Buckwheat Grains and Buckwheat Products – Nutritional and Prophylactic Value of their Components – a Review

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Abstract

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Buckwheat is introduced into the diet as an alternative crop of renewed interest due to its nutritive and health-promoting value. Experiments with animal models have demonstrated that buckwheat flour may alleviate diabetes, obesity, hypertension, and hypercholesterolemia. A number of nutraceutical compounds exist in buckwheat grains and other tissues. These are a rich source of starch, proteins, antioxidants, and dietary fibre as well as trace elements. The biological value (BV) of buckwheat proteins is comparable to BV of other protein sources. Besides high-quality proteins, buckwheat grains contain some components with prophylactic value: flavonoids, fagopyrins, or thiamin-binding proteins. For the food industry, buckwheat grains are a valuable raw material to be used for the production of functional foods. Buckwheat flour may be a valuable and important ingredient in diets or food products, taking into consideration its nutritive value and potential promotion of human health.

Keywords: buckwheat grains; nutritional components; resistant starch and dietary fibre; healing effect of components; dietary and prophylactic value; allergic reaction of buckwheat proteins

Buckwheat (*Fagopyrum esculentum* Möench) is an annual crop, it is a pseudocereal but its grains belong to cereals because of their similar use and chemical composition (Campbell 1997). Among a variety of buckwheat species, nine have agricultural and nutritional value. Two buckwheat species are commonly cultivated: common buckwheat (*F. esculentum*) and tartary buckwheat (*F. tartaricum*) (Krkošková & Mrázová 2005).

The main producers of buckwheat are China, Russian Federation, Ukraine, and Kazakhstan (Li & Zhang 2001; Bonafaccia *et al.* 2003). It is also produced in Slovenia, Poland, Hungary, and Brazil (Kreft *et al.* 1999a). There are some botanical and physiological similarities between buckwheat and weeds, one of them being the ability to correct growth without the use of artificial fertilisers or pesticides (Kreft *et al.* 1996). Moreover, buckwheat absorbs less water and lower amounts of nutrients from soil than other main crops (Li & Zhang 2001).

For many years, the cultivation of buckwheat was in decline, yet recently its has been observed to increase because of the health-promoting properties of its grains. Buckwheat grains and other tissues contain numerous nutraceutical compounds (Li & Zhang 2001) and they are rich in vitamins, especially those of B group (Fabjan *et al.* 2003).

The amino acid composition of buckwheat proteins is well balanced and of a high biological value (Kato *et al.* 2001), although the protein digestibility is relatively low (Liu *et al.* 2001). Buckwheat grains are an important source of microelements, such as: Zn, Cu, Mn, Se (Stibilj *et al.* 2004), and macroelements: K, Na, Ca, Mg (Wei *et al.* 2003). With 80% unsaturated fatty acids more than 40% are constituted by polyunsaturated fatty acid (PUFA) (Krkošková & Mrázová 2005). The significant contents of rutin, catechins and other polyphenols as well as their potential antioxidant activity are also of significance to the dietary value (Oomah & Mazza 1996; Wanatabe 1998). Moreover, buckwheat grains are a rich source of TDF (total dietary fibre), soluble dietary fibre (SDF), and are applied in the prevention of obesity and diabetes (Brennan 2005).

Chemical and nutritional components of buckwheat grains

Buckwheat grains contain a variety of nutrients, the main compounds being: proteins, polysaccharides, dietary fibre, lipids, rutin, polyphenols, micro- and macroelements (Kim *et al.* 2004). The total content of components depends on the variety or environmental factors (Bárta *et al.* 2004).

Proteins. In literature, the protein content of buckwheat grains has been reported to range from 12% to 18.9% (Table 1). The high stability of buckwheat species should be emphasised taking into consideration the content of protein in grains, in comparison with that determined currently in three Polish varieties of buckwheat (Stempińska & Soral-Śmietana 2006). It has been confirmed by the comparison of the content of proteins determined earlier in commercial tests of Polish and Brazilian buckwheat grains (Soral-Śmietana 1984). Bran milling fractions of buckwheat have been shown to be characterised by a high concentration of proteins (Qian & Kuhn 1999; Krkošková & Mrázová 2005), whereas the protein concentration in the hull is low, aboud 4%, however, in the embryo it reaches 55.9% (Pomeranz & Sachs 1972). Buckwheat flour contains from 8.5% to near 19% of proteins depending on the variety, pesticides used, and fertilisation that are likely to affect the total concentration of buckwheat proteins (Fornal 1999).

