

ANTIOXIDANT ACTIVITY OF RYE BREAD ENRICHED WITH MILLED BUCKWHEAT GROATS FRACTIONS

Mirosław Żmijewski¹, Anna Sokół-Łętowska¹, Ewa Pejcz¹, Dagmara Orzeł^{*2}

¹Department of Fruit, Vegetable and Cereals Technology, Wrocław University of Environmental and Life Sciences, 51-630 Wrocław, J. Chelmonskiego street 37/41, Poland

²Department of Human Nutrition, Wrocław University of Environmental and Life Sciences, 51-630 Wrocław, J. Chelmonskiego street 37/41, Poland

ABSTRACT

Background. Buckwheat, despite its broad nutritional benefits, is still not widely appreciated grain. It contains a protein with preferred amino acid composition and it is a valuable source of micronutrients and vitamins of the B group and vitamin E. Moreover, buckwheat groats have a high amount of polyphenols, including flavonoids and flavones. Eating rye bread is beneficial due to its high content of dietary fiber, phenolic acids and characteristic taste and aroma. Therefore, the use of rye flour and buckwheat mill products for bread may allow obtaining a product of high nutritional value and flavor.

Objective. The aim of the study was to evaluate the influence of buckwheat products addition and baking process on the antioxidant properties of rye-buckwheat blends and breads.

Material and methods. Experimental material was rye flour type 580 and buckwheat flour, wholegrain flour and bran obtained by grinding buckwheat groats. Buckwheat products share was 20 and 35%. The control was the rye flour. In the rye-buckwheat blends and bread loaves, the contents of selected flavonoids by HPLC method, total polyphenols content by Folin-Ciocalteu method and the antioxidant activity by the DPPH[•] radical scavenging method were determined.

Results. Buckwheat bran was significantly richer in total polyphenols, rutin, quercetin, orientin and isoorientin than other buckwheat products and rye flour. Bread after baking contained similar amount of total polyphenols and quercetin and have a comparable ability to scavenge 1,1-diphenyl-2-picrylhydrazyl radicals (DPPH[•]) than the corresponding blends. Baking process negatively affected the amount of rutin, orientin and isoorientin.

Conclusions. The use of buckwheat bran as a replacement for wheat flour in bread significantly increases its nutritional value. The process of baking unequally affects the content of particular groups of antioxidant compounds.

Key words: *antioxidants, buckwheat, flavonoids, rutin, quercetin, polyphenols*

STRESZCZENIE

Wprowadzenie. Gryka mimo swoich wszechstronnych właściwości prozdrowotnych, nie jest jeszcze wystarczająco docenionym zbożem. Zawiera ona między innymi białko o bardzo korzystnym składzie aminokwasowym, jest również cennym źródłem mikroelementów i witamin z grupy B oraz witaminy E. Ponadto orzeszki gryczane wyróżniają się dużą ilością polifenoli, wśród nich flawonoidów i flawonów. Spożywanie pieczywa żytniego jest natomiast korzystne ze względu na wysoką zawartość w nim błonnika pokarmowego i kwasów fenolowych oraz charakterystyczny smak i aromat. Dlatego też wykorzystanie do wypieku pieczywa zarówno z mąki żytniej, jak i produktów przemiału gryki może pozwolić uzyskać produkt o wysokiej wartości smakowej i odżywczej.

Cel badań. Celem badań była ocena wpływu dodatków gryczanych i procesu wypieku na wartość prozdrowotną mieszanek i pieczywa żytnio-gryczanego.

Materiał i metody. Materiał badawczy stanowiła mąka żytnia typ 580 oraz mąka, śruta i otręby gryczane, które otrzymano w wyniku przemiału kaszy gryczanej nieprażonej. Produkty gryczane dodawano do mąki żytniej w ilości 20 i 35%. Próbkę kontrolną stanowiła mąka żytnia typ 580. W mieszkankach żytnio-gryczanych i wypieczonym z nich pieczywie oznaczono zawartość wybranych flawonoidów metodą HPLC, polifenoli ogółem metodą Folina-Ciocalteu, oraz oznaczono aktywność przeciwutleniającą z wykorzystaniem rodników 1,1-difenyl-2-pikrylohydrazylowych (DPPH[•]).

