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Content of Phytosterols in Raw and Roasted Buckwheat Groats and By-Products

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Abstract

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We determined the content of phytosterols in buckwheat products. Additionally, the influence of technological processing applied during buckwheat groats production on the content of some phytosterols was investigated. The highest level of phytosterols was observed in lipids extracted from roasted buckwheat hulls and raw buckwheat hulls (51.7 mg/g of lipids and 40.9 mg/g of lipids, respectively). Sitosterol and campesterol were found in the largest quantities in each sample. Technological process affected the total content of phytosterols. An increase of phytosterol content in buckwheat grains (by 107.5%) was observed, while a reduction in phytosterol content in buckwheat groats (by 75.5%) was noted.

Keywords: *Fagopyrum esculentum*; grains; by-products; hull, roasting; technological process

Buckwheat is an annual plant from the knotweed (*Polygonaceae*) family (Krkošková & Mrázová 2005). It is not a plant with complex agricultural requirements, therefore it can be grown on poorer soils, of lower valuation classes. It is mainly grown in the Northern Hemisphere, especially in sub-Caucasian lands, China and Brazil, and to a lesser extent also in Japan, Korea, USA, Canada, Germany, Italy, Slovenia, and eastern Poland. Two buckwheat species are grown in Poland: common buckwheat (*Fagopyrum esculentum*) and a lot less frequent Tartary buckwheat (*Fagopyrum tataricum).* Only common buckwheat has an industrial significance, while Tartary buckwheat is mainly used as green fodder.

Buckwheat products are a source of biologically active substances, such as antioxidants, vitamins, amino acids, dietary fibre, and phytosterols (Cercaci *et al*. 2007; Christa & Soral-Śmietana 2008; Stojilkovski *et al*. 2013; Hęś *et al*. 2014). These bio-active compounds, found in buckwheat and buckwheat groats, are now the subject of many studies. Their positive influence in the prevention and prophylaxis of the so called 'diseases of affluence' has been well documented (Górecka *et al*. 2014). Buckwheat contains D-chiro-inositol, a constituent to insulin mediators, contributing to the regulation of blood glucose levels (Kawa *et al*. 2003; Yang *et al*. 2014). Buckwheat flour, made from crushed buckwheat groats, contains only trace quantities of proteins such as gliadin and glutenin, and thus can well be used as flour replacement for people with celiac disease. Buckwheat grains also contain high

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levels of vitamins B, mainly thiamine, therefore being a valuable dietary supplement especially for those people who cut down on meat products. Buckwheat is a rich source of phytosterols. Consumption of buckwheat products reduces cholesterol absorption in intestines due to similarities in the molecular structure between cholesterol and phytosterols contained in buckwheat (Christa & Soral-Śmietana 2008; Kaloustian *et al*. 2008; Ferretti *et al*. 2010; Dziedzic *et al*. 2012).

Technological processes applied in the industrial production of food products influence the content of biologically active compounds therein. Typically, mechanical processing is used in order to remove inedible or inassimilable parts or fractions, and thermal processing is applied to enhance digestibility or improve sensory attributes of food. Many technological processes used in the food industry as well as thermal processing applied in home cooking contribute towards degradation of phytosterols in ready to eat products (Kmiecik *et al*. 2009). Blanching and deodorisation of rice bran oil during the refining process lead to a decrease in phytosterol content by 38% (Van Hoed *et al*. 2006). When subjected to high temperatures, UV radiation, or when in the presence of heavy metal ions or pro-oxidants, sterols are oxidised and form derivative compounds called oxysterols or oxyphytosterols (Sosińska *et al*. 2013). An oxysterol level increases in meat during thermal processing (Derewiaka & Obiedziński 2009, 2010). These compounds have been found in nuts, rapeseed, rapeseed oil, also in fried potato chips and crisps (Rudzińska *et al*. 2005; Kmiecik *et al*. 2009). The resistance of phytosterols and stanols to oxidisation depends to a large extent on the temperature and duration of the applied processing. A significant decrease in the content of plant sterols was observed when temperatures exceeding 100°C were used in food processing. Also, longer frying times led to lower levels of these compounds (Panagiotis *et al*. 2011; Soupas *et al*. 2011).

