Influence of buckwheat by-products on the antioxidant activity of functional desserts

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Abstract. Using of buckwheat by-products (hull fine powder and melanin obtained from the hull) in formulations of desserts (by the examples of chocolate cream and honeysuckle mousse) can improve their sensory and physico-chemical characteristics, including antioxidant activity (AOA). The chemical composition of buckwheat hull fine powder was studied, and sensory evaluation of the powder and melanin was carried out. The values of AOA allowed one to determine the amounts of the powder and melanin in desserts as 1.5 and 0.037 g per serving accordingly. Sensory evaluation of dessert samples showed high-point values. There were also determined physico-chemical characteristics of dessert samples. Besides increasing of AOA, the buckwheat hull fine powder increases dietary fibers content in desserts. All dessert samples with addition of melanin satisfy more than 15% of the daily need in antioxidants, so the developed desserts can be considered as functional products.

1. Introduction

According to “The Strategy for Quality Improving of Food Production in Russian Federation by 2030”, the improvement of existing food processing technologies is closely related to the expansion of food production range by using processed non-traditional raw materials among with biologically active natural food supplements for the development of specialized and functional products.

Among various plant raw materials, which are used in food processing industry, one of the most valuable is buckwheat (Fagopyrum sagittatum Gilib.). It is known that buckwheat processed products have got high sensory characteristics and nutritional value and easy-to-digest. They can also perform preventive and therapeutic functions [1]. These products are obtained mostly from buckwheat grain. However, buckwheat by-products can be used in food production formulations too.

One of these by-products is buckwheat hull. Its yield during buckwheat grain obtaining is about 20%. Buckwheat hull contains several useful substances and thus can be used as a food supplement [2]. It is also advisable to use buckwheat hull in a state of fine powder or obtain melanin from it. This is because mechanochemical treatment of plant raw materials allows activation of useful substances contained in them, so they can possess new useful properties [3].

The purpose of the work was the obtaining of the buckwheat hull fine powder and melanin and developing functional desserts formulations on their basis.
The formulation of the problem

The chemical composition of buckwheat hull according to previously carried out researches [4–6] is presented in Table 1.

|                     | Value       |
|---------------------|-------------|
| Crude protein       | 4.09±0.1    |
| Crude fat           | 4.42±0.5    |
| Carbohydrates       | 0.4±0.1     |
| Hemicellulose       | 20.9±0.2    |
| Ash content         | 1.49±0.01   |
| Humidity            | 8.93±0.3    |
| Starch content      | 1.92±0.07   |
| Lignin              | 30.87±0.5   |
| Pectin              | 3.74±0.06   |
| TGP**               | 25.0±0.3    |
| Cellulose           | 18.8±0.2    |

* – easily hydrolysable polysaccharides;
** – hardly hydrolysable polysaccharides (mainly cellulose and part of hemicelluloses).

According to the data from the table, there is a significant amount of fiber in the hull (up to 80%), which content is more than in most cereal products. The content of crude protein and crude fat is about 4%, hemicellulose – 20%, cellulose – 18% and ash – 2%. In addition to polysaccharides and lignin, buckwheat hull contains biologically active polyphenolic complexes, flavonoids, microelements (potassium, sodium, copper, silver, calcium, magnesium, zinc, aluminum, iron, chromium and phosphorus). Their amounts depend on the type of buckwheat, but hulls of all buckwheat grades are characterized by high potassium content [5].

Monosaccharide composition of buckwheat hull includes halocuronic acid in amount of 7.7%, galactose – 13.7%, arabinose – 8.6%, rhamnose – 2.0% and xylose – 3.3%. The content of functional groups in pectin is: free COOH groups – 7.7%; COOCH₃ groups – 7.7%; OSOS₃ groups – 0.1%; degree of polymerization – 63. It is known that pectin from the hull belongs to the pectin substances of higher plants and characterized by a low degree of esterification. Xylans make up the bulk of buckwheat hemicellulose hull [7].

The hemicelluloses content in hull is 18.0…18.5% by dry weight, cellulose – 22.0…24.0% [5]. The flavonoid content in hull consists of 9 flavonoids: kenpferol, 3,5,7,3,4-pentaxiflavon, apigenin, luteolin, formononetin, hyperoside, rutin, orientin and homoorientin [8]. The amount of rutin in hull is about 0.17%, vitamin E – up to 0.023%, nicotinic acid – up to 0.056%, tannins – up to 7.5% and brown pigment – up to 10% [6].