Wyniki. Wykazano, że otręby gryczane były znacznie bogatsze w polifenole ogółem, rutynę, kwercetynę, orientynę i izoorientynę niż inne produkty gryczane i mąka żytnia. Po obróbce cieplnej, jaką jest wypiek, chleb zawierał więcej polifenoli

This work was financed by the National Science Centre within the research project No. NN312 425140, Poland.

***Corresponding author:** Dagmara Orzeł, Department of Human Nutrition, Wrocław University of Environmental and Life Sciences, The Faculty of Food Science, J. Chelmońskiego street 37/41, 51-630 Wrocław, Poland, phone; +48 713207726, fax. +48 713207744, e-mail: dagmara.orzel@up.wroc.pl

ogółem i kwercetyny oraz miał większą siłę gaszenia rodników DPPH niż mieszanki, z których go wypieczono. Proces wypieku niekorzystnie wpływał na ilość rutyny, orientyny i izoorientyny.

Wnioski. Zastosowanie otrąb gryczanych, jako zamiennika mąki żytniej w pieczywie znacznie zwiększa jego walory żywieniowe. Proces wypieku wpływa niejednakowo na zawartość poszczególnych grup związków przeciwutleniających.

Słowa kluczowe: przeciwutleniacze, gryka, flawonoidy, rutyna, kwercetyna, polifeole

INTRODUCTION

Traditional production of rye bread is based on sourdough. Sourdough rye bread, especially wholegrain, has a very beneficial effect on the human body, mainly due to the content of components with antioxidant properties [2]. Rye is a valuable source of dietary fiber and bioactive compounds such as alkylresorcinols present in bran, phenolic acids, phytosterols, tocopherols and folic acid. Fermented foods are one third of the world's food. Fermentation makes changes in the appearance, texture, taste, aroma and nutritional value; it also extends the shelf life of food products [5]. During the fermentation, lactic acid bacteria and yeast give the bread characteristic flavor and aroma. This is possible because of the indigenous microflora of rye flour [10].

Buckwheat is a pseudocereal characterized by unique nutritional properties, it is rich in vitamins, minerals and polyphenols, including flavonoids, flavones and phenolic acids [7]. The high content of flavonoids in diet reduces the risk of cancer and heart disease. The main flavonoid identified in buckwheat is rutin, wherein the amount ranges from 4 to 6% [11]. Other compounds with antioxidant properties found in buckwheat are quercetin, kaempferol, tocopherols [16]. The content of biologically active ingredients indicates that buckwheat has a positive impact on health of the human body. Some varieties of buckwheat have higher content of flavonoids than other cereals, fruits and vegetables, or even tea. Among the vitamins contained in buckwheat are thiamine, riboflavin, niacin, folate and pantothenic acid and antioxidant vitamins: vitamin E and small amount of β -carotene. Buckwheat is also a good source of minerals, contains zinc, copper, iron, potassium, phosphorus, manganese and rare elements such as bromine, cobalt and platinum and large amounts of magnesium (21-63 mg/100 g) [18]. Characteristics of buckwheat prove its unique properties; its compounds positively affect the functioning of the human body.

The aim of the study was to evaluate the effect of the addition of buckwheat products: flour, wholegrain flour and bran on the nutritional value of rye-buckwheat bread. Moreover, the impact of the fermentation and baking processes on the content of antioxidants and antioxidant activity of rye-buckwheat bread was determined

MATERIAL AND METHODS

The research material consisted of :

- Rye flour type 580 (mill Diamant Stradunia Ltd.)
- Blend of commercial buckwheat groats

Samples preparation

Buckwheat flour and bran were obtained by grinding the buckwheat groats in Quadrumat Junior mill. Buckwheat flour yield was 45%. Bran was also ground in a *Hagberg-Perten* mill to obtain smaller particles. Buckwheat wholegrain flour was obtained as a result of milling buckwheat groats in *Hagberg-Perten* mill. The levels of substitution of buckwheat products (flour, bran and wholegrain flour) in blends with rye flour were 20% and 35%. The control sample was rye flour.

