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A Review of Nutritional and Nutraceutical Components of Buckwheat

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ABSTRACT

Buckwheat, frequently classified as a pseudocereal, is one of the minor crops cultivated by ethnic groups in developed and developing countries which is an integral part of their diet and culture. When views on food components changed from only a source of basic nutrients into a resource of health promoting compounds, suddenly buckwheat was recognized as a food ingredient offering a variety of unique nutrients and nutraceuticals. The importance of buckwheat components is currently reflected by the large volume of research on nutritional and health aspects of this crop. In this paper we appraise recent findings in the macronutrients, nutraceuticals and unique components with astonishing properties present in buckwheat seed and plant.

Keywords: anthocyanins, *chiro*-inositol, diabetes, dietary fiber, fagopyritols, flavonoids, lignans, macronutrients, minerals, resistant starch Abbreviations: ACE, angiotensin converting enzyme; BPI, buckwheat protein isolate; DW, dry weight; ED, enterodiol; EL, enterolactone; IDF, insoluble dietary fibre; LDL, low-density lipoprotein; MAT, matairesinol; RDA, recommended dietary allowance; SDF, soluble dietary fibre; SDG, secoisolariciresinol diglycoside; SeMet, selenomethionine; TBP, thiamine-binding protein; TDF, total dietary fibre; VLDL, very low-density lipoprotein

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INTRODUCTION

Buckwheat has been an important part of the human diet for centuries and was introduced in Canada and the United States by European and Asian immigrants. Buckwheat has been grown for centuries in Eastern Europe and Asia but originated in the mountainous regions of southern China. There are many species of buckwheat; nevertheless only a few have agricultural significance: *Fagopyrum esculentum* Moench; *Fagopyrum tataricum* Gaertner; *Fagopyrum giganteum* Krotov; *Fagopyrum cymosum* Meissn.; *Fagopyrum suffruticosum* Fr. Schmidt; and *Fagopyrum ciliatum* Jaegt. Among these species only *F. esculentum* (common buckwheat) and *F. tataricum* (tartary buckwheat) are cultivated for human consumption (Ikeda 2002).

Common buckwheat has been a crop of secondary importance in many developed countries and yet it has persisted through centuries of civilization in the agriculture of nearly every country where cereals were cultivated. Buckwheat is a broad-leafed herbaceous annual, which belongs to the Polygonaceae family. This family includes rhubarb and sorrel. Buckwheat seed structurally and chemically resembles cereal grains and it is usually handled and classified with cereals (**Table 1**). Buckwheat seed is a fruit, strictly an achene (Campbell 1997). The seed, covered by a hull (pericarp), has a triangular shape and its flower can be white, pink or yellow. The exact shape, size, and colour of the seed may vary depending on the specie and variety. The hull may be glossy or dull and brown, black or gray in colour. The dehulled buckwheat seed is called the groat and resembles the cereal kernel in its gross chemical composition and structure (**Table 1**).

The first layer of the groat is a one-cell thick, light green coloured testa (seed coat). Under the testa, surrounding the starchy endosperm is a one-cell aleurone layer. The inner portion of the groat consists of a spermaderm and an
 Table 1 Proximate composition of buckwheat and other food grains (%).

Nutrient	Buckwheat		Wheat	Rye	Barley	Corn	Oat
	Common	Tartary		-	-		
Moisture	9.8	10.2	10.9	10.9	9.4	10.4	8.2
Energy	343	328	339	335	354	365	389
Protein	13.3	10.3	13.7	14.8	12.5	9.4	16.9
Lipids	3.4	2.5	2.5	2.5	2.3	4.7	6.9
Ash	2.1	1.8	1.8	2.0	2.3	1.2	1.7
Carbohydrates	71.5	74.3	71.1	69.8	73.5	74.3	66.3
Fiber	10.0	6.3	11.2	14.6	17.3	7.3	10.7
Protein in flour	19.0	18.9	10.3	14.3	10.5	6.9	14.7

Source: Compiled from USDA National Nutrient Database for Standard Reference, Release 21 (2008) and Bonafaccia and Fabian (2003)

Table 2 Composi	tion of buckwheat flour	produced from different	Canadian buckwheat	varieties (dry matter basis).
		•		

Milling products	Starch (%)		Fiber (%)	Protein (%)	Ash (%)	Fagopyritols ^A	D- <i>chiro</i> -Inositol ^B
		Total	Soluble			(mg/100 g)	(mg/100 g)
Koto ^E							
White flour ^D	79.2	4.6	1.6	6.5	0.8	101	3.4
Dark flour ^D	29.8	22.0	2.2	37.1	5.5	2220	43.4
Whole flour ^D	69.3	7.7	1.7	13.4	1.9	485	10.6
Koban ^E							
White flour	83.6	5.4	1.7	6.4	0.7	171	4.5
Dark flour	28.0	17.6	2.1	37.1	6.0	1470	30.6
Whole flour	69.0	8.3	1.8	14.2	2.1	491	10.9
BR01 ^C							
White flour	85.8	5.3	1.7	6.8	0.7	191	5.5
Dark flour	27.2	15.2	1.8	38.0	5.7	1420	32.8
Whole flour	69.8	7.9	1.7	15.1	2.1	521	12.8
BR06 ^C							
White flour	87.2	4.2	1.3	7.2	0.8	185	5.4
Dark flour	29.2	15.9	1.9	38.7	5.7	1630	37.9
Whole flour	73.5	6.7	1.4	14.2	1.9	503	12.5
Tartary ^F							
Grain	57.4	26.0	0.5	11.1	2.8		
Bran	37.6	24.8	1.2	25.3	5.0		
Flour	79.4	6.3	0.5	10.3	1.8		

A – Sum of all fagopyritols; B- Free D-chiro-inositol; C – New lines of Canadian buckwheat; D – Buckwheat seeds were milled to obtain three types of flour: White flour – mostly endosperm; Dark flour – mostly testa, germ and some fibrous parts of the endosperm; Whole seed flour – all seed parts combined. E – Standard large seeded Canadian buckwheat

Source: Adapted from Hatcher (2008); F - Adapted from Bonafaccia et al. (2003)

endosperm; a large embryo and two cotyledons extending in the shape of letter "S" are embedded in the center of the endosperm. The endosperm fraction and the embryo represent 74 and 26% of the mature seed (groat), respectively.