In addition to above-mentioned substances, buckwheat hull contains melanin, which is known to be one of the most powerful antioxidants with high UV-, radio-, gastro-, hepatoprotective and antioxidant activity antioxidant activity (AOA). Melanins have been widely used as therapeutic and prophylactic agents. They are involved in DNA repair processes, functioning of respiratory chain in cells as electron acceptors, serve as cellular metabolism systems modulators in photo- and radioprotection and neutralize lipid peroxidation products. In medicine melanins are used for protection from genetic damages after irradiation of persons exposed to prolonged exposure to ionizing radiation (for example, increased radiation background), as well as its further study in oncological practice [9, 10]. In food industry water-soluble melanin is used as preservative and dyestuff.
Melanins are characterized by the presence of unpaired electrons in their structure and have got the characteristics of stable free radicals. These properties are important for melanins to perform protective functions in the organism. Therefore, melanins do not only absorb various kinds of irradiation, but also neutralize and deactivate free radicals, which are formed under ionizing radiation and certain chemicals actions on living organisms [11].

The useful properties of buckwheat hull and melanins allow one to use them as food supplements in various food products and dishes (pates, beverages, cottage cheese products, desserts, etc.). In this work, there were developed formulations and technology of desserts with supplements from buckwheat hull fine powder and melanins. Previous researches (on the example of using Matcha green tea in marshmallow formulations) showed the advisability of addition of antioxidiant supplements into confectionery products and dessert formulations [12].

3. Materials and methods

The experimental researches were held at the Technology and Organization of Food Industries Department of Novosibirsk State Technical University in cooperation with the Laboratory of Solid State Chemistry of Institute of Solid State Chemistry and Mechanochemistry of the SB RAS.

From sowing buckwheat hull a fine powder was obtained. The grinding process was carried out using DESI-11 desintegrator (Estonia). The obtained powder had got brown color, strongly marked taste and smell of buckwheat grain. Powder particle sizes were determined using Microsizer 201 device (Russia), there values were 0.13…0.18 mm.

Obtaining of melanin included the following technological operations: buckwheat hull grinding, extraction, sedimentation and filtration. The solubility of the obtained melanin in the water at 23 °C is less than 0.087 g/l. The melanin yield was 5% from 20 g of hull.

The antioxidants presence in buckwheat hull fine powder and melanin were determined by AOA values using Yauza Color-01-AA device (Russia) according to the “Evaluation methodic of antioxidants for water-soluble samples” № 31-07 from May 14th, 2007 (№ 20706-05). The quercetin (B95% SigmaAldrich) was used as the control sample.

The base formulation of desserts were honeysuckle mousse and chocolate cream according to the formulation № 611 from “The Digest of Dishes and Culinary Products Formulations for Public Catering Enterprises” (1996).

The ingredients ratio in dessert formulations were calculated according to the methodical recommendations MR 2.3.1.1915-04 “The recommended levels of nutritional and biologically active substances consumption” by consumption norms of quercetin considering its toxicity.

For sensory evaluation of obtained buckwheat by-products, the descriptive and profile method was used. This method clearly demonstrates sensory characteristics of the obtained samples for their use in food products formulations [13].

The sensory evaluation of dessert samples was carried out according to Russian national standard GOST 31986-2012 “Public catering service. Method of sensory evaluation of catering products” on the 5-point scale for the following characteristics: appearance, aroma, smell of buckwheat, consistency, taste.

Chemical composition of buckwheat hull and physico-chemical characteristics of dessert samples were determined according to standard methods.

4. Results and discussion

The chemical composition of buckwheat hull fine powder is shown in table 2. It is seen that buckwheat hull fine powder can be used as a source of dietary fibers and sodium.