Rye and rye-buckwheat bread samples were prepared. Doughs were prepared in a Brabender farinograph mixer in single-phase method using dry rye sourdough as leavening agent (Spring R-10, Millbo, Poland). Rye flour or rye-buckwheat blend (of 14% moisture content) and additives: yeast (1%), salt (1,5%) and dry rye sourdough (3%) were mixed with tap water at 30°C in an amount necessary to obtain a dough consistency of 200 FU. Dough pieces were placed in forms with oil and fermented in a fermentation cabinet KL 864 (TecnoekaSrl) for 1.5 hours (30°C, 85% RH). Later on the dough was shortly kneaded and left for proofing (about 50-60 minutes). Dough pieces were baked in a laboratory oven (Brabender OHG) at 260°C for 35 minutes. After cooling, bread pieces were lyophilized and milled.

Antioxidant activity assay and HPLC analysis of phenolic compounds

A milled sample (4.0 g) of material (blend or bread) was mixed with 20 mL of 80% methanol, sonicated (15 min), left for 24 hours and sonicated (15 min) again and centrifuged (10000 rpm). This solution was directly injected into the HPLC after being filtered through a 0.45 μ m membrane (Millipore).

Phenolic compounds was determined using Dionex (Germany) HPLC system equipped with diode array detector model Ultimate 3000, a quaternary pump LPG-3400A, autosampler EWPS-3000SI, and thermostated column compartment TCC-3000SD and controlled by Chromeleon v.6.8 software. The reversed phase Cadenza 5CD-C18 (75 mm \times 4.6 i.d.) column

(Imtakt, Kyoto, Japan) with guard column Cadenza (5 × 4.6 i.d.) guard column (Imtakt, Kyoto, Japan) was used. The compounds were separated with gradient elution using 4.5% aqueous formic acid (A) and acetonitrile (B) as eluents. The elution system was as follows: 0 min 5% B; 0–20 min, linear gradient 5–20% B; 20–21 min 100% B, 21–26 min 100% B, 27 min 5% B, 30 min 5% B [19]. Flavonoids were monitored at 360 nm, hydroxycinnamic acids at 320 nm and hydroxybenzoic acids at 280 nm. The results were calculated as mg of quercetin, isovitexin, rutin or orientin/isoorientin in 100 g (for flavonols), as mg of (+)catechin in 100 g (for flavanols) or as mg ferulic acid in 100 g (for phenolic acids).

Free-radical scavenging activity of 1,1-diphenyl-2-picrylhydrazyl (DPPH, Sigma, Poznan, Poland) was measured spectrophotometrically according to the method described by Yen and Chen [20]. The results of this study were expressed as mM Trolox Equivalents per 100 g of (mM TE/ 100 g dw) by reference to a standard curve. All determinations were performed in triplicate. Measurements were made using a Shimadzu UV-2401 UV–VIS spectrophotometer. Total polyphenols were determined by the Folin-Ciocalteu method [14]. The results were calculated as mg of gallic acid in 100 g (mg GA/100 g of dw). All determinations were performed in

duplicate. Measurements were made using a Shimadzu UV-2401 UV–VIS spectrophotometer. All determinations were performed in duplicate.

Statistical analysis

The results were statistically analyzed with Statistica 10.0 software package (StatSoft, Tulsa, USA). Three-way ANOVA at $p = 0.95$ was calculated and homogeneous groups according to *Duncan* test were estimated.

RESULTS

Kind and amount of buckwheat fraction used as well as the breadmaking process significantly affected antioxidant activity of the products. Buckwheat bran was characterized by a significantly higher amount of total polyphenols (323.2 mg/100 g dw) and scavenging effect on DPPH[·] radical (1282.4 μmol TE/100 g) than buckwheat flour (respectively 34.3 mg/100 g dw and 82.1 μmol TE/100 g dw) and rye flour (respectively 23.7 and 17.5 mg/100 g dw μmol TE/100 g dw) (Table 1). This fraction also contained much more flavonoids such as quercetin, rutin, orientin and isoorientin than flours.