Oxidisation of sterols, which occurs when food is preserved and processed, is closely related to their degradation. Degradation of sterols in model systems can reach 100% depending on matrix, temperature and heating time (Rudzińska *et al*. 2005). Preserving (storing) products containing phytosterols at the temperature of 4°C for 12 months does not lead to any significant changes in their total content. Similarly, no changes have been observed in phytosterol and stanol levels in food products stored after pasteurisation, spray drying or in powdered milk stored for 12 months (Soupas 2007). The aim of this study was to determine the phytosterol content in raw buckwheat groats, roasted buckwheat groats, and buckwheat products.

MATERIAL AND METHODS

Reagents and standards. Methanol (pa), chloroform (pa), petroleum ether (pa) and *n*-hexane (pa) were purchased from PoCh S.A. (Gliwice, Poland). Sylon BTZ (BSA + TMCS + TMSI, 3 : 2 : 3, v/v/v) and sterol standards (campesterol 98%, stigmasterol 95%, sitosterol 95%, sitostanol 95%, cycloartanol 95%) were acquired from Sigma Aldrich (St. Louis, USA); avenasterol 95% and Δ-7-stigmasterol 95% from Red Analytical (Cambridgeshire, UK) while MTBE (Methyl-tert-Butyl Ether) from J. T. Baker (Center Valley, USA).

Plant material. Plant material for the research consisted of *Fagopyrum esculentum* buckwheat grains of Kora cultivar, obtained from Plant Breeding and Acclimatization Institute (IHAR) in Puławy (Poland). Raw buckwheat grains (BG-I) were exposed to two types of technological processing. Both processes were carried out under laboratory conditions. The first type of processing consisted solely of hulling buckwheat grains, the second – of roasting, then hulling. The application of this treatment led to the following range of research material samples: whole raw buckwheat groats (RBGR-I), raw buckwheat hulls (RBH-I), roasted buckwheat grains (BG-II), roasted whole buckwheat groats (RBGR-II), and roasted buckwheat hulls (RBH-II), where (I) and (II) denote the respective processing types (Figure 1).

Chemical composition. Dry matter content was determined according to AOAC 2001.12 (2001).

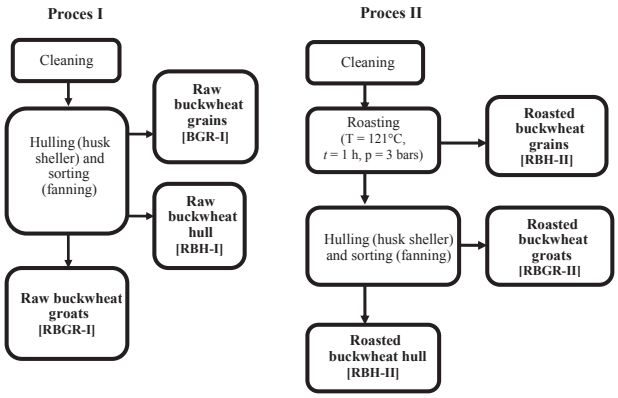

Figure 1. Draft of buckwheat groats production in laboratory conditions

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Ash content was determined by comparing the test portion weight prior to and after incineration (ICC 104/1:1990).

Protein content was determined by the classical Kjeldahl method. The conversion rate of 6.25 was used to convert the nitrogen content value to protein (AOAC 992.23:1992). Measurements were conducted using Kjeltec equipment from Foss Tecator (Sweden).

Total content of lipids. The total content of lipids was determined using petroleum ether, while the solvent was evaporated using a gravimetric method (AOAC 996.01:2000). Soxtec HT6 equipment from Foss Tecator (Höganäs, Sweden) was used for extraction.

Lipid extraction. Total lipids were extracted using a chloroform/methanol mixture (Folch *et al.* 1957). Each sample (2.5 g) was crushed and then incubated with a mixture of $CHCl_3$–MeOH (2 : 1, v/v) for 1 hour. Water (20%) was added and the system was thoroughly mixed to remove water-soluble substances. The chloroform fraction was collected and the solvent was evaporated to obtain the lipid fraction.