Buckwheat seed tastes harsh for *F. esculentum*, and slight bitter for *F. tataricum*. The bitter components in *F. tataricum* can be removed by isoelectric precipitation (Kawakami 1994).

Buckwheat has gained an excellent reputation as a nutritious ingredient in the human diet (Kreft *et al.* 1998). Its renewed popularity stems from its many proven and much sought after beneficial nutraceutical components. The unique bioactive components in buckwheat seeds provide human health benefits akin to flavonoids, fagopyritols, phytosterols, and the thiamin-binding proteins. Buckwheat should be used more often in formulation of functional and nutraceutical foods to exploit its positive medical benefits.

MACRONUTRIENTS

Protein

The protein content in common and tartary buckwheat varies from 7 to 21%, depending on the cultivar and environmental conditions during growth (**Table 1**). Currently grown cultivars yield seeds with 11-15% protein in a whole seed (Campbell 1997). The proteins in buckwheat are the best known source of high biological value protein in the plant kingdom, having 92.3% of the value of nonfat milk solids and 81.4% of the whole egg solids (Pomeranz and Robbins 1972). Buckwheat flour has the highest protein content among all cereals (**Table 1**). Flour produced from Canadian varieties of buckwheat verified high protein

content and elevated contribution of fiber and ash (Table 2). The composition of essential amino acids in buckwheat protein is close to egg protein, the latter is used as reference (Table 3). Compared to other cereals, the amino acids in buckwheat proteins are well balanced and rich in lysine, methionine, histidine and tryptophan which are generally recognized as the limiting amino acids in wheat and barley (Pomeranz and Robbins 1972). Buckwheat flour protein has à score of biological value (BV) of 93, which is calculated from amino acid composition. BV is very close to egg protein, and much higher than for any other cereals (Table 3). Comparison of amino acid composition and amount of protein in different buckwheat seed parts and different types of buckwheat indicates that the germ is the main place where protein is concentrated. Amino acid compositions among different buckwheat seed parts and products show very small differences (Table 4).

Buckwheat protein consists of 18.2% albumin, 43.3% globulin, 0.8% prolamin, 22.7% glutelin, and 5.0% other nitrogen containing components (Javornik and Kreft 1984; Ikeda *et al.* 1991b; Ikeda and Asami 2000). Immunological studies showed little cross-reactivity between buckwheat proteins and wheat prolamins, the main culprit for celiac disease (Skerritt 1986; Friis 1988). In the absence of gluten type proteins, buckwheat flour can be an important ingredient in gluten-free diet for people suffering from the celiac disease. Since buckwheat groat and flour are rich in many nutrients and nutraceuticals this pseudocereal can also be an excellent ingredient in bread and cereal formulation, improving the nutritional value of these products (Li and Zhang 2001).

Despite the balanced amino acid composition, buckwheat contains anti-nutritional components, such as pro-

Table 3 Comparison of essential amino acid composition and availability of proteins in buckwheat, cereals, and egg.

Amino acid		Am	ino acids contribution	(g/100 g protein)	
	Barley	Wheat	Corn	Buckwheat	$\mathbf{Egg}^{\mathbf{a}}$
Lysine	3.7	2.5	2.8	5.7	6.0
Methionine	1.8	1.8	2.4	2.3	3.8
Cysteine	2.3	1.8	2.2	2.2	2.4
Threonine	3.6	2.8	3.9	3.5	4.3
Valine	5.3	4.5	5.0	4.7	7.2
Isoleucine	3.7	3.4	3.8	3.5	5.9
Leucine	7.1	6.8	10.5	6.1	8.4
Phenylalanine	4.9	4.4	4.5	4.3	6.1
Histidine	2.2	2.3	2.4	2.5	2.2
Tryptophan	1.1	1.0	0.6	2.0	1.5
TD (%)	84.3	92.4	93.2	79.9	99
BV (%)	76.3	62.5	64.3	93.1	100
NPU (%)	64.3	57.8	59.9	74.4	94
UP (%)	7.3	7.3	6.0	9.1	12.2
TD - true protein digestib	ility; BV - biological value (based on amino acid compo	osition); NPU - net proteir	utilization; UP – utilizable pr	otein (protein x NPU/100); a -

values for whole egg.

Source: Compiled from Ikeda and Kishida (1993) and USDA National Nutrient Database for Standard Reference, Release 21 (2008)

Table 4 Amino acid composition of common and tartary buckwheat products (g/100 g protein).

Amino acid			Seed ^A	Germ ^A		
		Common		Tartary		
	Bran	Flour	Bran	Flour		
Alanine	4.4	4.6	4.3	4.7	4.5	3.6
Arginine	10.5	9.9	11.0	9.6	9.7	11.9
Aspartic acid	10.3	10.2	10.1	10.3	11.3	10.9
Cysteine	2.1	2.7	2.6	2.7	1.6	2.2
Glutamic acid	18.8	17.6	18.4	17.1	18.6	19.3
Glycine	6.1	6.1	6.0	5.9	6.3	6.0
Histidine	2.7	2.5	2.7	2.6	2.7	2.6
Isoleucine	3.8	3.9	4.0	4.2	3.8	3.5
Leucine	6.5	6.9	6.4	7.1	6.4	5.8
Lysine	5.5	5.8	5.9	6.2	6.1	5.6
Methionine	1.1	1.4	1.3	1.4	2.5	2.0
Phenylalanine	4.5	4.6	4.5	4.7	4.8	4.7
Proline	4.0	4.5	4.1	4.5	3.8	3.8
Serine	5.2	5.0	5.2	5.2	4.7	5.0
Threonine	3.6	3.7	3.5	3.7	3.9	3.7
Tyrosine	2.7	2.7	2.9	2.9	2.1	2.8
Protein (% DM)	4.3	19.0	4.1	18.9	13.8	55.9

Source: Adapted from Bonafaccia et al. (2003)

A – Pomeranz and Robbins (1972)

tease inhibitors, trypsin inhibitors, phytic acid and tannins (Farrell 1978; Javornik *et al.* 1981; Ikeda *et al.* 1986). These factors lower buckwheat protein digestibility in humans and in animals although it is comparable with other cereals (**Table 3**). Buckwheat trypsin inhibitors are resistant to thermal processing and treatment with acids (Ikeda *et al.* 1986). Germination of buckwheat seeds significantly reduces the activity of protease inhibitors; as such seedlings and young buckwheat plants are used as a food source showed improved digestibility and utilization of proteins (Kreft 1983). Also has been suggested that trypsin inhibitor can have beneficial effect for people with diabetes by stimulating activity of pancreas (Ookubo 1992).