Table 1. Antioxidants content and antioxidant capacity value of DPPH[·] of rye flour and buckwheat products

Product	Total polyphenols [mg/100 g dw]	DPPH [·] [μmol TE/100 g dw]	Quercetin [mg/100 g dw]	Rutin [mg/100 g dw]	Orientin+ Isoorientin [mg/100 g dw]
Rye flour type 580	23.7	17.5	0.09	0.20	0.13
Buckwheat flour	34.3	82.1	0.00	1.54	0.03
Buckwheat whole meal	188.9	275.0	0.07	17.19	0.17
Buckwheat bran	323.2	1282.4	0.19	34.16	0.35

Table 2. The average content of selected antioxidants and antioxidant capacity value DPPH[·] depending on factors

Factor	Feature	Total polyphenols [mg/100 g dw]	DPPH [·] [μmol TE/100 g dw]	Quercetin [mg/100 g dw]	Rutin [mg/100 g dw]	Orientin+ Isoorientin [mg/100 g dw]
Material	Blend	60.2 b	118.8 b	0.07 b	3.85 a	0.12 a
	Bread	63.4 a	131.5 a	0.31 a	1.46 b	0.09 b
	Flour	34.3 c	53.8 c	0.10 c	0.24 c	0.09 c
Buckwheat fraction	Wholemeal	56.2 b	124.1 b	0.17 b	2.40 b	0.10 b
	Bran	95.3 a	197.5 a	0.31 a	5.33 a	0.13 a
	0%	31.3 c	40.6 c	0.10 c	0.17 c	0.10 b
Level of substitution	20%	64.6 b	146.6 b	0.19 b	3.01 b	0.10 b
	35%	90.1 a	188.2 a	0.28 a	4.80 a	0.11 a

a, b, c – homogenous groups according to *Duncan's* test at $p = 0.95$

Table 3. The average content of selected antioxidants and antioxidant capacity value of DPPH[•] - interaction of the test material with buckwheat fraction type

Feature	Total polyphenols [mg/100 g dw]			DPPH [•] [μmol TE/100 g dw]			Rutin [mg/100 g dw]		
	Flour	Wholemeal	Bran	Flour	Wholemeal	Bran	Flour	Wholemeal	Bran
Buckwheat fraction	29.5 b	52.3 a	96.8 a	30.8 b	124.6 a	200.9 a	0.34 a	3.49 a	7.73 a
Blend									
Bread	39.1 a	58.0 a	93.8 a	76.9 a	123.5 a	194.1 b	0.14 a	1.30 b	2.93 b

a, b, c – homogenous groups according to *Duncan's* test at $p = 0.95$

Table 4. The average content of selected antioxidants and antioxidant capacity value of DPPH[•] - interaction of the test material with buckwheat fraction level of substitution

Feature	Total polyphenols [mg/100 g dw]			DPPH [•] [μmol TE/100 g dw]			Rutin [mg/100 g dw]		
	0%	20%	35%	0%	20%	35%	0%	20%	35%
Level of substitution									
Blend	26.8 b	62.8 a	89.1 a	19.8 b	147.0 a	189.5 a	0.20 a	4.29 a	7.07 a
Bread	35.5 a	66.3 a	91.0 a	61.4 a	146.3 a	186.9 a	0.13 a	1.72 b	2.52 b

a, b, c – homogenous groups according to *Duncan's* test at $p = 0.95$

Table 5. The average content of selected antioxidants and antioxidant capacity value of DPPH[•] - interaction of buckwheat fraction type and its level of substitution

