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Secondary Metabolites of Buckwheat and their Importance in Human Nutrition

Sekundarni metaboliti heljde i njihovo značenje u prehrani ljudi

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Summary

*Buckwheat (**Fagopyrum esculentum** Moench) has excellent nutritional value because of high content of essential amino acids, relatively high content of zinc and because of content of rutin and some other secondary plant metabolites – polyphenols. Nutritional characteristics and possibilities for reintroduction of some buckwheat foods are discussed in the paper. With HPLC (High Performance Liquid Chromatography) the variety of polyphenols in seeds of buckwheat Darja was studied. In milling fractions there is a positive correlation between the contents of proteins and polyphenols. Pre-cooking of buckwheat flour, pasta making and extrusion process do not influence much the amino acid composition of the products.*

Sažetak

*Heljda (**Fagopyrum esculentum** Moench) značajna je u prehrani ljudi zbog izvrsnog sastava esencijalnih aminokiselina, zbog relativno velikog udjela za organizam prijeko potrebnog cinka te zbog udjela rutina i nekih drugih sekundarnih biljnih metabolita (polifenola). U radu su prikazane mogućnosti ponovnog uključivanja različitih proizvoda od heljde u prehranu te njezino značenje u prehrani ljudi. S metodom HPLC (High Performance Liquid Cromatography) ispitana je raznovrsnost polifenola u sjemenu heljde Darja. Proizvodi mljevenja bogati proteinima sadržavaju više polifenola, dok ih frakcije s manje proteina imaju manje. Ovisno o tehnologiji pripreme proizvoda, bitno se ne mijenja udjel polifenola i aminokiselina.*

Introduction

Buckwheat (*Fagopyrum esculentum* Moench) is a crop of some importance in the Central European countries of Hungary, Austria, Croatia, Slovenia and in Northern Italy. It is used for groats, polenta, pasta products, and blended with other cereals for bread. More recently, it is being used for extruded products as well.

Buckwheat is known for excellent amino acid composition of proteins *(1)*. Buckwheat may be a valuable source of dietary zinc *(2)*. Zinc may be closely associated with diabetes mellitus *(3,4)*. In traditional Chinese medicine buckwheat is used in the treatment of patients with diabetes *(5)*. The real background for this use is not yet known in full detail. One of the factors involved in such beneficial effect could be zinc. Among other factors with possible beneficial effect for patients with diabetes mellitus, could be as well some specific secondary plant metabolites, for example rutin, or other polyphenolic substances of buckwheat plant, based on quercetin *(6)*. Rutin is known as an antioxidant of ascorbic acid and may be important in the prevention of diabetes mellitus, hypertension and cardiovascular diseases *(7)*. Buckwheat polyphenols may interfere with starch digestion, and this may result in slowly digestible starch or even in a part of starch being resistant to digestion.

This study was designed to further analyse the appearance of buckwheat polyphenols, along with some other nutritionally relevant substances, in buckwheat milling fractions and in some buckwheat food products.

Material and Methods

To obtain more detailed information about the distribution of polyphenols within different milling fractions, seeds of buckwheat cv. Darja, grown in Slovenia, were crushed in a mortar, separated by sieving into different size fractions and the material was further milled after the removal of husks by the Brabender laboratory mill. The procedure resulted in 10 milling fractions.

For HPLC studies, 50 % methanol extracts from crushed seeds of cv. Darja were used on Shimazu Corp.

LC-10A, SPD-10A HPLC Apparatus; Column Cosmosil $5C_{18}$-AR 6 × 150 mm. Solvent A $V(CH_3COOH$ 2.5 % diluted in water) : V(methanol) : $V(CH_3CN)$ = 35:5:10, solvent B (100 % methanol). Volume fraction of solvent A 0–5 min 100–30 %, 5–10 min 30 %, 10–30 min 0 % (solvent B respective up to 100 %), absorbance measured at 350 nm, flow rate 1 mL/min.

Pasta from domestic buckwheat cultivar from Bolzano region (Italy) was made as a thin, 1 mm thick spaghetti, using a PAT press with a capacity of 50 kg/h, in order to run tests on the product (water temperature 50 °C, head temperature 45 °C, cylinder temperature 25 °C, vacuum 720 mm Hg, head pressure 60 bar, water 36.00 %; drying process: in HT static cell, final moisture 10.13 %). A Pavan-Mapimpianti TT58W bi-screw extruder with screws 58 mm in diameter was used to produce extrusions for the study, using domestic buckwheat cultivar from Bolzano region, Italy (79.6 %), sugar (20 %) and malt (0.4 %). Two types of pasta were analysed: pasta 1, made from untreated buckwheat flour and pasta 2 made from 55 % pre-gelatinized buckwheat flour and 45 % untreated buckwheat flour.

Protein content was analysed by Kjeldahl method, with the application of nitrogen to protein conversion factor 5.75.

The content of polyphenols was quantitatively studied by the Vanillin-HCl method *(6)*, ash and dietary fibre were analysed according to AOAC methods *(8)*.

Results and Discussion

Results of analyses of buckwheat grain milling fractions are presented in Table 1. Protein content of some fractions may be as high as about 40 %. On the other hand some fractions contain less than 10 % of protein. Polyphenol content studied by the Vanillin-HCl method was in different fractions from less than 0.5 % up to more than 7 %. Some correlation between the content of polyphenols and the content of proteins was found (Fig. 1). Buckwheat milling fractions having more polyphenols have more proteins as well. This may be due to the composition of botanical structures of buckwheat kernel.