The low protein digestibility and utilization may not be beneficial for growing organisms and people with digestive track problems, since the consumption of insufficiently cooked buckwheat products can lead to diarrhea (Ikeda 1993, 2002). On the other hand, given that obesity is one of the prominent health problems in North America and the number of obese people is increasing in different parts of the World, the low digestibility of buckwheat protein may not necessarily be a negative property. "Resistant proteins", resistant to enzymatic digestion in digestive tract, such as those in buckwheat, can also beneficially affect blood cholesterol levels by limiting its absorption (Kayashita *et al.* 1996; Iwami 1998; Tomotake *et al.* 2000, 2001; Metzger *et al* 2007). Kayashita *et al.* (1995a) reported that both plasma and hepatic cholesterol levels were significantly lowered in rats fed a diet containing buckwheat protein extract compared to soybean protein or casein diet. Metzger et al. (2007) reported that 0.1 to 0.4% of buckwheat proteins added to cell culture reduced cholesterol solubility by 40%; in the presence of buckwheat protein cholesterol uptake was reduced by 36 and 47% when compared to bovine albumin and casein, respectively. Carroll and Hamilton et al. (1975) reported that the ratios of lysine to arginine and methionine to glycine are the main factors determining the cholesterol lowering properties of proteins, because these amino acids are involved in regulation of the hepatic low density lipoprotein (LDL) formation. In buckwheat, the ratios of these amino acids are lower than in the other plant proteins; nutritional studies have shown that buckwheat proteins have the highest cholesterol lowering properties among plant proteins (Huff and Carroll 1980). Moreover, high content of methionine in the diet negatively affects cholesterol level in serum, because methionine is a part of homocysteine catabolism which affects homocystine transferase (Carroll and Kurowska 1995).

Kayashita *et al.* (1997) reported that buckwheat protein isolate (BPI) was more efficient in cholesterol lowering than soybean protein isolate. The authors also showed that rats fed with BPI experienced the same body growth as casein-fed reference rats, suggesting that buckwheat proteins were sufficiently digested, absorbed and provided adequate amount of amino acids required for growing organisms. BPI was shown to be more effective in lowering LDL and very low density lipoprotein (VLDL), than any other plant and animal proteins (Saeki *et al.* 1990). BPI can also be used as a functional food ingredient to treat hypertension, obesity, as well as constipation (Kayashita *et al.* 1995b). As an example of unusual specific bioactivity of buckwheat protein, a patent has been issued in Japan to produce a buckwheat protein isolate which has lowering activity of angiotensin converting enzyme (ACE) and directly controlling hypertension (Koyama *et al* 1993).

Tomatoke *et al.* (2001) reported that high fat diets and overeating did not affect the rats' body weight when buck-wheat protein hydrolyzate was included in the diet. This protective effect was much weaker for soybean protein hydrolyzate. Mitsunaga *et al.* (1986) first reported the presence of thiamine-binding protein (TBP) in buckwheat seeds. Buckwheat TBP has a 1:1 binding stoichiometry with thiamin, offering protection for larger amounts of this vitamin (Mitsunaga *et al* 1986). After ingestion, this complex is digested by proteases, and thiamine is released and absorbed. The protein moiety in the TBP complex improves the stability of thiamine during food storage, processing and enhances its bioavailability particularly for people who suffer thiamin deficiency and cannot store it (Watanabe *et al* 1999).

Several epidemiological studies have shown that buckwheat proteins act like a dietary fibre and can retard mammary carcinogenesis (Kayashita et al. 1999) as well suppress the development of colon cancer (Cassidy et al. 1994; Lipkin et al. 1999). Absorption and blocking carcinogenic initiators in the colon may form a mechanism for anticarcinogenic activity of buckwheat protein. Additionally, difficult to digest proteins may interact with resistant starch and form a prebiotic, utilized by colon bacteria to produce short chain fatty acids that protect tissues and positively affect colon physiology (Scheppach et al. 1992; Morita et al. 1998). Among the unusual properties of buckwheat protein is evidence showing the potential to reduce the incidence of colonic adenocarcinomas by 47%. Further these proteins provide colon protection by reducing the proliferation and expression of carcinoma cells in colonic epithelium (Liu et *al.* 2001).

Carbohydrates

Starch is the major carbohydrate in buckwheat, and its amount in Canadian varieties of buckwheat may vary from 67 to 75% (Campbell 1997). The amylose content in buckwheat starch granules varies from 15 to 52% and its degree of polymerization fluctuates from 12 to 45 glucose units (Mazza 1993). The composition of starch isolated from different varieties of buckwheat grown in several countries in
 Table 5 is presented. In Polish varieties a significant amount
 of fiber and resistant starch were observed as components of buckwheat starch. Roasting of buckwheat seeds, which is used often before groats cooking, causes an increase in contribution of protein in starch and lowering the total amount of starch (Table 5). During roasting non-enzymatic browning is happening and proteins are bonded to carbohydrates (Christa et al. 2009). Raw buckwheat starch contains 17.1 to 26.1% of amylose and it contribution is dependent on variety and growing region, whereas amylopectin forms majority of starch granules (Table 5). Data about starch composition for other varieties and growing regions are limited to contribution of amylose and amylopectin (Praznik et al. 1999; Qian et al. 1999). Buckwheat starch granules are polygonal or round in shape with a diameter ranging from 2 to 12 μ m with flat areas due to the tide packing in the endosperm. The majority of granules are 2-6 µm in diameter; their small size defines the unusual properties and performance of buckwheat products during processing (Soral-Śmietana et al. 1984; Acquistucci and Fornal 1997; Campbell 1997).

Lipids

In the whole buckwheat grain the total lipids content range from 1.5 to 4.0% and 1.2 to 4.3% for common and tartary buckwheat, respectively (**Table 1**). The content of lipids

 Table 5 Composition of starch isolated from buckwheat seed (% DM).

