b – polyethylene wrap and a cardboard box](image)

From the given data (Fig. 4), it can be seen that within 15 days, the colour intensity of the products reduced by 5–38%. At the end of the shelf-life, changes amounted to 18–58%.

6. Discussion of the results of investigation of properties

According to the results of the sensory evaluation, it was found that marshmallow with Sudanese rose and black chokeberry cryopowder extracts possesses a regular shape with clear outlines without deformation. The surface of the products is dry, not sticky, without rough solids, evenly sprinkled with a mixture of starch and sugar powder, the consistency is soft, foam-like, viscous. The new products are of pink colour with a sour-sweet taste and Sudanese rose or black chokeberry flavour (Table 3). Almost all of the organoleptic characteristics (shape, consistency, taste, smell, colour) of the new products with natural anthocyanin dyes exceed the results of the control sample, manufactured without them (Table 4).

The results of determination of physicochemical characteristics (Table 5) proved that we provided the quality characteristics necessary for these products. Moreover, the use of natural anthocyanin dyes in marshmallow technology allows increasing the antioxidant properties of the finished product (Table 5). We can see it from the 2–2.5 times in-
crease of TAC for all of the developed samples compared to the control sample that doesn’t contain the dyes.

According to the obtained results (Fig. 1), moisture loss in marshmallow with natural dyes after 30 days of storage in polyethylene wrap was higher than in that without additives. An increase of moisture loss in MSR-3, MSR-4, MBC-5, MBC-6 samples during storage was probably due to a greater content of free moisture and probably the presence of volatile ethanol in the dye extracts. Moisture loss in MSR-1 and MSR-2 samples during 16–30 days increased, which was likely due to the greater fraction of free water in the samples.

In case of hermetic polyethylene packaging of marshmallow samples, moisture removal occurred until equilibrium in the packaging airspace was reached. However, polyethylene is characterized by the partial permeability of water vapor. With additional cardboard packaging, moisture loss in the marshmallow slowed down, therefore humidity did not decrease as much as during storage in polyethylene. Therefore, additional packaging of marshmallow in a cardboard box allows maintaining the humidity of products with a water extract of Sudanese rose cryopowder at 91–94% of the initial level, with water-alcohol extracts of cryopowders – at 74–82% of the initial level. This allows keeping a soft elastic consistency and holding the shape of marshmallow.

During storage of marshmallow, the value of the total acidity of the products at the end of the storage period did not depend on the type of packaging. After 30 days of storage, the total acidity of marshmallow with water extracts of cryopowders increased by 0.75–0.83 degrees, of marshmallow with water-alcohol extracts of cryopowders by 0.18–0.35 degrees and did not exceed allowable limits. At the same time, accumulation of reducing substances in marshmallow was due to the hydrolysis of sucrose.

It was determined that for all samples of marshmallow, there was a slight decrease in density during storage (Fig. 2). The greatest change in this characteristic for the samples stored in polyethylene wrap was observed for marshmallow with a water extract of Sudanese rose cryopowder – 15–16%. Additional cardboard packaging of the samples allowed reducing the density variation of the products, that is allowed preserving the elastic consistency of marshmallow.

According to the obtained data (Fig. 3), MSR-3, MSR-4, MBC-5, MBC-6 marshmallow samples with water-alcohol extracts of cryopowders are the most stable from the point of view of the antioxidant capacity. The peculiarity is that these marshmallow samples with water-alcohol extracts of cryopowders, packed in polyethylene wrap and cardboard possess higher TAC value than those, packed only in polyethylene wrap. An increase of TAC proved the occurrence of redox reactions in a complex food matrix: natural antioxidants with photochemical properties, food components, atmospheric oxygen and Maillard reaction products. Literature review showed that similar results were obtained for fruit and vegetable juices [28–30], extracts [31]. Maximal changes of the antioxidant capacity were observed for the samples of marshmallow with the Sudanese rose cryopowder extracts.

From the above data (Table 4), we can see that the mechanism of colour intensity variation of marshmallow for all of the samples is the same. It was found that additional packaging of marshmallow in a cardboard box allows decreasing the colour intensity variations of the products by 6%.

It was determined that introduction of a water-alcohol extract of Sudanese rose cryopowder to the composition of marshmallow allows making products with the colour intensity of 60–72% of the initial value at the end of the storage period (Fig. 4). It was proved that the products with the black chokeberry cryopowder extract possess a more stable colour than those with the Sudanese rose cryopowder extract. At the end of the storage period, the colour intensity is 78–84% of the initial value.

Gelatin-based marshmallow with solubilized substances at the end of the storage period was characterized by a more intense colour compared to gelatin-based marshmallow. So, the use of a structuring agent with solubilized substances allows making products with a more stable colour. The results of our research proved that during storage of marshmallow with natural anthocyanin dyes – Sudanese rose and black chokeberry cryopowders, the colour intensity decreases. But if stored in polyethylene wrap and a cardboard box, changes are less intense. Therefore, we recommend storing the new types of marshmallow in such type of packaging.

7. Conclusions

1. The results of sensory evaluation proved an improvement of organoleptic characteristics of the new types of marshmallow with natural anthocyanin dyes made of Sudanese rose and black chokeberry compared to control ones. Their complex quality index is 0.96–0.97 that is higher than the control result (0.92).

2. For the new types of marshmallow with natural anthocyanin dyes, the quality indexes necessary for the product were provided. Moisture content is within 19.0–21.5%, density is 0.51–0.67 g/cm³, reducing substances content does not exceed 13.6%, total acidity is 3.5 degrees. The use of natural anthocyanin dyes in marshmallow technology allows increasing the antioxidant properties of the finished product. The value of the antioxidant capacity for all of the developed samples is 2–2.5 times higher than that of the samples, made without the dyes.

3. It was found that short-term storage of marshmallow with natural anthocyanin dyes (up to 2 days) at a temperature of 15–18°C and relative air humidity of 75% is possible without packaging. Storage of the products during longer periods (up to 30 days) is possible only with using packaging materials.

4. Variation dependencies of organoleptic and physicochemical quality characteristics of marshmallow with natural anthocyanin dyes during 30 days of storage in different types of packaging were studied. It was found that storage of the products, hermetically packed in polyethylene wrap and cardboard provides high characteristics of quality.

5. It was proved that preservation of the colour intensity of marshmallow is ensured by packaging in polyethylene wrap and cardboard.

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References


