

Antioxidant activity in different morphological fractions of some cereal grains

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Abstract

*The purpose of this study was to examine the antioxidant properties of 70% ethanolic extracts of cereal grains and their different morphological fractions. Wheat (*Triticum durum* L.), barley (*Hordeum vulgare* L.), rye (*Secale cereale* L.), and buckwheat (*Fagopyrum esculentum*) were used. The total phenolic content (TPC), determined by the Folin-Ciocalteu method and antioxidant activities (AOA) were assessed using 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging capacity, ferric ion-reducing antioxidant power (FRAP) and thiobarbituric acid (TBA) methods. The following hierarchy of antioxidant activity was provided for 70% ethanolic extracts originated from whole grain: buckwheat > barley > wheat > rye. In respect to hulls, the antioxidant hierarchy was the same. The outer layers of grains had higher amount of phenolic compounds and subsequently higher antioxidant activity. Buckwheat had the highest amount of total phenolics, with the highest DPPH radical scavenging activity and capacity for Fe³⁺ reduction, but it had the lowest lipid peroxidation inhibition ability.*

Key words: Antioxidant activity, total phenolic compounds, cereal grain extracts, morphological fractions

1. INTRODUCTION

Food antioxidants might play a significant role as physiological and dietary antioxidants, thereby augmenting the body's natural resistance to oxidative damage. It has been suggested that antioxidants may contribute to the health benefits of cereal-based foods by reducing the incidence of aging-related chronic diseases including heart diseases and some types of cancer.

Significant levels of antioxidants have been detected in cereals and cereal-based products [1,2]. Cereals also contain a wide range of chemical classes with antioxidant activity [3]. Cereal grains are rich in phenolic acids. Whole-grain cereals are a major source of polyphenols, especially phenolic acids such as ferulic, vanillic, caffeic, syringic, sinapic and p-coumaric acids. All of them have potentially antioxidant properties due to the presence of an aromatic phenolic ring that can stabilize and delocalize the unpaired electron within its aromatic ring. Other phytochemicals occurring in cereals are phytosterines, saponins, and phytoestrogens. In cereals, flavonoids are present in small quantities.

Cereal products have significant antioxidant potentials in vitro. Miller et al, [4], used the DPPH assay to show that the average antioxidant activity of cereals and cereal products is higher (between 1200 and 3500 mmol Trolox Equivalents (TE)/100 g of fresh product) than that of common fruit (mean: 1200 mmol TE/100 g) and vegetables (mean: 400 mmol TE/100 g), but lower than that of common berries (around 3880 mmol TE/100 g).

Antioxidant properties of wheat based cereal products have been investigated by several research groups and reviewed by Baublis et al (2000). Research reports have been presented about the antioxidant potential of wheat bran and wheat flour [5]. The antioxidant capacity of the wheat bran fraction was 8500 mmol TE/100 g and that of the germ fraction was 5000 mmol TE/100 g [4]. Wheat extracts also have shown potential antioxidant properties as wheat phenolics appear to serve as powerful antioxidants through radical scavenging and/or metal chelation [6]. Phenolics in wheat are acids derived from benzoic acid or cinnamic acid. It has also been reported that phenolic compounds are concentrated in the bran portion of cereal kernels and may contribute to the total antioxidant activities of wheat, suggesting wheat bran a potent source of antioxidants.

Barley is an excellent source of natural antioxidants either for food preservation, or for disease prevention. There is growing interest in barley products because of their high content of antioxidants such as benzoic and cinnamic acid derivatives, proanthocyanidins, quinines, flavonols, chalcones, flavones, flavanones, and amino phenolic compounds [7]. Barley contains substantial amounts of phenolic antioxidants that effectively scavenge peroxy, DPPH, and hydroxyl radicals, and effectively control oxidation of LDL cholesterol, thereby having a great potential in the development of nutraceuticals rich in antioxidants [8].