Component	Buckwheat				
	Native	Roasted	Seed ¹	Different varieties ²	
Starch	90.2	82.5	95.8		
Amylose	17.1	12.4	24.0	21.3 - 26.4	
Amylopectin	73.1	70.1	76.0	78.7 - 73.6	
Resistant starch	5.1	5.1			
Dietary fiber	5.6	4.2			
Proteins	1.1	4.0			
Ash	0.2	0.2			

Adapted from Christa (2009)

¹ Adapted from Praznik et al. (1999)

 2 Starch from different buckwheat varieties and growing area. Adapted from Qian *et al.* (1999)

Table 6 Fatty acid composition of common and tartary buckwheat (g/100 g fat).

Fatty acid	Buckwheat				
	Common	Tartary			
Myristic	0.3	0.4			
Palmitic	15.6	19.7			
Palmitoleic	0.1	0.2			
Stearic	2.0	3.0			
Oleic	37.0	35.2			
Linoleic	39.0	36.6			
Linolenic	1.0	0.7			
Arachidonic	1.8	1.8			
Eicosenoic	2.3	2.0			
Behenic	1.1	0.8			
Saturated	20.5	25.3			
Unsaturated	79.3	74.5			
Unsaturated/saturated	3.9	2.9			

Source: Adapted from Bonafaccia et al. (2003) and Kim et al. (2004)

varies by seed part and is usually in: the embryo 9.6-19.7%, the endosperm 2.0-3.0% and the hulls 0.4-0.7% (Campbell 1997). Buckwheat oil contains 16-25% of saturated and 74-79% of unsaturated fatty acids (**Table 6**). Among these fatty acids palmitic, oleic and linoleic are dominant with contribution of 15-20, 30-45 and 31-41%, respectively (Campbell 1997). Other typical fatty acids for plant lipids were also detected although their contribution was below 10% (**Table 6**). Sterols, the main source of signalling and metabolic components, are found in the buckwheat embryo and endosperm at levels of 2.1 and 0.55 ppm, respectively (Horbowicz *et al* 1992). This very low amount of phytosterols in buckwheat may affect absorption of cholesterol only when this crop will forms a significant portion of a daily diet.

BUCKWHEAT NUTRACEUTICALS

Dietary fiber

Dietary fiber is a part of a plant or analogous carbohydrates that is resistant to digestion and absorption in the human small intestine but is partially or completely fermented by microflora in the large intestine (AACC Report 2001). The amount of total dietary fiber (TDF) in buckwheat may be affected by both variety and environmental factors during growth. The major components of TDF are: cellulose, nonstarch polysaccharides, resistant starch and lignins. These components are concentrated in the cell walls of the starchy endosperm, aleurone, seed coat, and hull. The content of TDF in groats may range from 5.0 to 11.0% (Yoshi and Rana 1995; Zheng et al. 1998; Steadman et al. 2001; Izydorczyk et al. 2004). Smaller groats have less endosperm and, therefore, relatively more seed coat, resulting in more dietary fiber. Bran fractions obtained by milling buckwheat were especially enriched in dietary fiber (15-22%) because the outer layer covering the seeds contains non-starch polysaccharides (Table 2). Hatcher et al. (2008) reported that dark flours from cross- and self-pollinating Canadian common buckwheat were richer in dietary fiber (15.2-22.0%)



Fig. 1 Chemical structure of fagopyritols from B series. Linkage between D-chiro-inositol and galactose molecules. Adapted from Horbowicz et al. (1998).

than white flours containing mostly starch. However, the majority of TDF in dark flours was insoluble, whereas the dietary fiber associated with white flours were mainly water soluble (Hatcher *et al.* 2008). The amount of fiber in buck-wheat flour is affected by the milling process and the number of fractions produced. The fiber is distributed among fractions and the amount in each fraction can be 1.7-8.5% as reported by Steadman *et al* (2001).

From a functional point of view TDF is classified into soluble and insoluble dietary fiber. The insoluble part of dietary fiber (IDF) decreases transit time through the digestive tract and at the same time increases fecal mass, preventing or ameliorating constipation. Soluble dietary fiber (SDF), due to its absorption of large amounts of water and formation of high viscosity solution, slows gastric emptying, reduces and preventing absorption of nutrients. Among nutrients which are the most affected by this type of fiber are glucose and cholesterol. SDF is fermented by gut microflora producing short chain fatty acids, implicated with health of colon and preventing cancer development (Scharlau et al. 2009). He et al. (1995) observed that SDF affected blood pressure and suggested that buckwheat consumption, due to its high content of fiber, may prevent and/or ameliorate both hypertension and hypercholesterolemia. Dietary fiber may also negatively affect minerals and proteins by binding them and making non-available for absorption (Ikeda et al. 1986; Torre 1991; Roberfroid 1993).

Some portion of buckwheat dietary fiber is soluble (**Table 2**). Asano *et al.* (1970) isolated water-soluble nonstarch polysaccharides from buckwheat and reported that the main chain of this polysaccharide consists of xylose, mannose, galactose, and glucuronic acid. More recently, arabinose and glucose residues have also been identified in water-soluble buckwheat polysaccharides (Izydorczyk *et al.* 2004). One of the most important characteristics of buckwheat water-soluble non-starch polysaccharides is their very high molecular weight; as a consequence, they can form very viscous solutions when hydrated (Izydorczyk *et* al 2004).

Resistant starch

Starch is a major component of buckwheat (**Table 1**). Although the majority of buckwheat starch is readily digestible, a small portion (4.0-7.0%) is resistant to enzymatic hydrolysis (Christa *et al.* 2009). The so-called resistant starch – including physically inaccessible starch, native granular starch, retrograded starch, and chemically and thermally modified starch – is another source of dietary fiber in buckwheat and may exhibit nutritionally advantageous effects similar to those of dietary fiber (Christa and Soral – Śmietana 2008). There are indications that resistant starch is similarly fermented in the large intestine as soluble fiber, and similar metabolites with positive health effects are produced (Englyst *et al.* 1992).

The factors influencing starch availability include its botanical origin, physical properties and form of starch, the ratio of amylose to amylopectin, and its interactions with other constituents. Raw buckwheat grain may contain 33-38% of resistant starch; however cooking reduces its content three-fold (Christa and Soral-Śmietana 2008). Processing of buckwheat starch or foods-containing buckwheat by autoclaving, cooling cycles, extrusion, boiling, baking, increase the amount of resistant starch (Skrabanja and Kreft 1998; Skrabanja et al. 1998a). During storage, development of the retrograded amylose in starches may result in limited accessibility to amylases (Berry 1986). Other components may interact with starch or inhibit starch degrading enzymes and thus reduce starch digestibility (Thompson and Gabon 1987). Consumption of boiled buckwheat groats or bread with 50% of buckwheat flour lower blood glucose and insulin responses compared with white wheat bread (Skrabanja et al. 2001). Thus, buckwheat has potential to be used as functional ingredient in the formulation of food with lowered glycemic index, which in turn positively affects blood glucose level.