Table 1. Content of proteins in buckwheat grains

N (% d.m.) × 6.5	Authors
12.0 –13.0	Steadman *et al.* (2001)
12.11	Li and Zhang (2001)
13.30–15.55	Wei *et al.* (2003)
8.51–18.87	Krkošková and Mrázová (2005)
12.02	Stempińska and Soral-Śmietana (2006)

The major protein fractions of the grains are water-soluble and salt-soluble albumins and globulins representing almost one-half of all buckwheat proteins. Globulins consist of 12–13 subunits with molecular weights from 16 kDa to 66 kDa (Krkošková & Mrázová 2005).

The main storage protein of buckwheat grains is 13S globulin (Aubrecht & Biacs 1999; Li & Zhang 2001). It has a hexametric structure with disulfide-bonded subunits composed of bonded acidic and basic polypeptides. This structure is common for all legumin-like storage proteins (Aubrecht & Biacs 1999). Buckwheat globulins are also composed of 8S vicilin-like proteins (Radović *et al.* 1999). The average albumin content is 21%, whereas the highest one reaches 30–33% (Bharali & Chrungoo 2003). Buckwheat prolamins have a different characteristic in comparison to wheat, barley, and rye prolamins, which enables buckwheat grains application in the prophylactic of gastrointestinal tract diseases, mainly celiac disease (Kreft *et al.* 1996). Buckwheat grains may constitute a valuable source of dietary proteins with a high content of essential amino acids, which is important for people who do not tolerate glutenproteins (Aubrecht & Biacs 2001) or with proteins deficiency in the diet.

Buckwheat proteins are rich in arginine and lysine, the primary aminoacids limiting the content of proteins in cereals, whereas the contents of methionine and threonine in buckwheat proteins are low (Table 2).

Thiamin-binding proteins (TBP) serve as B1 vitamin transporters in the plant and stabilise it during technological processing. They can also improve thiamin stability during storage as well as its bioavailability. Mistunaga *et al.* (1986) were the first to isolate the thiamin-binding proteins (TBP) from buckwheat grains. TBP in buckwheat represent an oligomer, during SDS-PAGE they migrate as a single band corresponding to the molecular weight of 42 kDa to 45 kDa. They have a 1:1 binding stoichiometry with thiamin (Li &

Table 2. Aminoacids of buckwheat grains (% w/w)

Aminoacids	Soral-Śmietana (1984)	Wei *et al.* (2003)	Tomotake *et al.* (2006)
Lysine	6.17	4.9	5.68
Histidine	2.44	1.4	2.52
Arginine	8.85	5.4	11.16
Glutamic acid	15.37	9.7	19.38
Aspartic acid	9.10	5.2	9.54
Threonine	4.04	1.9	3.5
Serine	4.89	2.4	4.61
Proline	4.57	2.6	7.93
Glycine	6.23	4.2	5.66
Alanine	4.82	3.0	3.89
Valine	4.97	3.4	4.26
Isoleucine	3.41	2.6	3.12
Leucine	6.12	2.8	5.94
Methionine	0.99	1.6	2.3
Tyrosine	1.94	1.5	3.03
Pnenylalanine	4.42	2.0	4.3
Tryptophane	2.14	1.5	2.0

Zhang 2001). TBP may be used in the cases of thiamin deficiency and difficulties in its storage (Wanatabe *et al.* 1999).

An increasing incidence of allergy manifestations or symptoms is observed in people who consume buckwheat-containing food products often and in high quantities. The main reason for such immunological disorders are low molecular weight proteins, particularly those with molecular weights of 15, 22, or 26 kDa (Yoshioka *et al.* 2004; Handoyo *et al.* 2006; Morita *et al.* 2006).

Polysaccharides and dietary fibre. Starch is the major storage component of buckwheat grains. It is accumulated in the endosperm as an energetic material necessary for the plant growth. In the whole grain of buckwheat, starch content varies from 59% to 70% of the dry mass, demonstrating fluctuations under variable climatic and cultivation conditions (Qian & Kuhn 1999). However, current results of starch analysis in buckwheat grains of three Polish varieties have shown that the starch content lies in a narrow range, i.e. from 63% to 66% d.m. (Stempińska & Soral-Śmietana 2006).