Sterol content. Lipid extracts (0.05 g) with 2 ml of 1 M methanolic KOH were incubated at room temperature for 18 hours. The unsaponifiable fraction was extracted with a mixture of hexane and MTBE (1 : 1 v/v), then the solvent was evaporated using nitrogen and silylated using Sylon BTZ.

GC-analysis. Chromatographic analysis was conducted using a Hewlett-Packard 6890 chromatograph equipped with flame ionization detector and DB-35MS capillary column (25 m × 0.2 mm × 0.33 m; J&W Scientific, Folsom, USA). Sterols were separated using programmed oven temperatures: the temperature program was initially set to 100°C for 5 min, then raised at a rate of 25°C/min to 250°C and held for 1 min; in the next phase the temperature was raised by 3°C/min up to 290°C and held for 20 minutes. Injector and detector temperature was 300°C. Splitless injection was used. Hydrogen was used as the carrier gas, at a flow rate of 1.5 ml/minutes. 5α-Cholestan was used for the internal standard, and sterols were identified based on retention time of standards and literature data (AOCS 6-91:1997) (Figure 2).

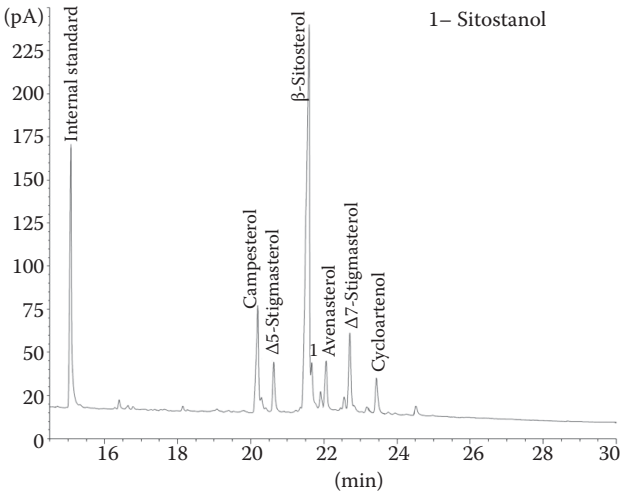

Figure 2. GC chromatogram of phytosterols from BG I (raw buckwheat grains)

Statistical analysis. Results of determinations reported in this study constitute a mean of three replications. For the purpose of objectivity of inference the recorded results were subjected to statistical analysis (Statistica software). For the determination of significance of differences between means a one-way analysis of variance was conducted using

Table 1. The content of total lipids and proteins in buckwheat samples (g/100 g of product)

Buckwheat products	Total content		Ash	Dry matter
	protein	lipid		
Technological process I				
BG-I	11.84 ± 0.22^{bc}	1.79 ± 0.04^{c}	2.20 ± 0.03^{b}	91.04 ± 0.13^{c}
RBGR-I	16.88 ± 0.21^{d}	3.45 ± 0.02^{e}	1.98 ± 0.11^{a}	92.54 ± 0.31^{e}
RBH-I	3.59 ± 0.24^{a}	0.77 ± 0.03^{b}	2.44 ± 0.02^{c}	93.68 ± 0.24^{f}
Technological process II				
BG-II	11.51 ± 0.00^{b}	2.80 ± 0.03^{d}	1.8 ± 0.127^{a}	89.50 ± 0.28^{a}
RBGR-II	11.96 ± 0.02^{bc}	2.80 ± 0.01^{d}	2.53 ± 0.02^{c}	90.07 ± 0.12^{b}
RBH-II	3.19 ± 0.12^{a}	0.37 ± 0.01^{a}	2.56 ± 0.11^{c}	91.50 ± 0.00^{d}

Data are mean values of triplicate determinations ± standard deviation; means with different letters in each column differ significantly ($P < 0.05$); BG-I – raw buckwheat grains; BG-II – roasted buckwheat grains; RBGR-I – raw buckwheat groats; RBGR-II – roasted buckwheat groats; RBH-I – raw buckwheat hulls; RBH-II – roasted buckwheat hulls

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Tukey's test. Dependences were considered statistically significant at the level of significance $\alpha < 0.05$.