Table 7 Composition of vitamins in buckwheat and selected food grains (unit/100 g)

Vitamin	Units	Rye	Buckwheat	Barley	Corn	Wheat
Vitamin C	mg	0.0	0.0	0.0	0.0	0.0
Thiamin	mg	0.32	0.42	0.65	0.39	0.51
Riboflavin	mg	0.25	0.19	0.29	0.21	0.11
Niacin	mg	4.27	6.15	4.61	3.63	5.71
Pantothenic acid	mg	1.46	0.44	0.28	0.42	0.94
Vitamin B-6	mg	0.29	0.58	0.32	0.62	0.34
Folate	μg	60	54	19	19	43
Choline, total	mg	30.4	54.2	37.8	21.6	31.2
Vitamin A	IU	11	0	22	214	9
Lutein + zeaxanthin	mg	0.21	0.22	0.16	1.36	0.22
Vitamin E	mg	1.3	0.32	0.57	0.49	1.01
Vitamin K	μg	5.9	7.0	2.2	0.3	1.9

Fagopyritols and other soluble carbohydrates

Fagopyritols are specific carbohydrates formed by joining D-chiro-inositol with galactose, where series B have 2-1 while A series 3-1 α -galactosyl bond, firstly identified in buckwheat and named after the Latin name of this crop (Fig. 1). Fagopyritols are mono-, di-, and tri-galactosyl derivatives of D-chiro-inositol that accumulate specifically in the embryo and the aleurone tissues of buckwheat. These components hold water, preventing desiccation of seed. Among plant sources, buckwheat is the richest in these carbohydrates (Horbowicz et al. 1998; Obendorf et al. 2000).

Buckwheat embryos usually have two mono-galactosyl chiro-inositol isomers (Fagopyritol B1 and Fagopyritol A1), two di-galactosyl chiro-inositol isomers (Fagopyritol B2 and Fagopyritol A2) and small amounts of tri-galactosyl chiro-inositol (Fagopyritol B3). In buckwheat embryos the amount of fagopyritol B1 [O- α -D-galactopyranosyl-(1 \rightarrow 2)-D-chiro-inositol] was at 40% whereas sucrose accounted for 42% of all soluble carbohydrates, indicating importance of these sugars to it function and survivability (Horbowicz et al. 1998). Other soluble carbohydrates found in buckwheat embryos include D-chiro-inositol, myo-inositol, galactinol, raffinose and stachyose. The latter two oligosaccharides contribution was below 1% of the total soluble components in buckwheat embryos (Horbowicz et al. 1998).

Bran fractions contain the highest amount of fagopyritols among all milling fractions, reflecting the high amount of embryo and aleurone tissues. It has been reported that the bran milling fractions may contain 2.6 g of fagopyritols per 100 g of dry weight, whereas dark and light buckwheat flours contain 0.7 g and 0.3 g/100 g, respectively (Steadman et al. 2000). Dark flour is formed by milling embryo, aleurone tissue and hull from buckwheat seed and it contains the highest amounts of fygopyritols and D-chiro-inositol (Table 2).

Fagopyritols are readily hydrolyzed by α -galactosidase releasing D-chiro-inositol (Horbowicz et al. 1998). Published literature indicates that D-chiro-inositol could positively affect the blood glucose level and insulin activity (Ortmeyer et al. 1993; Fonteles et al. 2000). Work done at the University of Manitoba has shown that buckwheat extract was equally efficient in lowering blood glucose level and activating insulin as synthetic D-chiro-inositol (Kawa et al. 2003). Further work by this group showed that single dose of buckwheat extract can keep blood glucose level lowered by 20% for extended period of time. However, this effect was not related to the content of either D-chiroinositol or fagopyritols, indicating that buckwheat contains other components that can replace insulin and regulate glucose level. There is also evidence that D-chiro-inositol may obstruct development of polycystic ovary (Nestler et al. 1999). The digestion of fagopyritols in the human digestive system and the amounts required for consumption to achieve beneficial effects remain unknown and necessitate further investigation.

Vitamins

Buckwheat is unique from other cereals in its content of minerals and vitamins, each is discussed separately. Buckwheat contains various vitamins with content comparable to other grains (Pomeranz 1983). However, buckwheat contains higher levels of niacin, B₆, vitamin K and choline. The latter is an important component of the neurotransmitter acetylcholine and body can synthesize choline from methionine; however this amino acid is often in short supply in our diet (Clemens et al 2009). On the other hand buckwheat does not contain vitamin A while carotenoids such as lutein and zeaxanthin are present in similar amounts as in other cereals (Table 7).

Minerals

The ash content of buckwheat varies from 2.0-2.2%, depending upon the variety and conditions during growth (Campbell 1997). Different parts of the buckwheat seed contains different amounts of minerals; hull, aleurone tissues and embryo are the main locations of the most of the minerals (Tables 2, 8) (Sokolov et al. 1981; Ikeda et al. 1995). Buckwheat seeds are a good source of many essential minerals; whereas the amounts are similar to other cereals (**Table 8**).

The mineral content in buckwheat seeds and their morphological fractions reach: 2.0-2.5% in the whole grains, 1.8-2.0% in the kernel, 2.2-3.5% in the dehulled grains, 0.8-0.9% in flour, and 3.4-4.2% in the hulls (Li and Zhang 2001). In comparison with rice, wheat, corn flour, buckwheat contains the highest amounts of zinc, copper, and manganese. Trace elements, e.g. selenium or chromium, are also present in buckwheat, however at very low levels. As in other plant material, mineral content is highly influenced by the presence of these elements in soil where the crop was produced (Ikeda et al. 1991a, 1998; Steadman et al. 2001). Minerals are cofactors in antioxidative enzymes. Activity of the following enzymes is maintained by: superoxide dismutase on zinc, copper and manganese; glutathione peroxidase and thioredoxine reductase on selenium; and catalase on iron (Fardet et al. 2008).