The composition of starch isolated from buckwheat grains differs from that of cereal starches. It may contain higher amounts of proteins, ash, and phosphorus (Soral-Śmietana *et al.* 1984b). The content of bound lipids is two times higher than that of free lipids. Upon hydrothermal processing of buckwheat grains, the content of free lipids fraction was observed to increase, however, buckwheat starch was shown to be predominated by both lipid fractions (Soral-Śmietana *et al.* 1984a).

Amylose content of buckwheat starch granules fluctuates between 15% and 52% and its degree of polymerisation varies from 12 to 45 glucose units (Campbell 1997). Buckwheat starch granules are spherical, oval and polygonal in shape with noticeable flat areas due to compact packing in the endosperm, the granule size distribution ranges from 2 to 6 μm (Soral-Śmietana *et al.* 1984b; Acquistucci & Fornal 1997).

From the nutritional point of view, there exist three fractions of starch: rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS). Resistant starch is not absorbed in the small intestine and is partly or completely available for fermentation by microflora in the large intestine. It could show similarity to dietary fibre. In uncooked buckwheat grains, RS consti-

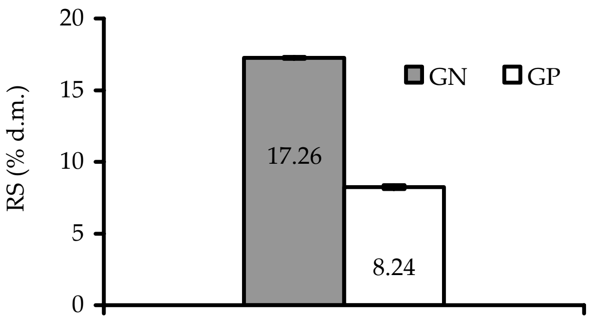

Figure 1. Content of resistant starch in native and processed buckwheat grains (Stempińska *et al.* 2007)

tutes 33–38% of total starch, but after cooking – only 7–10% (Figure 1). Resistant starch in buckwheat grains of three Polish varieties constituted from 16% to over 18% d.m., while the Kora variety stood out from the other varieties (Stempińska & Soral-Śmietana 2006). The factors influencing starch availability include its botanical origin and physical properties, the ratio of amylose to amylopectin, and starch interactions with other constituents (Kreft *et al.* 1996). It was proved that, in the presence of milk proteins and cereal flour (corn), the complexing factor is buckwheat starch and its lipids induced by the extrusion process (Soral-Śmietana 1992). Starch is not only a significant source of energy for humans, it is also reported to interact with the gut microflora (Bird *et al.* 2000; Wronkowska *et al.* 2006).

Soluble carbohydrates, including fagopyritols, are concentrated mainly in the embryo, their concentration is low in endosperm whereas their total contents ranges from 1% to 6% (Steadman *et al.* 2000).

Fagopyritol A1 and Fagopyritol B1 are the most remarkable of all the fagopyritols accumulated. Fagopyritol A1 (Obendorf *et al.* 2000) is an active substance that may be used in the treatment of e.g. diabetes and polycystic ovarian syndrome (PCOS) (Horbowicz *et al.* 1998; Janet *et al.* 2005).

According to the current definition, dietary fibre is the edible part of a plant or analogous carbohydrates that is resistant to digestion and absorption in the human small intestine but is partly or completely fermented by microflora in the large intestine (AACC Report 2001). Dietary fibre consists also of oligosaccharides, polysaccharides, and other hydrophilic derivatives (Gibson *et al.* 2000). Non-starch polysaccharides such as cellulose, hemicelluloses, pectins, gums, and non cellulosic polysaccharides are the main components of dietary fibre. They are concentrated in tissues with thicker cell walls, aleurone, seed coat and hulls. Total dietary fibre (TDF) is classified in view of its affinity to water as either insoluble dietary fibre (IDF) or soluble dietary fibre (SDF). In general, IDF includes cellulose, lignins, and certain non-cellulosic polysaccharides, while SDF includes pectins and some associated non-cellulosic polysaccharides (Asp *et al.* 1993; Brennan 2005; Young *et al.* 2005). The whole grains contain 7% TDF, while bran with hull fragments has 40% TDF (Steadman *et al.* 2001).

Lipids. Buckwheat grains contain from 1.5% to 4% of total lipids (Steadman *et al.* 2001), but the content of raw fat in buckwheat flour exceeds 3% (Soral-Śmietana 1987). Free lipids isolated from buckwheat grains constitute 2.5% of d.m., whereas bound lipids – about 1.3% d.m. (Soral-Śmietana *et al.* 1984a). It was demonstrated that in buckwheat flour the content of free lipids is higher than that of bound lipids, but reverse situation was observed after the extrusion process (Soral-Śmietana 1987). The highest concentration of lipids was found in the embryo (7–14%), whereas the lowest in the hull (0.4-0.9%) (Bonaffacia *et al.* 2003).