Rye is typically consumed in Scandinavian countries, especially as whole-grain rye bread. Ferulic acid is

the predominant hydroxycinnamic acid, and the concentrations of its free and bound forms range from 900 to 1170 mg/g dry matter [9].

Buckwheat is an alternative crop belonging to the *Polygonaceae* family and is usually grouped with cereals because of similarity in cultivation and utilization though it is not cereal grain. Buckwheat grains have been well known as a plant source of rutin, quercetin, kaempferol-3-rutinoside, and a trace quantity of a flavonol triglycoside [10]. Buckwheat contains more rutin than most of the other plants, which exhibits antioxidative, antihemorrhagic and blood vessel protecting properties [11,12].

It has been shown that several factors, namely grain variety, environmental and growing conditions or milling and refining process of grains, can influence the presence and distribution of phenolic compounds and the final antioxidant power of cereal products [1,3,13,14]. Outer layers of grain usually contain a greater amount of polyphenolic compounds, as expected from their protective function in the plants. The bran fraction has been reported to have more antioxidant activity than other fractions. The total flavonoid concentrations of buckwheat seed and hull are 18.8 and 74 mg/100 g flour, respectively [14]. Phenolic compounds in buckwheat have been reported to possess antioxidant activity and higher concentrations of these compounds are found in the outer layers of the grain containing bran [10,12].

In this study, the effect of milling on the antioxidant activity and phenolic composition of some cereal grains was studied using in vitro models.

2. MATERIALS AND METHODS

2.1. Materials

The cereal samples used in this study included buckwheat (*Fagopyrum esculentum*) manufactured by Organic Biopharm, China, and wheat (*Triticum durum*), rye (*Secale cereale*) and barley (*Hordeum vulgare*) manufactured by KLAS d.o.o., Sarajevo. The compounds 1,1-diphenyl-2-picrylhydrazyl (DPPH), thiobarbituric acid (TBA) and gallic acid were purchased from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany), Folin-Ciocalteu reagent was purchased from Merck & Co., Inc. (New York, USA), and all other chemicals and solvents were the highest commercial grades purchased from Lachema Ltd. (Brno, Czech Republic) and Fluka Chemie GmbH (Buchs, Switzerland), and used without additional purification.

2.2. Preparation of cereal extracts

Samples of whole grains, dehulled grains and hulls were grounded in mill Olovo (Bosnia and Hercegovina) and were obtained as flour. Samples were stored at -30 °C until extraction. Samples of each cereal fractions were prepared in triplicate.

The samples of cereal fractions (100 g each) were extracted with 70% (v/v) ethanol (700 ml) for 3 h on the magnetic paddle (Heidolph MR 3001, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany), and then centrifuged at 3060 g (4500 rpm) for 10 min using the SIGMA 2-16 Versatile Centrifuge (MBI, Dorval, Canada). Extracts residues were re-extracted and the extracts were combined. Before drying samples were concentrated using the Büchi rotavapor R 210/215 (Büchi Labortechnik AG, Flawil, Switzerland) (temperature 50 °C, pressure 50–150 mbar). Concentrated extracts were dried using the Büchi Mini Spray Dryer B-290 (Büchi Labortechnik AG, Flawil, Switzerland). Inlet temperature and pump were adjusted to 120–125 °C and 15–20%, respectively, leading outlet temperature of 60–63 °C. Dried samples were kept in hermetically sealed dishes in a freezer until further analysis.

2.3. Determination of total phenolics content

The content of total phenolics in extracts was determined by a modified Folin-Ciocalteu method [15]. Briefly, 100 µl with 10–200 µg of each dried extract were shaken for 1 min with 500 µl of Folin-Ciocalteu reagent and 6 ml of distilled water. After the mixture was shaken, 2 ml of 15% Na₂CO₃ were added and the mixture was shaken once again for 0.5 min. Finally, the solution was brought up to 10 ml by adding distilled water. After 2 h, the absorbance was read on the UV/visible spectrophotometer (Ultrospec 3300 pro, Amersham Bioscience, Sweden) at 750 nm (25 °C). The TPC was assessed by plotting the gallic acid calibration curve.