The bioavailability of zinc, copper and potassium from buckwheat is especially high (Ikeda et al. 1990). It has been reported that 100 g of buckwheat flour can provide approximately 13-89% of the daily recommended dietary allowance (RDA) for zinc, copper, magnesium, and manganese. However, the phytic acid, mainly located in bran fractions, may reduce minerals bioavailability by forming undigestible salts (Thompson 1993). Foliar fertilization makes buckwheat grains a rich source of dietary selenium and a useful raw material to enrich food products (Stibilj et al. 2004). Spraying plants with selenium solution may enrich buckwheat grain with selenium. Soaking buckwheat seeds in selenate solution before seeding yielded buckwheat herbs with high levels of selenium (Stibilj et al. 2004; Smrkolj et al. 2006; Ozbolt et al. 2008). Buckwheat accumulates selenium predominantly as organic compounds including

Table 8 Comparison of minerals composition in buckwheat and food grains (mg/100 g).

Mineral	Corn	Barley	Rye	Wheat		Buckwhe	at
					Seed	Hull	Flour ^A
Calcium	7	33	33	25	18	33.3	41
Iron	2.7	3.6	2.7	3.6	2.2	6	4.1
Magnesium	127	133	121	124	231	5991	251
Phosphorus	210	264	374	332	347	1353	337
Potassium	287	452	264	340	460	1416	577
Sodium	35	12	6	2	1	46	11
Zinc	2.2	2.8	3.7	2.8	2.4	7.3	3.1
Copper	0.3	0.5	0.5	0.4	1.1	1	0.5
Manganese	0.5	1.9	2.7	4.1	1.3	4.6	2.1
Selenium	15.5	37.7	35.3	70.7	8.3	6.8	5.7

A-Flour from whole groats.

Source: Compiled from USDA National Nutrient Database for Standard Reference, Release 21 (2008)



OH

OH

OH

ĊH₃



Quercetrin

ÓH Ö

Fig. 2 Buckwheat flavonols. Adapted from Oomah et al. (1996).

seleno-methionine, methyl-selenocysteine and γ -glutamylmethyl-selenocysteine. These compounds are part of an antioxidative system and may reduce the risk of cancer development (Ip *et al.* 2000; Nomura *et al.* 2000; Burke *et al.* 2003; Kitaguchi *et al.* 2008).

Flavonoids

Flavonoids and anthocyanins are phenolics, a large group of components produced mainly by plants. Oomah and Mazza (1996) reported the amount of phenolics in buckwheat at 0.7% in the hulls and 0.8% in the groats. Phenolics content and composition in buckwheat seeds is affected by specie, growing phase, growing conditions. New varieties with high levels of these compounds were developed in Canada, Japan and Germany (Ohsawa et al. 1995; Oomah et al. 1996; Jiang et al. 2007; Olschlager et al. 2008; C. Campbell, pers. comm.). The average total flavonoids contents were significantly different for the buckwheat species, 2.04% in F. tataricum, 0.35% in F. homotropicum, and 0.04% in F. esculentum (Jiang et al. 2007). Many different flavonoids have been isolated and identified in buckwheat grains including rutin, orientin, vitexin, quercetin, isovitexin, quercetrin and isoorientin in the hull, and rutin and small amounts of isovitexin in the groats (Table 9). Rutin, the main buckwheat flavonoid, is a quercetin aglycon attached to rutinose and the chemical structure of rutin, quercetrin (quercetin with rhamnose) and aglycon quercetin are presented in **Fig. 2**. Rutin attributed 54, 29, and 82% of the total flavonoid content in *F. esculentum, F. homotropicum*, and *F. tataricum*, respectively (Oomah and Mazza 1996; Li and Zhang 2001; Jiang *et al.* 2007). In the flowers, leaves and stems of *F. tataricum* the content of flavonoids can exceed 10% of wet plant weight (Park *et al.* 2000). New Canadian varieties, selected for plant flavonoids production achieved up to 18% of rutin in fresh plant tissues (C. Campbell, private communication). The average rutin seed content differs significantly depending on the buckwheat species, and was found 1.7% in *F. tataricum*, 0.1% in *F. homotropicum*, and 0.02% in *F. esculentum* (Jiang *et al.* 2007).

Table 9 Composition and content of flavonoids and catechins in buckwheat (µg/g DM).

(188)			
Flavonoids	Groat	Hull	
Isoorientin	8.5	8.4	
Orientin	8.6	14.3	
Vitexin	17.8	30.4	
Rutin	176.5	33.1	
Isovitexin	21.6	20.4	
Total	233.0	106.5	
Flavanols			
Catechin	31.3		
Epicatechin	203.5		
Epicatechin gallate	12.3		
	1 (0005) D 11	1 (0005)	

Source: Adapted from Zielinska et al. (2007), Danila et al. (2007)

Steadman *et al.* (2001) reported that the tartary buckwheat hull contained a similar amounts of rutin (4.4 g/kg) as the hull of common buckwheat, but the rutin level was much higher in groats of tartary buckwheat (81 g/kg) than in common buckwheat (0.2 g/kg). Fabjan *et al.* (2003) reported that content of rutin in seeds of three Tartary buckwheat cultivars were at 0.8-1.7% while at 0.01% in common buckwheat seeds (Minami *et al.* 1992).

Therapeutic doses of rutin, derived from buckwheat, were reported to be in the range of 180-350 mg, when 10 g of fresh buckwheat leaves were consumed (Dietrych-Szostak and Oleszek 1999). To exploit the variety and content of different nutraceuticals, particularly flavonoids, the buckwheat plant is utilized in some countries as a vegetable and often parts of buckwheat plants are collected a few times during the growing season (Lipkin *et al.* 1999; Li and Zhang 2001; Kim *et al.* 2004).

Biofunctionality displayed by rutin includes anti-inflammatory, antimutagenic, antitumoral, anticarcinogenic, smooth muscle relaxation, and estrogen receptor binding (Pisha and Pezzuto 1994; Ushida *et al.* 2008). It has been established that rutin can positively affect the activity of angiotensin I, enzyme involved in the controlling of blood pressure (Kawakami *et al.* 1995). The amount of rutin present in buckwheat seed usually included in the daily diet is effective in ameliorating blood cholesterol level, high blood pressure, keeping capillaries and arteries strong and flexible, arteriosclerosis and assisting in prevention of brain and lung hemorrhage (Yildzogle-Ari *et al.* 1991; Santos *et al.* 1999; Li and Zhang 2001; Gao *et al.* 2003).

