Food Chemistry 115 (2009) 982–988

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Effects of hull-less barley flour and flakes on bread nutritional composition and sensory properties

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ARTICLE INFO

Article history:
Received 1 September 2008
Received in revised form 5 November 2008
Accepted 9 January 2009

Keywords:
Bread
Hull-less barley
Composition
β-Glucans
Minerals
Selenium
Heavy elements
Intakes
Sensory properties

ABSTRACT

Barley is a desirable food ingredient, with health benefits provided by a β-glucan fibre fraction. A hull-less barley flour and flakes were incorporated into white and wholegrain wheat bread in quantities usually applied in practice. The breads were evaluated for nutritional composition and sensory properties and compared to standard products as controls. The supplemented breads were high in fibre, zinc and selenium content. It was estimated that a 300-gram daily portion of such breads could meet up to 40% of dietary recommended intakes for selenium and 70–75% of recommended daily values for β-glucan. Regarding sensory quality, the only significant differences ($p < 0.05$) were higher taste and lower volume in the white supplemented breads and lower crumb elasticity in the white bread made with barley flour. Hull-less barley can substantially contribute to an adequate intake of selenium and β-glucan. In addition, supplemented breads were not found to pose a significant risk, with regard to excessive intakes of heavy elements (Pb, Cd, As).

1. Introduction

In recent years, improving the nutritional profile of white wheat bread has been of much interest. This is usually realised by supplementing wheat flour with a number of flours of different origin that contribute to enhanced mineral, vitamin, protein or dietary fibre composition and content in the end product.

Although barley has been of little importance in the modern diet, when compared to other cereals, like wheat, rye and oats, recent evidence about considerable amounts of nutritionally important β-glucans found in barley has focused a lot of attention on the matter of designing new foods containing barley. β-Glucans are recognised as having important positive health impacts, centred on their benefits in coronary heart disease, cholesterol lowering and reducing the glycaemic response. Inclusion of barley flour in plain wheat bread formulation enhances the β-glucan content of bread, which may have a beneficial effect on human health. The Food and Drug Administration (FDA) concluded that β-glucan soluble fibre (3 g/day) from oat bran and rolled oats or wholegrain barley and dry milled barley products are efficacious in lowering total and LDL-cholesterol serum concentrations (Food and Drug Administration, 2003). Human clinical trials have shown that barley β-glucan gives on average 7–10% reductions in total and LDL-cholesterol in mildly and moderately hypercholesterolaemic persons, over a dose range of 3–8 g/day (Behall, Schofield, & Hallfrisch, 2004a,2004b; McIntosh, Whyte, McArthur, & Nestel, 1991).

The nutritional value of food supplemented with barley depends on the level of supplementation as well as on the type of barley used. Barley genotypes have been classified as hull-less and hulled. Hull-less cultivars have better nutritional value than hulled ones as they contain more proteins, lipids and soluble dietary fibres (Soares, De Francisco, Rayas-Duarte, & Soldi, 2007; Zhang, Junmei, & Jinxin, 2002). However, besides the advantages resulting from an increased content of nutrients, hull-less barley is at a potentially higher risk as a vehicle for some environmental pollutants, due to the absence of the husk that protects the kernel.

The maximum level of barley flour recommended by most authors for incorporation in yeast breads is 10% (flour basis) (Bhatty, 1986) although there are reports of successful incorporation of 20 and 26% of hull-less barley (Berglund, Fastnaught, & Holm, 1992; Swanson & Penfield, 1988). In general, substitution levels ranging from 15–20% are the most usual in practice (Bojat, Vukobratović, & Kiš, 1994).

In this report, we investigated how the incorporation of hull-less barley flour and flakes in white and wholegrain wheat bread

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doi:10.1016/j.foodchem.2009.01.028

affected the composition as well as the sensory properties of the products. Especially highlighted was the nutritional adequacy of the obtained products, with regards to the adequate intake of β-glucan and essential minerals including the risk estimation coming from potential exposure to heavy elements.

2. Materials and methods

2.1. Materials

Wholegrain flour and flakes originated from an experimental cultivar of hull-less barley Balša and were generously donated by the Centre for Agricultural and Technological Research (Zaječar, Serbia). The material was prepared from barley harvested in 2006.