RESULTS AND DISCUSSION

Chemical composition. The content of total proteins, lipids, dry matter, and ash is presented in Table 1. The content of buckwheat proteins depends on the technological process used. The sample of raw buckwheat groats (RBGR-I) was the richest in protein, with 16.88 g/100 g of product. The technological process caused a reduction in the total content of protein in buckwheat groats (by 29%), while in buckwheat grains and buckwheat hulls the high temperature did not cause any significant differences. The value of the total protein content in raw buckwheat grain (BG-I) and roasted buckwheat grain (BG-II) was similar (about 11.5 g/100 g of product). The lowest protein content was observed in raw (RBH-I) and roasted (RBH-II) buckwheat hull (about 3.5 g/100 g of product). Krkošková and Mrázová (2005) reported that the total content of protein depends on morphological parts of the plant. They observed the highest content of total protein in groats and grains (about 12 g/100 g of product). The sample of raw buckwheat groats (RBGR-I) was the richest in lipids, with 3.45 g/100 g total lipids extracted on a dry weight basis. The amount of total lipids in roasted buckwheat grains (BG-II) was comparable (2.8%) to that in roasted buckwheat groats. The lowest level of lipids was observed in roasted buckwheat hulls (RBH-II) and raw buckwheat hulls (RBH-I), 0.37 and 0.77%, respectively. The highest level of total lipids in buckwheat grains and buckwheat groats can be explained by the occurrence of the germ, where the majority of fatty substances are found. Krkošková and Mrázová (2005) reported that buckwheat grains contained 2.3% of lipids, which generally agrees with our findings. According to many authors, the content of components in buckwheat grains and buckwheat groats is determined by growing conditions, cultivation, and buckwheat variety (Bonafaccia *et al*. 2003; Krkošková & Mrázová 2005; Licen & Kreft 2005; Guo & Yao 2006).

Total content of phytosterols. The average dietary consumption of phytosterols is approximately 250 mg/day (Moreau *et al*. 2001). Plant sterols found in buckwheat seeds show positive effects in a lowering of the blood cholesterol level (Krkošková & Mrázová 2005). The total quantification of phytosterols is summarised in Tables 2 and 3 and Figure 3. The lipids extracted from roasted buckwheat hulls (RBH-II) and raw buckwheat hulls (RBH-I) contained the highest amount of phytosterols, 51.7 and 40.9 mg/g of lipids, respectively. Therefore lipids extracted from buckwheat hulls contained more phytosterols than those extracted from buckwheat grains and groats. Jiang and Wang (2005) observed a similar dependence in their experiments. Nurmi *et al*. (2012) also identified the highest phytosterol content in the outer layers of wheat grains. The total content of phytosterols in buckwheat products was comparable to the value reported by others (Bajguz & Tretyn

Table 2. The content of total phytosterols in buckwheat samples

Buckwheat products	Total content of phytosterols	
	(mg/g of lipids)	(mg/g of product)
Technological process I		
BG-I	29.81 ± 0.53^{b}	0.53 ± 0.00^{d}
RBGR-I	40.36 ± 1.34^{cd}	1.39 ± 0.05^{f}
RBH-I	40.94 ± 2.61^{e}	0.32 ± 0.02^{b}
Technological process II		
BG-II	39.38 ± 2.03^{cd}	1.10 ± 0.05^{e}
RBGR-II	12.02 ± 0.38^{a}	0.34 ± 0.01^{c}
RBH-II	51.66 ± 2.39^{f}	0.19 ± 0.01^{a}

Data are mean values of triplicate determinations ± standard deviation; means with different letters in each column differ significantly in the same group ($P < 0.05$); BG-I – raw buckwheat grains; BG-II – roasted buckwheat grains; RBGR-I – raw buckwheat groats; RBGR-II – roasted buckwheat groats; RBH-I – raw buckwheat hulls; RBH-II – roasted buckwheat hulls