Flavonoids also act as strong antioxidants protecting lipids, DNA, proteins and lipoproteins (Noroozi 1998; Przybylski *et al.* 1998; Cao *et al.* 2008). Due to higher content of flavonoids in tartary buckwheat, this crop is more effective in antioxidant activity (Cao *et al.* 2008). However newer varieties of common buckwheat offer even higher content of rutin as typical tartary buckwheat (Campbell private communication). Jiang *et al.* (2007) reported that *Fagopyrum tataricum* exhibit superior inhibition of LDL oxidation compared to common buckwheat. When buckwheat was thermally treated, including roasting, a common practice in preparation of the seeds for cooking, significant reduction in antioxidant activity and amount of flavonoids was observed (Dietrych-Szostak and Oleszek 1999; Zielińska *et al.* 2007).

Buckwheat may improve antioxidant capacity of foods when seed, flour or parts of plant are used as ingredients. In the Far East, buckwheat leaves are often used as component of herbal tea and vegetables, while the flour is applied in bread formulation. Significant enhancement in antioxidant activity was observed in bread, however due to the lack of gluten these formulations produced bread with poor physical and sensory properties (Kalinova *et al.* 2006; Gawlik-Dziki *et al.* 2009; Lin *et al.* 2009). Lack of gluten which is the main component forming dough and bread structure, causes poor textural property of baked goods, when transglutaminase was applied during dough formation, good quality bread was produced (Dal Bello 2007).

Buckwheat flavonoids also retarded proliferation of breast cancer cells and peripheral blood lymphocytes (Hirano *et al.* 1989a, 1989b). Interestingly, flavonoids are transferred from mother to fetus across placenta, and further into the fetus brain. This fact suggests that flavonoids are important as essential components for brain development and for maintenance of the nervous system (Lin *et al.* 2009).

Anthocyanins are widely spread pigments in the plant kingdom and have been found in buckwheat sprouts. However, these compounds have not been detected in buckwheat seeds, probably due to low concentration. This large group of components is intensely colored with red, purple, or blue water-soluble pigments; colors important in attracting consumers to flowers, fruits, and leaves. Positive health effects were also established for these components. The anthocyanin profiles and differences of anthocyanin concentrations in common and tartary buckwheat sprouts have been studied. Four anthocyanins namely: cyanidin 3-O-glucoside, cyanidin 3-O-rutinoside, cyanidin 3-O-galactoside, and cyanidin 3-O-galactopyranosyl-rhamnoside were found in common buckwheat sprouts while the last two in tartary buckwheat sprouts. Cyanidin 3-O-glucoside and cyanidin 3-Orutinoside were found in sprouts at the level of 0.2 mg/g and 5.5 to 6.6 mg/g DM, respectively. The amount of these components is highly affected by the intensity and type of light, forming higher amounts under intensive UV light (Kreft et al. 2002; Jovanović et al. 2006; Kim et al. 2007). Formation of more anthocyanins is related to the protective properties of these compounds against radiation and oxidative stress, suggesting that these compounds are strong antioxidants and radiation protectants. Pigmentation of plants is not the only function of anthocyanins, it has been established that components from this group have bioactivity similar to the flavonoids discussed above, including strong antioxidative capacity and activation of resistant insulin (Kim et al. 2007; Zhang et al. 2009).

Lignans

Lignans are the most researched group of nutraceuticals with the diverse activity proven by nutritional testing. They are compounds with a dibenzyl butane skeleton, and have been found in many plants (Fig. 3) (Setchell 1995). These components act in mammalians as hormone-like phytoestrogens, affecting many metabolic processes. Human gut microflora in large intestine is converting them into active compounds such as enterodiol (ED) and enterolactone (EL) (Thompson et al. 1991). The concentration of plant lignans acting as precursors of mammalian lignans are measured by subjecting a particular food ingredient to fermentation by intestinal microorganism and by measuring the released amount of ED and EL (Setchell 1995). In animals, the excretion of ED and EL measured in the urine indicates the amount of consumed plant lignan components (Rickard and Thompson 2000). The pathway of plant lignans transformation into mammalian lignans by bacteria is presented in Fig. 3. Flaxseed is one of the richest sources of plant lignans, and it contains 75-800 times more that other oilseeds, cereals, legumes, fruits and vegetables. Buckwheat is placed as the fourth highest in the amount of excreted ED and EL lignans among cereals and oilseeds (Fig. 4). The main plant lignans found in buckwheat are secoisolariciresinol diglycoside (SDG) and matairesinol (MAT) (Thompson et al. 1991; Kurzer et al. 1995). Mammalian lignans are often called enterolignans and are also found as converted and active forms in cereals, oilseeds and nuts (Smeds et al. 2007).

Lignans are considered to prevent and control some forms of cancer, particularly ones where hormones play a role (Thompson 1993). It was established that the urinary excretion of ED and EL was significantly lower in omnivore patients with breast cancer than in vegetarians who have a lower risk of cancer development due to the higher consumption of lignans (Adlercreutz et al. 1986). Also lignans reduced mammary tumor size by 50% and the number of tumors by 37% when cancer was developing in experimental rats (Setchell 1995; Rickard and Thompson 2000). Furthermore, it has been suggested that lignans have antimiotic, antiestrogenic, antiviral, antibacterial, and antifungal properties (Setchell et al. 1995; Thompson et al. 1995, 1996; Rickard and Thompson 2000). Epidemiological studies show that a high serum level of EL is associated with a reduced risk of coronary heart disease (Ayres 1990; Vanharanta et al. 1999). Lignans and their metabolites also display antioxidant activity towards different lipids, however low antioxidant activity was observed for components of the genetic system (Kitts et al. 1999; Pool-Zobel et al. 2000).

Food uses

Buckwheat has favorable composition in terms of high biological value of proteins, variety of nutraceutical compo-



Fig. 3 Formation of mammalian lignans and their plant precursors. Adapted from Thomson (1993).



Fig. 4 Total excretion of mammalian lignans in the urine of rats after diet supplementation with various foods. Sources: Compiled from Smeds *et al.* (2007), Thompson (1993, 1995).

nents with high health impact, trace elements and dietary fiber. Many functional foods are formulated with different forms of buckwheat around the globe; however nutritional tradition is the main factor affecting type of food produced. For some rural populations in countries such as Nepal, Bhutan, and China, buckwheat is the staple food. In Europe, however, buckwheat is mainly grown and consumed as an alternative crop and mostly in the Eastern European countries.