Feature	Total polyphenols [mg/100 g dw]			Quercetin [mg/100 g dw]			Rutin [mg/100 g dw]			Orientin+ Isoorientin [mg/100 g dw]		
	Flour	Wholemeal	Bran	Flour	Wholemeal	Bran	Flour	Wholemeal	Bran	Flour	Wholemeal	Bran
Level of substitution												
0%	31.1 b	31.1 c	31.1 c	0.10 a	0.10 c	0.10 c	0.17 a	0.17 c	0.17 c	0.11 a	0.11 a	0.11 c
20%	31.7 b	57.9 b	104.2 b	0.11 a	0.17 b	0.30 b	0.26 a	2.45 b	6.31 b	0.09 b	0.10 a	0.12 b
35%	40.1 a	79.4 a	150.9 a	0.10 a	0.24 a	0.51 a	0.28 a	4.58 a	9.52 a	0.07 c	0.11 a	0.15 a

a, b, c – homogenous groups according to *Duncan's* test at $p = 0.95$

No presence of vitexin and trace amounts of isovitexin were detected in tested

Breads contained more polyphenols (63.6 mg/100 g dw) than mixtures from which they were produced (60.2 mg/100 g dw) (Table 2). Blends and breads with buckwheat bran share contained the highest amount of polyphenols (95.3 mg/100 g dw), while the least those with the addition of buckwheat flour (34.3 mg/100 g dw). The increase in buckwheat fraction share caused an increase in polyphenols content. In materials with 35% of buckwheat products share polyphenol content reached 90.1 mg/100 g dw, and without the buckwheat addition 31.3 mg/100 g dw. Breads with buckwheat flour contained more polyphenols than the corresponding blends (Table 3). Bread and blends with buckwheat wholegrain and bran had a comparable amount of polyphenols. Rye bread contained more polyphenols (35.5 mg/100 g dw) than rye flour (26.8 mg/100 g dw) (Table 4). Blends and breads containing 20 and 35% of the buckwheat products had a similar amount of polyphenols. Samples with 35% share of buckwheat flour had higher content of polyphenols (40.1 mg/100 g dw)

than those with 0% and 20% share of buckwheat flour (respectively 31.1 and 31.7 mg/100 g dw) (Table 5). The increasing share of buckwheat wholegrain and bran in blends and breads positively affected the polyphenols content.

In present study breads had higher antioxidant capacity (131.5 μmol TE/100 g dw) defined as ability to scavenge DPPH[•] radicals than blend from which they were obtained (118.8 μmol TE/100 g dw) (Table 2). Among the analyzed fractions of buckwheat bran had the greatest ability to react with DPPH[•] radical (197.5 μmol TE/100 g dw), while the smallest buckwheat flour (53.8 μmol TE/100 g dw) (Table 1). Along with the amount of buckwheat products in blends the ability to reduce DPPH[•] radical increased. Breads with the addition of buckwheat flour were characterized by a greater reduction of DPPH[•] ability than corresponding mixtures (Table 3). Samples containing buckwheat bran showed an inverse relation, the mixture had a higher DPPH[•] radical scavenging capacity than bread. Blends and bread with buckwheat wholegrain had similar antioxidant capacity. Rye bread was characterized by higher

DPPH[•] scavenging activity (61.4 μ mol TE/100 g dw) than rye flour (19.8 μ mol TE/100 g dw) (Table 4). With 20 and 35% buckwheat products level of substitution this ability was on the same level for blends and bread.

Quercetin content was higher in breads (0.31 mg/100 g dw) than in the corresponding flour blends (0.07 mg/100 g dw) (Table 2). The content of rutin, orientin and isoorientin was lower in breads (1.46 and 0.09 mg/100 g dw) than in the blends (3.85 and 0.12 mg/100 g dw). The highest amount of these components contained samples with bran and the lowest with buckwheat flour. Quercetin and rutin quantity in blends increased with the amount of buckwheat fraction level of substitution. Isoorientin and orientin content increased slightly with 35% buckwheat products share. Bread and blend with buckwheat flour contained a similar amount of rutin (Table 3), while breads with buckwheat wholegrain and bran had less rutin than the corresponding blends. Rye bread had the same rutin content (0.13 mg/100 g dw) as rye flour (0.20 mg/100 g dw) (Table 4). In samples with 20 and 35% of buckwheat fraction, breads had lower levels of rutin (respectively 1.72 and 2.52 mg/100 g dw) than the corresponding blends (respectively 4.29 and 7.07 mg/100 g dw). Rutin quantity increased with the increasing wholegrain and bran substitution level in the samples. There were no changes in the amounts of this flavonoid with the increasing share of buckwheat flour. Orientin and isoorientin content decreased with increasing buckwheat flour share (from 0.11 to 0.07 mg/100 g dw). A higher share of buckwheat bran affected an increase in this flavonoid quantity (from 0.10 to 0.15 mg/100 g dw). Different quantity of buckwheat wholegrain in samples had no influence on this component content. Different share of buckwheat flour did not result in different quercetin quantity (0.10 to 0.11 mg/100 g dw). However, increasing buckwheat wholegrain and bran share resulted in an increased amount of quercetin. This flavonoid was present in similar amounts in blends with different buckwheat fractions (Table 6). The highest content of quercetin had bread with buckwheat bran (0.53 mg/100 g dw) and the least