2.4. Determination of DPPH radical scavenging activity

Antioxidant activity of the ethanol extract was measured on the basis of scavenging activities of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical [16]. In a lab dishes containing 50 µl of test samples of various concentrations were added: 3.95 ml of methanol and 1 ml 0.2 mM of DPPH methanol solution. After 30 min of incubation in the dark at room temperature, the absorbance was measured against a blank (methanol) at 517 nm using the UV/visible spectrophotometer (Ultrospec 3300 pro, Amersham Bioscience, Sweden). Inhibition of DPPH radical was calculated as a percentage (%) using the formula:

$$\text{Percentage inhibition (\%)} = \{(A_{\text{control}} - A_{\text{sample}}) / A_{\text{control}}\} \times 100$$

where, A_{control} is the absorbance of the control reaction (containing all reagents except test compound), and A_{sample} is the absorbance of the test compound.

IC₅₀ values (concentration of sample required to scavenge 50% of free radicals) were calculated from the regression equation, prepared from the concentration of the samples and percentage inhibition of free radical formation (percentage inhibition DPPH was assayed). Synthetic antioxidant L-ascorbic acid was used as a positive control and all tests were carried out in triplicates.

2.5. FRAP method

In the FRAP method the yellow Fe^{3+} -TPTZ complex is reduced to the blue Fe^{2+} -TPTZ complex by electron-donating substances under acidic conditions. Any electron donating substance with a half reaction of lower redox potential than $\text{Fe}^{3+}/\text{Fe}^{2+}$ -TPTZ (2,4,6, tri[2-pyridyl]-s-triazine) will drive the reaction and the formation of the blue complex forward. To prepare the FRAP reagent, a mixture of 300 mmol/l acetate buffer pH 3.6 (containing 6.4 ml 2 mol/l sodium acetate solution and 93.6 ml 2 mol/l acetic acid solution diluted in a volumetric flask, 10 mmol/l TPTZ in 40 mmol/l HCl) and 20 mmol/l ferric chloride (10:1:1, v:v:v) was made. 150 μl of ethanol plant extract were mixed with 4.5 ml of FRAP reagent. The absorbance readings were started after 5 min and they were performed at 593 nm using the UV/visible spectrophotometer (Ultrospec 3300 pro, Amersham Bioscience, Sweden). The blank consisted of FRAP reagent. The final absorbance of each sample was compared with those obtained from the standard curve made from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The results were expressed in nmol Fe^{2+} /mg dried extracts [17].

2.6. Thiobarbituric acid test (TBA)

Thiobarbituric acid tests were performed to determine the TBA reactive substance (TBARS) from lipid peroxidation [18]. Lipid peroxidation was measured in the liposome rimifon Lipotech 10 (0.3 g lecithin/ml). The mixture contained 20 μl FeSO_4 (0.075 mol/l), 50 μl liposomes, 10 μl of test samples of various concentrations (1–10% w/v), 20 μl L-ascorbic acid (0.1 M) and 3.9 ml phosphate buffer pH 7.4 (containing 5 ml of 0.2 mol/l monopotassium phosphate solution and 3.91 ml of 0.2 mol/l sodium hydroxide solution diluted in a volumetric flask (20 ml)).

The mixture maintained at 37 °C for 1 h in thermostat and then mixed with 0.2 ml ethylenediaminetetraacetic acid (EDTA) (0.1 mol/l) and 1.5 ml TBA reagent (3 g thiobarbituric acid, 120 g trichloroacetic acid and 10.4 ml perchloric acid in 800 ml demineralised water). After heating at 100° C for 15 min, and centrifugation at 1107g (3000 rpm) for 10 min using the SIGMA 2-16 Versatile Centrifuge (MBI, Dorval, Canada), the absorbance of the supernatant was measured at 532 nm using the UV/visible spectrophotometer (Ultrospec 3300 pro, Amersham Bioscience, Sweden). Inhibition of lipid peroxidation was calculated as percentage (%) by the formula:

Percentage of inhibition (%) = $\{(A_{\text{control}} - A_{\text{sample}}) / A_{\text{control}}\} \times 100$
 where, A_{control} is the absorbance of the control reaction (containing all reagents and distilled water against test compound), and A_{sample} is the absorbance of the test compound).