Buckwheat flour and groats are used for a wide variety of dishes. In Asia they are consumed as noodles, dumplings and as unleavened chapattis. The buckwheat flour, called 'sobako', is mixed with wheat flour for the production of buckwheat noodles called 'soba noodles' in Japan. The buckwheat flour content ranges from 50 to 80% depending on the type of noodle produced. The Japanese Food Agency stipulates that a minimum of 35% buckwheat must be present for noodles to be called 'soba'. Some handmade 'soba noodles', available only in selected restaurants, are made with 100% buckwheat flour. In addition to their unique taste, buckwheat noodles have a superior protein makeup, high lysine level, contain an abundance of vitamins B1, B2, minerals and dietary fibre (Fu 2008). 'Soba noodles' prepared with 60% of dark buckwheat flour contain considerably higher amounts of minerals, proteins, dietary fibre, fagopyritols and flavonoids than noodles prepared with white flour, the potential health benefits of dark buckwheat noodles may be substantially greater (Hatcher *et al.* 2008). In the Japanese market, there are many kinds of buckwheat products presently available including: buckwheat wine, buckwheat sauce, and buckwheat lotus confectionery.

The buckwheat flower itself is one of the most important honey-producing plants. It is available for bees in time when other plants are deficient and very important for the survival of honeybees (Krkošková and Mrázová 2005). Honey produced from buckwheat flowers, usually contains high amounts of flavonoids and other phenolic components, protects human blood lipoproteins against oxidation more effectively than sucrose analogues (Gheldof *et al.* 2003). In Japan, buckwheat inflorescences are utilized as a functional food, due to their high rutin content. Rutin-rich herb tea and green buckwheat flour are the most commonly used buckwheat herb products (Fabjan *et al.* 2003). Green flour obtained by milling the dried flowering buckwheat plants is added as a natural food colorant to pasta, ice cream, and other products in Japan and South Korea (Kim *et al.* 2001).

In the early 2000s, buckwheat sprouts were introduced as functional vegetables because of their beneficial nutritive value, including amino acids, fibre, minerals, and protein (Kim *et al.* 2001). However, compared to the sprouts of common buckwheat, those of 'tartary buckwheat' (*F. tataricum*) have received greater attention as a functional food given their two fold higher content of rutin known to strengthen blood vessels (Mukoda *et al.* 2001).

In Europe, particularly Eastern Europe, roasted, hulled buckwheat kernels, usually cracked into coarse, medium, or fine granules, also known as 'kasha' are used in dishes ranging from pilafs to mixtures with meat and as basic ingredient used in the preparation of porridges and soups. In North America, the main use has been in pancakes, however, utilization of buckwheat has been increasing in the form of noodles, cereals and various ethnic dishes. The functional properties of buckwheat also create an opportunity for developing a new puffed snack product and buckwheat grit cakes (Im *et al.* 2003). Buckwheat is also used in pastries and as a meat extender.

In Europe and North America, buckwheat has been blended with other grains to produce multigrain pasta, energy bars, waffles, cereal flakes, bagels, and bread. Buckwheat, which is added to bread as a supplement, can provide beneficial health effects and prevent bread from oxidative degradation during processing and storage (Lin *et al.* 2009). The investigations of the effect of buckwheat ingestion in a rat model showed an increase of aerobic, mesophilic and lactic acid bacteria content in rats' intestines, concurrently significant decrease in pathogenic bacteria was also observed (Prestamo *et al.* 2003). Thus, buckwheat products could be considered as potential prebiotics for human gastrointestinal track.

As discussed above buckwheat is very rich source of a variety of nutraceutical components which can directly improve our diet and through it, positively affect our health and well being. Every coming year offers more data specifying new bioactive components found in buckwheat seed and plant. The crop stands apart from other cereals or plant sources as it contains immensely more nutraceuticals utilizable in our food supply that can ameliorate many chronic and civilization based health problems.

FUTURE PERSPECTIVES

Buckwheat is the rich source of nutraceutical and functional food ingredients; however, years of neglect and treating it as marginal crop caused that considerable development is required to utilize those components for food and drugs. The main challenge for buckwheat is keeping continues production of good quality seeds to provide food industry with source of unusual food ingredients to allow development of new products. The current technologies used for cereals processing need adaptation to accommodate buckwheat seed and to protect nutraceutical components present in it. Many novel techniques are required to improve traditional buckwheat products and to produce new with improved amount of functional and nutraceutical components. For buckwheat processing low temperature technologies need to be developed to protect functional components. Extrusion often used in cereals processing requires modification to accommodate unique buckwheat starch properties and to protect health impacting compounds.

Progress need to be made in the utilization of buckwheat seed and plant for new nutraceutical and main stream food products for everyday consumption. Many components of buckwheat plant and seed are rich in nutrients and nutraceuticals. Flowers and green parts of plant can produce large amounts of flavonoids; newly developed varieties can produce up to 18% of rutin in plant tissues. To utilize this component new technologies have to be developed to transfer it from plant to supplement and/or food ingredient.

Buckwheat is gluten-free and can be an important ingredient in celiac food formulations where considerable economical impact can be made for producers and processors. Example of the new applications of buckwheat is in the production of gluten-free malt, beer and novel functional drinks, where major modifications to processing were required to obtain proper quality product.

In the area of breeding, new varieties of buckwheat containing higher amounts of already know nutraceuticals are currently under development. Dr. Campbell developed new varieties of buckwheat seed which produce multiple amounts of fagopyritols compared to standard crop; however its utilization is lacking. It is expected that new health impacting components will be found in this crop and new variety containing higher amounts of specific component or multitude of compounds needs to be developed. However, breeding of new varieties of buckwheat is hampered by minimal food market interest.

Buckwheat has to be treated as potential source of drugs, especially for chronic and resistant diseases such as cardiovascular and diabetes. Many buckwheat components posses mysterious health activity, for example controlling insulin activity and type II diabetes, nevertheless further research is needed to establish bioactivity of compounds present in buckwheat.

In summary, to fully utilize generous amounts of bioactive components present in buckwheat seed and plant, substantial advancement in breeding, production, processing and health assessment is needed in the near future.

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