with buckwheat flour (0.14 mg/100 g dw). With the increase in buckwheat products share the quantity of quercetin slightly decreased in blends and increased in breads.

DISCUSSION

Antioxidants are substances which significantly delay or inhibit the oxidation reaction, being at many times lower concentration than oxidizing agents. Providing proper supply of these compounds in the diet reduced the risk of diabetes, obesity, coronary heart disease, and even tumors [4]. Polyphenols content in materials as well as their activity depends on the plant species, cultivars, as well as the state of maturity and changes during the technological processing. It was found that the predominant phenolic acid in rye grain is ferulic [17]. Buckwheat groats contain several components having specific properties of biological activity. Their content and composition are dependent on a variety of buckwheat and environmental conditions during growth. Six flavonoids were isolated from buckwheat kernels: rutin, quercetin, orientin, vitexin, isovitexin and isoorientin. Most of which are rutin [18]. To allow comparison of test results obtained by different methods, antioxidant capacity is expressed as the synthetic water soluble tocopherol - Trolox, usually in micromoles Trolox per 100 g dry weight of the sample. These methods include 1,1-diphenyl-2-picrylhydrazyl radical (DPPH), 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid radical cation (ABTS) or ferric reducing antioxidant power (FRAP).

The total concentration of phenolic acids in the whole rye grain is assessed at 65-300 mg/100 g dw [2]. The total polyphenol content of the tested rye flour was mg/100g 26.8 dw. *Lin et al.* [8] showed that the addition of buckwheat flour for wheat bread resulted in increased antioxidant properties, which was confirmed in this study on rye bread - the addition of buckwheat products, both to blends and the loaves, contributed to the increase in polyphenols content and total antioxidant capacity. Tested blends and breads with buckwheat bran had much more polyphenols including flavonoids than those with the addition of flour or wholegrain, it resulted the greater antioxidant activity of buckwheat bran among the other buckwheat fractions.

Chłopicka et al. [3] studied wheat bread with 15% and 30% share of pseudocereal flours (buckwheat, amaranth and quinoa). The addition of buckwheat flour to wheat bread, particularly at higher levels of substitution, caused significant increase of the antioxidant activity (DPPH[•] and FRAP), compared to other flours used. Total antioxidant activity was higher in bread with 30% buckwheat flour than in the ones with

Table 6. The average content of quercetin [mg/100 g dw] – interaction of the test material with buckwheat fraction type and its level of substitution

Factor		Blend	Bread
Buckwheat fraction	Flour	0.07 a	0.14 c
	Wholemeal	0.07 a	0.27 b
	Bran	0.08 a	0.53 a
Level of substitution	0%	0.09 a	0.12 c
	20%	0.07 a b	0.32 b
	35%	0.06 b	0.51 a

a, b, c – homogenous groups according to *Duncan's* test at $p=0.95$

15% of buckwheat flour. This study showed that the content of total polyphenols, selected flavonoids and DPPH[·] radical scavenging effect increased with the share of buckwheat wholegrain and bran in rye-buckwheat blends and breads. Due to the lower content of quercetin, orientin and isoorientin in buckwheat flour than rye flour, its addition did not favorably affect the amount of these compounds in the samples with a higher proportion of buckwheat flour.