3. RESULTS AND DISCUSSION

3.1. Total phenolics and antioxidant activities of whole grains

The antioxidant activities and total phenolics of extracts of whole grains are shown in Table 1. All plants showed a significant amount of total phenolics and effective antioxidant activities. Buckwheat had the highest amount of total phenolics, with the highest DPPH radical scavenging activity and capacity for Fe^{3+} reduction, but it had the lowest lipid peroxidation inhibition ability. These data suggest that it might be more critical, in delaying lipid peroxidation, to suppress the initiation of radical chain reaction than to terminate it by quenching or removing the radicals generated during propagation of the radical chain reaction [19]. Other plants had similar TPC or AOA.

3.1.1. Total phenolic content

It has been shown that several factors, namely grain variety, environmental and growing conditions or milling and refining process of grains, can influence the presence and distribution of phenolic compounds and the final antioxidant power of cereal products [3, 13, 14].

As shown in Table 1, total phenolic compound contents in the examined whole seed extracts were the highest in buckwheat, 50.7 mg GAE/g dry extract. Lower total phenolic compound contents were present in wheat and barley (16.2 and 16.4 mg GAE/g dry extract, respectively) and the lowest in rye 13.2 mg GAE/g dry extract.

An asymmetric distribution of antioxidative components through the cereal grains was evident. The concentration of phenolic constituents was greater in the outer layers of the grain. The data reported had shown that phenolic acids are predominantly found in the outer bran layer of a wheat grain [6,18].

As shown in a Table 1, the greatest source of phenolics is buckwheat hull (62.6 mg GAE/g dry extract). Other cereal brans have similar contents of phenolics (16.1-19.4 mg GAE/g dry extract). Content of total phenolics in examined cereal fractions of wheat, barley and rye were not very different. These results can be explained by the fact that the majority of phenolics in cereal grains are insoluble and bound by ester and ether linkages with polysaccharides, such as arabinoxylan and lignin, in the cell wall.

Covalently bound phenolic acids are concentrated in the cell walls of the various grain tissues especially the aleurone and the pericarp-seed coat where they are esterified to the arabinose side groups of arabinoxylans [19]. On the other hand, free and other soluble phenolics are mainly found in the aleurone layer and starchy endosperm of barley. The phenolic acids are mainly located in the outer layers of grain in free forms, which can be easily extracted using ethanol or methanol solutions. In contrast, the flavonoids existed in the buckwheat grain in the bound forms, which were

bound to cell wall materials and needed further treatments to extract. However, rutin, one of main flavonoid in buckwheat grain, existed mostly in the free phenolic extracts using ethanol solution. The results of this study show that the phenolic compounds in buckwheat existed primarily in free form contrary to other cereals investigated.

The solubility of individual phenolics varies and the results may not be representative of the true phenolic content of grain fractions. The data reported by Zhou and Yu [13] had shown that the contents of TP in wheat and barley grain were affected by the extraction solvents in the following descending order: acetone > ethanol > methanol, which can be used to explain lower amounts of phenols present in this plants (Table 1).

Besides, although the Folin–Ciocalteu method is widely used to determine total phenolic contents in botanical and biological samples, it has its own limitations. Other reducing agents, such as L-ascorbic acid and sulphur dioxide, may also react with the Folin–Ciocalteu reagent and contribute to total absorbance, which generally results in overestimated levels of total phenolic contents. In addition, individual phenolic compounds may have different reactivities toward the Folin–Ciocalteu reagent, which could result in potential errors in total phenolic content measurements [5].