Triacylglycerides are the main components of the neutral fraction of lipids containing fatty acids from C_{12} to C_{22}, with a predominating contribution of: oleic (42%), linolic (32%), and palmitic acids (16%) (Soral-Śmietana *et al.* 1984a). By analysing the composition of fatty acids, these authors found that bound lipids in the whole buckwheat grains and those in buckwheat starch differ in terms of the concentrations of dominant acids: palmitic (16 and 26%, respectively), oleic (32 and 40%, respectively), and linolic (46 and 22%, respectively). The application of two hydrothermal processes with different intensities evoked changes in the proportions of saturated fatty acids and unsaturated fatty acids in buckwheat grains. An in-depth research of the free to bound lipids ratio was showed its valus to reach 1:2. Predominance of linolic acid is marked in the polar fraction of free lipids of buckwheat starch both before and after hydrothermal processes. The observed changes in the concentration of stearic acid in glyco- and phospholipids of free lipids was also evoked by hydrothermal processes (Soral-Śmietana *et al.* 1984a). Fatty acids may play a role in modifying the risk of breast, colon, and prostate cancer incidence. Polyunsaturated fatty acids (PUFA), such as n-3 and n-6, are often referred to as factors provoking the modulation of the immunological system in humans (Jelińska 2005).

Minerals and vitamins. Generally, the content of minerals in buckwheat grains and their morphological fractions (dry base) reaches: 2–2.5% in whole grains, 1.8–2.0% in kernel, 2.2–3.5% in dehulled grains, about 0.9% in flour, and 3.4–4.2% in hulls (Li & Zhang 2001). Buckwheat is rich in potassium (K), magnesium (Mg), calcium (Ca), and sodium (Na). P, K, and Mg are most concentrated in bran, particularly in the bran from which the hulls were removed before milling the grains. Buckwheat may be an important nutritional source of such microelements as iron (Fe), manganese (Mn), and zinc (Zn) (Wei *et al.* 1995). Trace elements, e.g. chromium (Cr) or selenium (Se), are occasionally detected at very low levels. Stibilj *et al.* (2004) reported after cultivation experiments reported that foliar fertilisation makes buckwheat grains a rich source of dietary Se and a useful raw material for enriched food products (Steadman *et al.* 2001; Wei *et al.* 2003; Stibilj *et al.* 2004).

Buckwheat grains were also demonstrated to contain vitamins: B_1, B_2, B_6 (Fabjan *et al.* 2003). These are concentrated in the peripheral parts of endosperm and embryo, hence the highest quantity of B vitamins is found in the bran. Tartary buckwheat bran contains about 6% of daily therapeutic doses of pyridoxine (Schynder *et al.* 2001), effective in the reduction of blood plasma homocysteine levels.

Buckwheat components with healing effects

Buckwheat grains and hull consist of some components with healing properties and biological activity, i.e.: flavonoids and flavons, phenolic acids, condensed tannins, phytosterols, and fagopyrins. Their contents and compositions differ depending on the buckwheat species and growing conditions. Generally, flavonoids content of *F. tartaricum* (about 40 mg/g) is higher than that of *F. esculentum* (10 mg/g) (Oomah & Mazza 1996; Li & Zhang 2001; Chao *et al.*, 2002). Xuan and Tsuzuki (2004) rank buckwheat (*Fagopyrum* sp.) among alleopathic plants.

Antioxidant activity is the fundamental prophylactic property important for the human organism. A variety of biological functions, e.g. antimutagenic, anticarcinogenic, antiaging, originate from that property (Holasová *et al.* 2002).

About six flavonoids have been isolated from buckwheat grains. Of the total pool of buckwheat grains flavonoids, rutin wass been observed to predominate (Kreft *et al.* 1999b). Rutin, quercetin, orientin, vitexin, isovitexin, and isoorientin were identified in buckwheat hulls (Dietrych-Szóstak & Oleszek 1999, 2001). Some types of buckwheat flour could be considered as food with a high content of flavonoids, expressed as rutin (Figure 2), since their contents are higher than in cereal grains, cabbage, apple, red wine or tea (Zieliński & Kozłowska 2000).