It is known that the heat treatment causes chemical changes in food products such as flavonoids degradation and reducing the antioxidant capacity of ABTS and DPPH[·] [1]. *Stempińska* et al. [15] observed a significant reduction in the antioxidant capacity (ABTS and DPPH[·] radicals analysis) of the buckwheat grains after heat treatment compared to buckwheat before the thermal process. *Sensoy* et al. [13] studied the effect of different thermal methods, including roasting at 200 °C for 10 minutes on the antioxidant activity of buckwheat flour and the amount of polyphenols and found that this treatment significantly reduced the DPPH[·] radical scavenging effect and the amount of polyphenols showed a slight decrease compared with the amount of flavonoids. The author suggested that the significant decrease in antioxidant activity can be related to the interactions that occur between proteins and flavonoids, which can mask some oxidative activity. Own study showed that after the process of fermentation and baking flavonoids such as rutin, orientin and izoorientin content decreased but there was also an increase in the antioxidant capacity of DPPH[·] (from 118.8 to 131.5 μmol TE/100 g dw), the amount of quercetin and total polyphenols. Higher antioxidant potential may be related to higher availability of certain antioxidants by enzymatic hydrolysis of the cell walls during the fermentation of the dough [6].

Heat treatment of cereals, such as baking, can also cause the synthesis of substances having antioxidant properties, such as certain *Maillard* reaction products in the crust of bread [12]. *Zhang* et al. [21] demonstrated that heat treatment of the buckwheat did not affect any change in total amount of polyphenols due to the formation of *Maillard* products. *Nicoli* et al. [9] found that heat-treated vegetables have increased their antioxidant capacity. The increase their antiradical activity with increasing temperature and time of treatment also justified *Maillard* reactions. *Zielinski* et al. [22] reported that processing of the grain can release phenolic acids and other compounds from the cell walls, which leads to a higher antioxidant capacity. Present study shown that in mixtures with different share of buckwheat fractions the amount of quercetin is similar, however in bread with an increasing share of buckwheat the selected flavonoid content increased. This may be related to the release of quercetin from the cell wall decomposition during the dough fermentation.

Rye-buckwheat bread should be popularized, due to its enrichment nutritionally valuable, classified as a functional food. It can contribute both to diversify the diet and above all to improve the health of society.

CONCLUSIONS

Buckwheat bran was significantly richer in total polyphenols, rutin, quercetin, orientin and isoorientin than other buckwheat fractions of and rye flour. The use of this product as a substitute for rye flour in breadmaking has significantly increased its nutritional value.

After baking breads contained a similar amount of total polyphenols and more quercetin than mixtures from which they were made. Blends and breads were also characterized by comparable DPPH[·] radical scavenging activity.

Bread after baking contained more total polyphenols, quercetin and have a greater ability to scavenge DPPH[·] radicals than the corresponding blends. The process of baking negatively affected the amount of rutin orientin and isoorientin.

Acknowledgments

This study was supported by the National Science Centre (Poland) within the research project No. N N312 425140.

Conflict of interest.

The authors declare no conflict of interest.

REFERENCES

1. *Blaszczak W, Zielińska D, Zieliński H, Szawara-Nowak D, Fornal J.*: Antioxidant properties and rutin content of high pressure-treated raw and roasted buckwheat groats. *Food Bioprocess Technol* 2013; 6: 92-100.
2. *Bondia-Pons I, Aura AM, Vuorela S, Kolehmäinen M, Mykkänen H, Poutanen K.*: Rye phenolics in nutrition and health. *J Cereal Sci* 2009; 49: 323 – 336.
3. *Chłopicka J, Pasko P, Gorinstein S, Jedryas A, Zagrodzki P.*: Total phenolic and total flavonoid content, antioxidant activity and sensory evaluation of pseudocereal breads. *Food Sci Technol* 2012; 46: 548 – 555.
4. *Chu KO, Chan KP, Wang CC.*: Green tea catechins and their oxidative protection in the rat eye. *J Agr Food Chem* 2010; 58: 1523-1534.
5. *Esteller MS, Lannes SCS.*: Production and characterization of sponge – dough bread using scalded rye. *J Texture Stud* 2008; 39: 56 – 67.
6. *Grajek W.*: Changes in the antioxidant potential of plant materials in processing and digestion. *Food. Science. Technology. Quality* 2003; 4: 26-35 (in Polish).