3.1.2. DPPH radical scavenging activity

The DPPH radical has been widely used for assessment of radical scavenging activity because of the ease and convenience of the method. The scavenging effect of plant extracts using the highest sample concentra-

tion (200 µg/ml), as shown in Table 2, was weak for the wheat extract, with only 31% DPPH radical inhibition. In other investigations, wheat extracts also demonstrated weak activity in scavenging the DPPH radical at this sample concentration [5]. Stronger scavenging effects on the DPPH radical were found for barley and rye (36.6% and 45%, respectively) (Table 2). The results of this work, showing significant DPPH radical inhibition ability for barley, are consistent with data reported by others, apart from differences in data interpretations. Madhujith and Shahidi (2006) demonstrated that barley contained substantial amounts of phenolic antioxidants that effectively scavenged free radicals, especially peroxy, DPPH, and hydroxyl radicals [8]. The strongest scavenging effects on the DPPH radical were found for buckwheat extract (82.5%) (Table 2).

The DPPH radical scavenging effect observed in this work is in agreement with literature data [20].

No correlation existed between TPC and DPPH radical scavenging activity in cereals (Table 1). The cereals with higher TPC values were not necessarily better in DPPH inhibition. Ferulic acid, the main phenolic acid in cereal grains, showed a weak antiradical effect in experiments with the DPPH radical, which may explain the discrepancies. Generally, there are several explanations of the ambiguous relationship between the antioxidant activity and total phenolics. The first, total phenolic content did not include all antioxidants, such as ascorbic acid, carotenoids and tocopherols. The synergism between antioxidants in the mixture made the antioxidant activity not only dependent on antioxidant concentration but on the structure and interactions

Table 1. Total phenolics and antioxidant activities of whole grains and their milling fractions

Tabela 1. Sadržaj ukupnih fenola i antioksidativna aktivnost nekih žitarica i njihovih morfolokih frakcija

Sample name	Fraction	TPC ^A (mg GAE/g dried extract)	DPPH ^B (IC ₅₀) (µg/ml)	FRAP ^C (nm Fe ²⁺ /mg dried extract)	TBARS inhibition ^D (%)
Buckwheat (<i>Fagopyrum esculentum</i>)	<i>whole grain</i>	50.7	76.7	49.43	45.6
	<i>bran</i>	62.6	69.2	57.42	58.9
	<i>flour</i>	41.8	105.2	40.19	42.1
Barley (<i>Hordeum vulgare</i>)	<i>whole grain</i>	16.4	176.6	15.56	50.8
	<i>bran</i>	19.4	155.8	18.5	56.8
	<i>flour</i>	12.1	191.9	12.3	41.6
Wheat (<i>Triticum durum</i>)	<i>whole grain</i>	16.2	206	12.15	55.2
	<i>bran</i>	18.9	195.2	15.35	57.2
	<i>flour</i>	11.9	232	11.9	45.4
Rye (<i>Secale cereale</i>)	<i>whole grain</i>	13.2	243	8.94	57.6
	<i>bran</i>	16.1	169.6	12.13	59.8
	<i>flour</i>	10.6	256	7.98	55.2

A. Total phenolics content (TPC) by Folin–Ciocalteu method.

B. DPPH radical scavenging activity.

C. Ferric reducing ability of plasma (FRAP).

D. Thiobarbituric acid method (TBA).

Table 2. DPPH radical scavenging activity of whole grains and their milling fractions (%)

Tabela 2. Antioksidativna aktivnost nekih žitarica i njihovih morfoloških frakcija određena DPPH metodom