Rutin, a flavonol glycoside, is a plant metabolite that was discovered in 1842. Rutin content depends on the variety and growth conditions (Ohsawa & Tsutsumi 1995). Kitabayashi *et al.* (1995) reported that its content in buckwheat grains ranges from 12 to near 36 mg/100g dry basis.

C-Glycosylflavons present in buckwheat seedling cotyledons are vitexin, isovitexin, orientin and isoorientin. Condensed catechins, phenolic acids, including hydrobenzoic acids, synigric, *p*-hydroxy-benzoic, vanillic, and *p*-coumaric acids, are present in the bran-aleurone layer of buckwheat grains (Przybylski *et al.* 1998). Soluble oligomeric condensed catechins occur in common buckwheat grains which, along with phenolic acids, provide astringency and affect the colour and biological activity of buckwheat products.

Plant sterols (so-called phytosterols), although identified in buckwheat grains at low levels, also exert a positive effect on the blood cholesterol level. β-Sitosterol, which represents at least 70% of total sterols, occurs in the endosperm and embryo tissues of buckwheat grains. It cannot be absorbed in human body and displays a considerable competitive inhibitory effect on cholesterol absorption

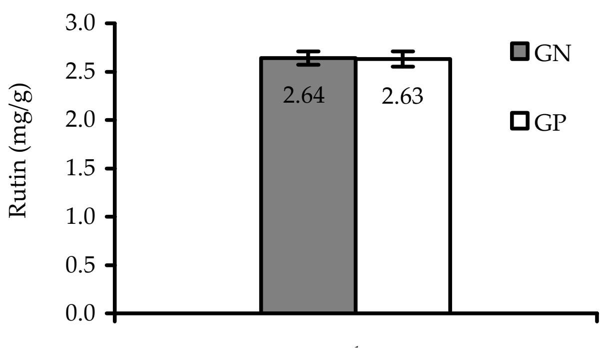

Figure 2. Flavonoids contents in the native and processed buckwheat grains cultivar Kora (Stempińska *et al.* 2007)

in vivo (Bryngelsson *et al.* 1999; Normén 2001; Krkošková & Mrázová 2005).

The level of fagopyrins in buckwheat grains is very low and their isolation is difficult. It was reported that fagopyrins found in buckwheat can be utilised in the treatment of type II diabetes (Li & Zhang 2001; Bonafaccia *et al.* 2003; Horbowicz & Obendorf 2005).

Dietary and prophylactic value of buckwheat grains or products

Buckwheat is nutritionally interesting due to, e.g., a very low content of prolamins in its grains. Buckwheat flour can be a valuable ingredient in diets or food products for coliac patients. Coliac disease (also known as gluten-sensitive enteropathy) is a genetically-determined disease of the small intestine linked with gluten intolerance. However, an increase is also observed in the incidence of the so-called potential celiac disease, particularly in adult patients. Prolamins of the gluten proteins complex found in wheat, barley, rye, and probably also oat react with the mucosa of small intestine, causing damage by activating the immune system to attack the delicate lining of the gut, which is responsible for absorbing nutrients and vitamins (Kunachowicz 2001; Rujner 2002).

Buckwheat proteins may show a strong supplemental effect with other vegetable proteins due to the well balanced aminoacid composition (Li & Zhang 2001). The Lys/Arg and Met/Arg ratios in buckwheat proteins are lower than those in most plant proteins. This indicates that buckwheat should be characterised by the properties capable of lowering blood cholesterol level. According to Huff and Carroll (1980) and Sugiyama *et al.* (1985), buckwheat proteins can exert a strong cholesterol-lowering effect and have a high biological value (BV).

The addition of protein products of buckwheat to diets significantly lowers the levels of cholesterol in serum, liver, and gallbladder of hamsters and suppresses the formation of gallstones by altering cholesterol metabolism (Tomotake *et al.* 2002), whereas protein extracts are more efficient in lowering the blood cholesterol level, particularly that of LDL and VLDL (Kayashita *et al.* 1995; Misawo & Iwao 1996; Tomotake *et al.* 2006). The hypocholesterolemic effect in humans is linked with a lower digestibility of buckwheat proteins and the presence of fibre-like substances, which is indicated by an increase in the contents of neutral and acid sterols in rat faeces observed upon the administration of a diet rich in buckwheat protein products (Kayashita *et al.* 1997; Tomotake *et al.* 2001).