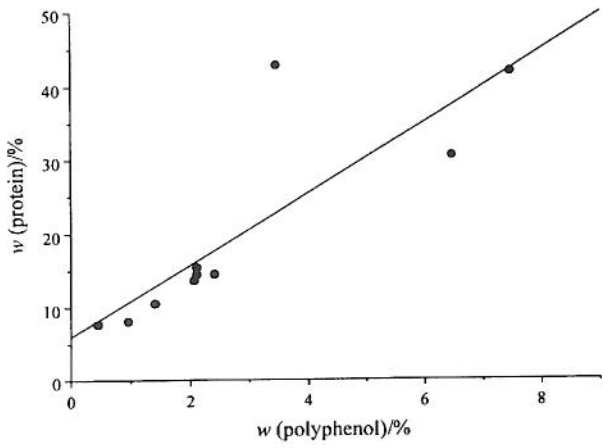

Fig. 1. Correlation between the content of polyphenols and protein in 10 milling fractions of Darja buckwheat
Slika 1. Odnos između postotka fenola i proteina u 10 mljevenih frakcija heljde

Table 1. Polyphenol and protein content of Darja buckwheat grain and milling fractions, expressed as mass fractions of polyphenols and proteins in dry matter
Tablica 1. Udjel polifenola i proteina u zrnu i mljevenim frakcijama heljde, izražen kao maseni udjeli polifenola i proteina u suhoj tvari

Fraction	Chemical composition	
	Polyphenols w/ %	Protein w/ %
Whole grain	2.15	12.28
Husked grain	2.08	14.52
Husk	2.55	4.69
Fraction 1	2.05	13.66
Fraction 2	2.10	15.46
Fraction 3	6.45	30.49
Fraction 4	0.45	7.77
Fraction 5	1.40	10.58
Fraction 6	2.40	14.54
Fraction 7	2.10	14.49
Fraction 8	7.45	41.86
Fraction 9	3.45	42.87
Fraction 10	0.95	8.19

Buckwheat polyphenols were fractionated by the application of reverse-phase HPLC and several fractions were found. One of the major fractions was rutin (quercetin-3-O-rutinoside). The presence of rutin may be a part of the explanation, as to why buckwheat is used in traditional Chinese medicine. Further HPLC studies on buckwheat milling fractions indicate that rutin and some other secondary metabolites are not equally distributed in different parts of buckwheat kernel. In preliminary studies no free quercetin was found in the Darja seed milling fractions studied. This might suggest that a considerable part of secondary metabolites in buckwheat is present as glycoside conjugates.

Results of chemical analyses of pre-cooked buckwheat flour, pasta and extruded products are presented in Tables 2 and 3. In Table 2 are not included data on content of lipids or on content of polysaccharides other than those included in dietary fibres. Differences in protein, ash and fibre content between buckwheat flour and extruded product may be attributed to the dilution after the addition of sugar in the process. But the change in polyphenol content could not be explained solely in this

Table 2. Chemical composition of buckwheat pre-cooked flour, pasta and extruded product, based on dry matter
Tablica 2. Kemijski sastav heljdinog prethodno kuhanog brašna, tjestenine i ekstrudiranih proizvoda, računajući na suhu tvar

	Pre-cooked flour	Pasta 1	Pasta 2	Extruded product
	w/ %			
Protein	11.40	12.20	11.30	8.30
Ash	2.36	2.41	2.18	2.12
Total dietary fibre	5.15	5.19	4.98	4.72
Insoluble	4.36	4.13	3.96	3.81
Soluble	0.79	1.06	1.02	0.91
Polyphenols	0.25	0.28	0.24	0.12

Table 3. Amino acid composition (g/100 g of protein) of buckwheat pre-cooked flour, pasta and extruded product
Tablica 3. Sastav aminokiselina (g/100 g proteina) heljdinog prethodno kuhanog brašna, tjestenine i ekstrudiranih proizvoda

	Pre-cooked flour	Pasta 1	Pasta 2	Extruded Product
Aspartic acid	8.94	5.58	7.88	7.52
Threonine	3.57	2.98	3.40	3.26
Serine	4.71	5.09	4.99	4.91
Glutamic acid	20.39	30.88	20.63	24.46
Proline	6.30	13.45	7.38	8.05
Glycine	5.18	4.08	4.83	4.61
Alanine	4.50	3.50	4.82	4.10
Cystine	2.47	2.53	2.62	2.58
Valine	5.80	4.85	4.69	5.84
Methionine	2.15	1.97	2.23	1.63
Isoleucine	4.46	4.07	3.58	4.62
Leucine	8.15	7.23	7.23	7.91
Tyrosine	2.72	2.90	2.77	4.14
Phenylalanine	4.81	4.91	4.91	5.43
Lysine	5.25	4.17	4.39	4.12
Histidine	3.05	2.11	3.13	3.11
Arginine	7.98	5.20	7.28	6.65

way. Maybe, during the hydrothermal procedure, a part of polyphenols bound to some other substances, or became in some other way less soluble in the solvent applied in the analysis (methanol at the room temperature). Anyway, it indicates some changes in content and/or condition of polyphenols during the industrial process. In pasta and extruded buckwheat products there is a slightly higher part of valuable soluble fibres and a somewhat lesser part of insoluble ones. In buckwheat pasta and extruded products it was found slightly less lysine in proteins (Table 3), in comparison with pre-cooked buckwheat flour. But it is in any case higher than it normally is in cereals or cereal products.

Conclusion

Buckwheat milling may result in a number of different flour fractions with different polyphenol and protein contents and quality. In studied experimental buckwheat products, despite thermal and other treatments, the excellent amino acid composition of buckwheat proteins and the content of polyphenols were mainly conserved.

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