Sample name	Fractions	Inhibition of DPPH radical, (%)				
		Sample concentration, µg/ml				
		10	20	50	100	200
Buckwheat (<i>Fagopyrum esculentum</i>)	<i>whole grain</i>	11.6	21.	34.8	63.3	82.5
	<i>bran</i>	13.8	25.2	39.7	72.2	96.4
	<i>flour</i>	7.3	17.4	29.2	48.6	68.2
Barley (<i>Hordeum vulgare</i>)	<i>whole grain</i>	4.5	6.5	17.9	29.0	36.6
	<i>bran</i>	5.8	7.5	23.3	35.0	64.2
	<i>flour</i>	2.8	5.7	13.4	28.5	32.1
Wheat (<i>Triticum durum</i>)	<i>whole grain</i>	6.7	12.2	15.6	23.4	31.0
	<i>bran</i>	7.4	14.1	19.9	32.0	50.2
	<i>flour</i>	5.2	11.1	13.2	19.8	27.8
Rye (<i>Secale cereale</i>)	<i>whole grain</i>	10.6	18.9	25.8	32.7	45.0
	<i>bran</i>	12.2	23.8	28.7	38.6	59.1
	<i>flour</i>	7.2	16.9	19.4	26.3	30.2

among antioxidants as well. Different methods used for measuring antioxidant activity based on different mechanisms may lead to different observations.

DPPH radical scavenging activity of morphological fractions was decreased in the following order: buckwheat hull, barley hull, rye hull and wheat bran (Table 2). These findings were not quite in agreement with total phenolic compounds which not decreased in the same order.

The grain fractions of wheat (whole-grain, bran and flour) have different antioxidant capacities [6]. Wheat bran extracts contain several phenolic acids, including vanillic, p-coumaric and, largely, ferulic acid. These compounds, particularly ferulic acid, are not evenly distributed in the wheat; most are found in the bran [20]. Extract of wheat bran, having high concentration of phenolic acids, was shown to have stronger antioxidant activity than other fractions of wheat. The aleurone layer is therefore the fraction with the highest antioxidant activity, followed by the bran fraction and whole grain. Some of industrial processes have been developed to isolate the aleurone layer, and then to enrich cereal products with it [21].

The antioxidant capacity of barley and barley extracts has been particularly studied in the field of beer production, since most of the phenolics in beer are derived from barley malt. Unlike wheat and oat, there has been little research on the antioxidant potential of barley and its fractions. However, the total phenolic content of barley is significantly correlated with the antioxidant capacity, as measured by the DPPH and ABTS assays [22].

The antioxidant activity of rye extracts (whole-grain, bran and flour) is significantly correlated with the total content of monomeric and dimeric hydroxycinnamic acids, with rye bran having the greatest antioxidant capacity [9].

3.1.3. FRAP method

Ferric reducing antioxidant power (FRAP) of the examined cereals, as shown in Table 1, correlated with total phenolic content. The highest FRAP value, expressed in nmol of Fe²⁺/mg dry extract, was found in buckwheat (49.43 nmol Fe²⁺/mg dry extract), followed by lower FRAP in barley and wheat (15.56 and 12.15 nmol Fe²⁺/mg dry extract, respectively), and the lowest ferric reducing antioxidant ability was found to be in rye (8.94 nmol Fe²⁺/mg dry extract). Difficulty in the interpretation at comparison of data is even more obvious with the FRAP method. In our work, the results were expressed in nmol of Fe²⁺/mg dry extract, however other authors reported their results in nmol or mmol Fe²⁺ in mg or g of grains or flour [23]. Besides, extraction solvents and methods of sample preparation used in other studies were different, and both were shown to have influence on FRAP. It is interesting that rye, which had significant DPPH radical inhibitory activity, showed the lowest ferric-reducing power (Table 1). It appears that care should be taken when using free radicals as a basis for antioxidant activity tests because the measured antioxidant activity of a biological sample depends on the free radical or oxidant that is being used in assay.

Wheat bran has been reported to be able to inhibit lipid oxidation catalyzed by either iron or peroxy radicals [20]. Most recently, Zhou, and Yu [13] reported that wheat grain, bran and fractions had different antioxidant activities and total phenolic contents (TPC). Their study also showed that ferulic acid was a major contributor to the antioxidant activity. In a phosphatidylcholine liposome system, the percentage of liposome oxidation is reduced by increasing the concentration of isolated phenolic acids from whole-grain cereals [20].