Buckwheat proteins products (BWP) are acknowledged as preventive nutrients (Liu *et al.* 2001). They are also associated with the suppression of colon carcinogenesis by reducing cell proliferation, and with the suppression of mammary carcinogenesis by lowering serum estradiol.

They can suppress gallstone formation better than can soy protein isolates (Tomotake *et al.* 2000, 2001). Numerous experiments have proved that buckwheat proteins extract may be used as a potential functional food additive to treat hypertension, obesity, alcoholism, as well as constipation (Kato *et al.* 2001; Tomotake *et al.* 2002).

In buckwheat grains dietary fibre contains about 7% of the soluble fraction whereas resistant starch (comparable with it in terms of the physiological functions) constitutes about 28% of total starch in the whole grain (Stempińska & Soral-Śmietana 2006). Préstamo *et al.* (2003) investigated the effect of buckwheat products ingestion on the microbial composition of the colon of rats, the detection having been carried out on *Enterobacteria* and *Bifidobacteria*. The researchers reported an increase in the numbers of aerobic, mesophilic and lactic acid bacteria with the buckwheat products as compared to control. They observed a slight decrease of *Enterobacteria* and less pathogenic bacteria. These results confirm that buckwheat products may be considered as potential prebiotic components in human gastrointestinal tract.

In the technological cycles of experimental buckwheat products for fast consumption, the so-called convenient food, buckwheat flour was used as a component mixed with milk proteins and cereals (Śmietana *et al.* 1985, 1988). During the extrusion process (Fornal *et al.* 1987a), biopolymers like proteins and starch coming from several sources underwent physicochemical and structural transformations (Fornal *et al.* 1985, 1987b), as a result of factors such as heat, friction, pressure, and limited amounts of free water. Hence, as a consequence of hydrothermal transformations, this process resulted in the improvement of the true digestibility examined in the intestinal tract of rats, yet with a rise in the temperature of the extrusion process the biological value (BV) and NPU index of extruded products indicated a slight decrease in comparison with the proteins of non processed buckwheat flour (Kozikowski *et al.* 1989).

The changes in the structure of cereal starches and buckwheat starch prove the possibility of small and weak crystallites formation at various levels of aggregation and random distribution upon extrusion (Soral-Śmietana 1992). This indicates that thermally-induced amylose-lipid complexes in this products can cooperate with B type crystallites and behave as an amorphous material.

Honey obtained from buckwheat flowers increases the antioxidative potential of human blood serum and *in vitro* studies indicated that it protects lipoproteins of blood serum against oxidative processes more effectively than saccharic analogues (Gheldof *et al.* 2003).

The most interesting fact for the food industry is the improvement of functional properties of food as well as the health-promoting benefits resulting from food consumption. Buckwheat flour is used to produce multicomponent mixtures to obtain food of a complex nutritive value, but buckwheat flour can be also abtained characterised by decreased activities of proteases and α-amylase (Fornal 1999).

Buckwheat proteins in the aspect of allergic reactions

Although buckwheat grains contain a significant amount of proteins of well-balanced aminoacid composition and display a high biological value, the newest results signalise that some buckwheat proteins may provoke allergies. Allergic reactions after the consumption of buckwheat food are noticed and, in their worst form, they may cause hemorrhagic disease, connected with a rapid decrease of blood pressure known as the anaphylactic shock. The main symptom of allergy to buckwheat products is eczema or uritcaria, appearing in a short time after their consumption. The detection of allergic protein of buckwheat with IgE immunoblotting shows that allergic reactions are triggered by numerous low molecular weight legumin-like proteins (15–29 kDa). According to Yoshioka *et al.* (2004), the protein of 22 kDa is the major protein binding IgE antibodies. Morita *et al.* (2006) confirmed this information and showed another allergic protein of 15 kDa. Moreover, the proteins of 24, 19, 16, 9 kDa are known as strong allergens (Ličen & Kreft 2005).

Bearing in mind the nutritive and health – promoting value of buckwheat products, researchers try to eliminate allergic proteins of buckwheat grains. They use advisable modifications, e.g. enzymatic modifications that consist in enzymatic separation of allergenic constituents or controlled fermentations performed by yeast or mould strains (Handoyo *et al.* 2006).

The conditions of our health depend on the quality of food in diet. To sum up, because of the valuable chemical composition of buckwheat grains, these are an important component in the diet and, taking into consideration the biological activity of other components presented in this review, they can play prophylactic or therapeutic roles.

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