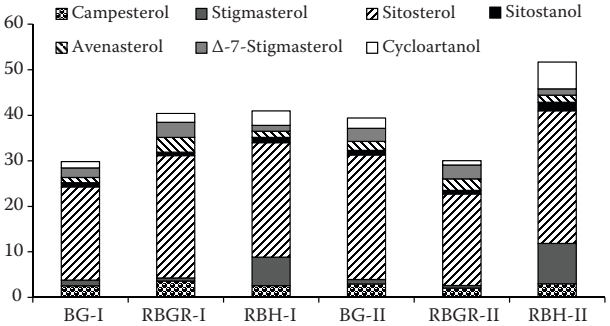

Figure 3. The content of total phytosterols and its fraction composition (mg/g of lipids)

BG-I – raw buckwheat grains; BG-II – roasted buckwheat grains; RBGR-I – raw buckwheat groats; RBGR-II – roasted buckwheat groats; RBH-I – raw buckwheat hulls; RBH-II – roasted buckwheat hulls

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Table 3. Composition of phytosterols (mg/g of lipids)

Buckwheat products	Campesterol	Stigmasterol	Sitosterol	Sitostanol	Avenasterol	Δ-7-Stigmasterol	Cycloartanol
Technological process I							
BG-I	2.53 ± 0.05^{bc}	1.26 ± 0.06^{d}	20.48 ± 0.37^{ab}	0.87 ± 0.03^{abc}	1.20 ± 0.03^{a}	2.09 ± 0.03^{b}	1.38 ± 0.07^{ab}
RBGR-I	3.55 ± 0.12^{d}	0.72 ± 0.06^{abc}	26.85 ± 1.02^{def}	0.79 ± 0.02^{ab}	3.20 ± 0.02^{d}	3.33 ± 0.18^{d}	1.93 ± 0.10^{bc}
RBH-I	2.57 ± 0.28^{bc}	6.26 ± 0.22^{e}	25.16 ± 2.43^{cde}	1.11 ± 0.04^{d}	1.37 ± 0.15^{a}	1.30 ± 0.13^{a}	3.17 ± 0.05^{d}
Technological process II							
BG-II	2.95 ± 0.16^{c}	0.99 ± 0.06^{bcd}	27.33 ± 2.13^{def}	1.02 ± 0.06^{cd}	1.98 ± 0.18^{b}	2.85 ± 0.12^{c}	2.26 ± 0.11^{c}
RBGR-II	2.00 ± 0.18^{a}	0.60 ± 0.01^{ab}	20.09 ± 0.15^{ab}	0.80 ± 0.08^{ab}	2.53 ± 0.16^{c}	3.07 ± 0.11^{cd}	0.92 ± 0.02^{a}
RBH-II	2.98 ± 0.13^{c}	8.87 ± 0.26^{f}	29.15 ± 2.36^{ef}	1.83 ± 0.03^{e}	1.54 ± 0.04^{a}	1.45 ± 0.05^{a}	5.85 ± 0.72^{e}

Data are mean values of triplicate determinations ± standard deviation; means with different letters differ significantly ($P < 0.05$); BG-I – raw buckwheat grains; BG-II – roasted buckwheat grains; RBGR-I – raw buckwheat groats; RBGR-II – roasted buckwheat groats; RBH-I – raw buckwheat hulls; RBH-II – roasted buckwheat hulls