The higher phenolic contents in the phenolics rich fractions exhibited the stronger antioxidant capacity than the phenolics less rich fraction. Ferulic acid and

rutin were the major antioxidant compounds of buckwheat and existed mostly in the outer layers of grain. As a result, the outer layers of buckwheat grains with higher amount of phenolic compounds along with higher amounts of protein, lipid, ash and dietary fiber are considered to be good materials for cereal-based food processing with significant health benefits [12,25,26].

3.1.4. Thiobarbituric acid test (TBA)

As shown in Table 1, there is a lack of correlation between TPC and the ability of lipid peroxidation inhibition in cereals. The cereals with higher TPC values were not necessarily better inhibitors of lipid peroxidation. An explanation of this may be in the complex mechanism of lipid peroxidation inhibition, which includes not only un-compounded phenols, but also high-molecular polyphenols and other nonphenolic antioxidants. According to results, rye had the greatest capacity for inhibition of lipid peroxidation of all cereals examined (57.6%), followed by wheat and barley (55.2% and 50.8%, respectively), while the weakest results in TBA tests were for buckwheat (45.6%) (Table 1). Besides, wheat extracts, for instance, demonstrated a high ability to inhibit lipid peroxidation in liposomes, but showed the lowest ability to directly react with and quench DPPH radical (Table 1). As already mentioned, these data may suggest that it might be more critical to suppress the initiation of radical chain reaction than to terminate it by removing the radicals generated during propagation of radical chain reaction [23,24].

4. CONCLUSIONS

This study indicates, as we shown in our previous studies (2,27) that cereals, used widely for human consumption, exhibit significant free radical scavenging activities, ferric-reducing power, capacity for inhibition of lipid peroxidation and total phenolic contents. Several significant differences were found among the cereals regarding these characteristics, which warrant further study, especially in terms of their effects on human health. Milling and refining process of grains can influence the presence and distribution of phenolic compounds and the final antioxidant power of cereal products. Processing of cereals may thus have a significant effect on their antioxidant activity. The concentration of grain antioxidants will be drastically reduced during the refining process. As phenolic compounds are found to be concentrated in the outermost layers, the bran fractions obtained as milling by-products may be used as a natural source of antioxidants and as a value-added product in the preparation of functional food ingredients and/or for enrichment of certain products.

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ANTIOKSIDATIVNA AKTIVNOST RAZLIČITIH MORFOLOŠKIH FRAKCIJA ZRNA NEKIH CEREALIJA

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Kratak sadržaj

*Cilj rada je bio da se ispita antioksidativna aktivnost etanolnog ekstrakta zrna cerealija i njihovih morfoloških frakcija. Ispitivani se: pšenica (*Triticum durum* L.), ječam (*Hordeum vulgare* L.), raž (*Secale cereale* L.) i heljda (*Fagopyrum esculentum*). Određivan je sadržaj ukupnih fenola (TPC) metodom po Folin-Ciocalteu i antioksidativna aktivnost (AOA) po tri najčešće korišćene metode: DPPH (sposobnost neutralizacije 2,2-difenil-1-pikrilhidrazil radikala), FRAP (antioksidativna sposobnost redukcije Fe III jona) i TBA (metoda sa tiobarbiturnom kiselinom). Antioksidativna aktivnost etanolnog ekstrakta celog zrna opada u sledećem nizu: heljda > ječam > pšenica > raž. Isti odnos je dobijen i za mekinje. Spoljni slojevi zrna imaju veći sadržaj polifenola, pa sledstveno tome i veću antioksidativnu aktivnost. Heljda sadrži najviše polifenola i ima najveću antioksidativnu aktivnost određenu DPPH i FRAP metodom, ali ima najmanju sposobnost inhibicije lipidne peroksidacije.*

Gljučne reči: antioksidativna aktivnost, ukupan sadržaj polifenola, ekstrakt zrna cerealija, morfološke frakcije

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