7. *Li S, Zhang QH*: Advances in the development of functional foods from buckwheat. *Crit Rev Food Sci Nutr* 2001; 41(6): 451 – 464.
8. *Lin Y, Liu HM, Yu YW, Lin SD, Mau JL*: Quality and antioxidant property of buckwheat enhanced wheat bread. *Food Chem* 2009; 112: 987 – 991.
9. *Nicoli MC, Anese M, Parpinel M*: Influence of processing on the antioxidant properties of fruit and vegetables. *Trends Food Sci Tech* 1999; 10: 94-100.
10. *Ostasiewicz A, Ceglińska A, Skowronek S*: The quality of rye bread with the addition of sourdough. *Food. Science. Technology. Quality* 2009; 2 (63): 67 – 74 (in Polish).
11. *Panda R, Taylor SL, Goodman RE*: Development of a Sandwich Enzyme-Linked Immunosorbent Assay (ELISA) for Detection of Buckwheat Residues in Food. *J Food Sci* 2010; 6: 110 – 117.
12. *Sakač M, Torbica A, Sedej I, Hadnađev M*: Influence of breadmaking on antioxidant capacity of gluten free breads based on rice and buckwheat flours. *Food Res Int* 2011; 44: 2806 – 2813.
13. *Sensoy I, Rosen RT, Ho ChT, Karwe MV*: Effect of processing on buckwheat phenolics and antioxidant activity. *Food Chem* 2006; 99: 11-12.
14. *Slinkard K, Singleton VL*: Total phenol analyses: automation and comparison with manual methods. *Am J Enol Viticult* 1977; 28: 49-55.
15. *Stempińska K, Soral-Śmietana M, Zieliński H, Michalska A*: Effect of heat treatment on the chemical composition and antioxidant properties of buckwheat kernels. *Food. Science. Technology. Quality* 2007; 5 (54): 66 – 76 (in Polish).
16. *Tian Q, Li D, Patil BS*: Identification and determination of flavonoids in buckwheat (*Fagopyrum esculentum* Moench, Polygonaceae) by high-performance liquid chromatography with electrospray ionization mass spectrometry and photodiode array ultraviolet detection. *Phytochem Analysis* 2002; 13: 251-256.
17. *Weider S, Amarowicz R, Karamać M, Frączek E*: Changes in endogenous phenolic acids during development of *Secale cereale* caryopses and after dehydration treatment of unripe rye. *Plant Physiol Bioch* 2000; 38: 595-602.
18. *Wijngaard HH, Arendt EK*: Buckwheat. *Cereal Chem* 2006; 83(4): 391-401.
19. *Wojnicz D, Sycz Z, Walkowski S, Gabrielska J, Włoch A, Kucharska A, Sokół-Lętowska A, Hendrich AB*: Study on the influence of cranberry extract Żuravit S·O·S® on the properties of uropathogenic *Escherichia coli* strains, their ability to form biofilm and its antioxidant properties. *Phytomedicine: international journal of phytotherapy and phytopharmacology* 2012; 19(6): 506-514.
20. *Yen GC, Chen HY*: Antioxidant activity of various tea extracts in relation to their antimutagenicity. *J Agric Food Chem* 1995; 43: 27 – 32.
21. *Zhang M, Chen H, Li J, Pei Y, Liang Y*: Antioxidant properties of tartary buckwheat extracts as affected by different thermal processing methods. *Food Sci Technol* 2010; 43: 181-185.
22. *Zieliński H, Kozłowska H, Lewczuk B*: Bioactive compounds in the cereal grains before and after hydrothermal processing. *Innov Food Sci Emerg Technol* 2001; 2: 159 – 169.

Received: 09.09.2014

Accepted: 12.02.2015