The results of sensory evaluation of obtained functional ingredients are shown in figure 1. According to the profilogram, buckwheat hull fine powder has got higher characteristics of taste and smell, then melanin. This defines their content in dessert formulations.
Table 2. Chemical composition of buckwheat hull fine powder

| Index          | Value       |
|----------------|-------------|
| Water, %       | 7.00±0.3    |
| Proteins, %    | 4.83±0.1    |
| Crude fat, %   | trace       |
| Sugar, %       | 41.31±0.15  |
| Cellulose, %   | 36.27±0.31  |
| Pectin, %      | 3.74±0.1    |
| Crude ash, %   | 6.82±0.4    |
| Minerals:      |             |
| Na, mg%        | 1000.0±0.21 |
| K, mg%         | 840.0±0.36  |
| Ca, mg%        | 260.0±0.2   |
| Fe, mg%        | 48.0±0.1    |

Figure 1. Profilogram of sensory evaluation of buckwheat hull fine powder and melanin

Table 3. Antioxidant activity of buckwheat by-products

| Samples                   | AOA, mg quercetin / g sample |
|---------------------------|-----------------------------|
| Buckwheat hull fine powder| 2.0                         |
| Melanin                   | 119.0                       |

The results of antioxidant activity of buckwheat by-products evaluation are shown in table 3. The AOA of melanin is approximately 60 times higher than AOA of buckwheat hull, because melanin is meant to be highly concentrated product.

Empirically it was found that the addition of buckwheat hull fine powder and melanin into desserts’ formulations in the amount of 1.5 and 0.037 g per serving accordingly, provides the functionality of desserts in case of their AOA.

The results of honeysuckle mousses samples sensory evaluation (figure 2) showed that they had fine consistency, gentle taste and nice color. The mousse sample with buckwheat hull fine powder had a slight tinge of buckwheat, however it didn’t spoil the overall picture of dessert’s sensory profile. In the dessert sample with melanin addition, there weren’t detected the smell or tinge of buckwheat.

Similar results were obtained for chocolate cream samples.
At a daily norm of quercetin is ~ 30 mg / day (according to MR 2.3.1.1915-04 norms), its content in a functional product is 4.5 mg / portion of the product.

To justify the functionality of the developed desserts’ formulations, the studies of physico-chemical characteristics were carried out. The results are presented in tables 4 and 5 for chocolate cream and honeysuckle mousse samples accordingly.

Table 4. Physico-chemical characteristics of chocolate cream samples

| Physico-chemical characteristics | Chocolate cream (control sample) | Chocolate cream with melanin | Chocolate cream with buckwheat powder |
|----------------------------------|----------------------------------|------------------------------|---------------------------------------|
| Humidity, %                      | 30.5±0.2                         | 30.0±0.2                     | 25.0±0.2                              |
| Acidity, °Т                      | 40.0±0.1                         | 44.0±0.1                     | 42.0±0.1                              |
| Total sugar, %                   | 22.0±0.15                        | 22.0±0.15                    | 23.0±0.15                             |
| Total fiber, mg%                 | 1.765±0.01                       | 1.765±0.01                   | 2.305±0.01                            |
| Ash content, g                   | 0.2±0.01                         | 0.2±0.01                     | 0.26±0.01                             |
| AOA, mg quercetin/g sample       | 0.09±0.01                        | 0.126±0.01                   | 0.12±0.01                             |

Table 5. Antioxidant activity of honeysuckle mousse samples

| Samples                           | AOA, mg quercetin / g sample |
|-----------------------------------|------------------------------|
| Honeysuckle mousse (control sample) | 0.075±0.004                 |
| Honeysuckle mousse with melanin   | 0.16±0.011                  |

According to MR 2.3.1.1915-04 norms, the daily norm of dietary fibers is ~ 20 g. The results show that the enrichment of desserts with buckwheat processed by-products increases their AOA. The addition of buckwheat hull powder also increases fibers content in desserts. All dessert samples with addition of melanin satisfy more than 15% of the daily need in antioxidants, so they can be considered as functional products.

5. Conclusion
We developed the formulations of desserts of functional purpose with buckwheat by-products (buckwheat hull fine powder, melanin). The supplementation of desserts with buckwheat hull in a state of fine powder increases the AOA of samples and enriches their chemical composition with dietary
fibers. All experimental samples had got high points on their sensory characteristics. The antioxidants content in dessert samples with melanin satisfy more than 15% of its daily need. Therefore, the developed formulations of desserts are recommended for practical implementation on public catering enterprises.

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