2003; Liu 2007). Technological process affected the total content of phytosterols in various ways. Roasted buckwheat grains (BG-II) from technological process (II) contained more phytosterols than those obtained from technological process (I): an increase from 29.8 mg/g to 39.4 mg/g of lipids, or in other terms, an increase from 0.5 mg/g to 1.1 mg/g of product. The results obtained for roasted buckwheat hulls (RBH-II) are less clear: an increase was observed for the total content of lipids (from 40.9 mg/g to 51.7 mg/g of lipids) while a decrease was noted in phytosterol content per gram of product (from 0.3 mg to 0.2 mg/g of product). In the case of roasted buckwheat groats (RBGR-II) the thermal processing caused a decrease in phytosterol levels by approximately 70% both in terms of lipid and product content. Kaloustian *et al.* (2008) found that high temperature and pressure caused a reduction in the total content of phytosterols in beans and vegetables. Qui'lez *et al.* (2006) reported that baked muffins contained a lower total content of phytosterols than muffin dough. In terms of the raw material, buckwheat groats obtained from technological process I (RBGR-I) had the highest phytosterol content, i.e. 1.39 mg/g of product (Table 2). Roasted buckwheat grain (BG-II) was the second richest source of phytosterols (1.1 mg/g of product), followed by raw buckwheat grain (BG-I) – 0.53 mg/g of product, roasted buckwheat groats (RBGR-II) – 0.34 mg/g of product, raw buckwheat hulls (BH-I) – 0.32 mg/100 g of product and roasted buckwheat hulls (BH-II) – 0.19 mg/100 g of product. The highest sterol content in raw buckwheat grains (1.39 mg/g of product) can be attributed to their highest lipid content. Roasted buckwheat hulls (RBH-II) contained the smallest amount of phytosterols (0.19 mg/g) and the smallest amount of lipids (0.37 g/100 g of product).

Phytosterols composition. In the lipids obtained from the investigated buckwheat products, regardless of the processing, sitosterol (60–70%) was the predominant sterol, followed by campesterol (5–10%). Bacchetti *et al.* (2011) identified that the most abundant phytosterols are β-sitosterol, campesterol, and stigmasterol. Roasted buckwheat hulls (BH-II) contained very high concentrations of sitosterol, which made up over 56% of the total phytosterols. Sitosterol was also detected in raw buckwheat grains (BG-I) – 20.5 mg/g of lipids, roasted buckwheat grains (BG-II) – 27.3 mg/g of lipids, raw buckwheat groats (RBGR-I) – 26.9 mg/g of lipids, roasted buckwheat groats (RBGR-II) – 20.1 mg/g of lipids and raw buckwheat hulls (BH-I) – 25.2 mg/g of lipids. Cycloartanol was detected in all investigated buckwheat products. The highest concentration of this unique sterol was detected in roasted buckwheat hulls (BH-II) – 5.9 mg/g of lipids and raw buckwheat hulls (BH-I) – 3.2 mg/g of lipids. When comparing the phytosterol composition of raw (BG-I) and roasted (BG-II) buckwheat grains, raw buckwheat grains (BG-I) had much more stigmasterol (1.3 mg/g of lipids), while the contents of campesterol, sitosterol, sitostanol, avenasterol, Δ-7-stigmasterol, and cycloartanol were significantly lower. Raw buckwheat groats (RBGR-I) contained more campesterol (3.6 mg/g of lipids), avenasterol (3.2 mg/g of lipids) and cycloartanol (1.9 mg/g of lipids) in comparison with roasted buckwheat groats (RBGR-II). The process of roasting of buckwheat hulls had a significant effect, increasing the cycloartanol (85%), sitostanol (65%), and stigmasterol (42%)

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levels, but no influence of the roasting process on the content of campesterol, sitosterol, avenasterol and Δ-7-stigmasterol was observed. This could be attributed to partial degradation, transformation or isomerisation of the identified sterols (Kaloustian *et al*. 2008). Differences in the sterol composition between morphological parts of grains were also reported by Jiang and Wang (2005) and Harrabi *et al*. (2008). Kmiecik *et al*. (2011) reported that heating of oil had an impact on the content of some phytosterols to a different extent. The sterol composition and oil content are affected by geographical growing area, difference in species or processing and the ripening stage of fruits or seeds (Rivera del Alamo *et al*. 2004; Phillips *et al*. 2005).

CONCLUSIONS

Buckwheat products are carriers of various sterols, particularly sitosterol and campesterol. Cycloartanol was detected as a unique sterol in roasted and raw buckwheat products. Technological processing applied in the production of buckwheat groats influenced the content of phytosterols in various ways, which can be used when designing various products or diets with health-promoting properties. Raw buckwheat groats are a rich source of proteins, lipids and sterols, in comparison with roasted buckwheat groats. It was therefore concluded that process I of production of buckwheat groats is recommended for the preservation of functional components of buckwheat groats.

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