Wholegrain barley flour was stone-milled. Barley flakes were prepared by a specific procedure which involved hydrotreatment of grains in lye, soaking in warm water (30 °C) for 1.5 h, draining and drying. Lye was prepared by leaching hard wood ash with previously shortly boiled water.

Commercial bread wheat flour was supplied from Žitko (Bačka Topola, Serbia). Vegetable fat, fresh compressed yeast and salt were purchased from a local store. Gluten and improver were from Puratos (Groot-Bijgaarden, Belgium).

2.2. Baking procedure

The formulations of breads are detailed in Table 1. The improver was dosed as recommended by the manufacturer. Breads were prepared in triplicate using a straight dough baking procedure. The ingredients were mixed in a high-speed Diosna mixer with low speed (85 rpm) for 1 min and high-speed (120 rpm) for 7 min. Barley flakes were soaked in lukewarm water (flake to water ratio, 1:2.5) for one hour prior to mixing. Dough was fermented for a period of 45 min at 30 °C, and then it was divided into 340 g portions, manually rounded, rolled and put into tin pans (24.5 × 9 × 6.5 cm). Final fermentation lasted 70 min for white breads and 60 min for wholegrain breads. The breads were baked at 230 °C in a deck type oven.

2.3. Bread quality assessment

The breads were evaluated 24 h after baking. Loaf volume was measured using a rapeseed displacement method. The following bread attributes were analysed: crumb elasticity, crumb grain structure, crumb grain uniformity, porosity according to Dallmann (1958), crust colour and flavour. Ranking scale for porosity according to Dallmann ranged from 1 (open grain structure) to 8 (close grain structure). Intensity of other parameters was determined on a rating scale which ranged from 1–5. In general, number one corresponded to the lowest intensity and number five to the highest intensity of the attribute. Terms which describe the intensity of the selected sensory attributes are given in detail in Škrbić and Filipčev (2008).

Crumb texture measurements were performed using a PNR6 SUR Berlin penetrometer with spherical probe (25 mm diameter).

2.4. Chemical analyses

The chemical composition was determined according to standard methods of analysis (AOAC, 2000). Starch content was determined according to ICC Standard No. 123/1 (1994).

The content of essential minerals and heavy elements was assessed by atomic absorption spectrophotometry according to a procedure described in detail in Škrbić and Čupić (2005).

The β-glucan content of samples was determined enzymatically by modification (McCleary & Codd, 1991; McCleary & Mugford, 1992; McCleary & Nurthen, 1986) of the method of McCleary and Glennie-Holmes (1985).

3. Results and discussion

3.1. Chemical composition

In general, breads supplemented with barley flour or flakes did not differ significantly in the content of fat and proteins, except for the wholegrain wheat bread made with barley flour which was the highest in the protein content (Table 2). The wholegrain bread samples had significantly lower starch content but significant variability within each bread group was not observed. Whereas the ash and crude fibre contents of breads increased significantly with the addition of barley ingredients as compared to the controls, the difference in these parameters was not significant within the supplemented breads. As a result of supplementation with barley flour and flakes, the content of β-glucans in the bread samples increased – in the case of white breads the β-glucan content increased approximately four-fold, whereas in the case of wholegrain bread's the increase was two-fold, as compared to the corresponding control. The barley ingredients also significantly increased the reducing sugar content in both bread groups.

In terms of Dietary Reference Intakes (DRIs) (NRC (National Research Council), 2001) of an adult male and female, an average daily portion of bread (300 g) would meet 53.6–59.2% and 64.9–72.0% of DRIs for proteins, respectively (Table 3). High intakes for carbohydrates were calculated for the group of white wheat breads (ranging from 118.8% to 127.6% of DRIs). In this group, barley ingredients slightly lower the intake of carbohydrates, when compared to the control. In the group of wholegrain breads, barley ingredients increase the intake of carbohydrates, as compared to the control. The wholegrain breads would provide lower intakes of carbohydrates in comparison to the group of white breads.

Table 1
Formulations of control and hull-less barley-supplemented breads.

Ingredients (g)	White breads			Wholegrain breads		
	Control	With hull-less barley flour	With hull-less barley flakes	Control	With hull-less barley flour	With hull-less barley flakes
White wheat flour, type 500	100	85	85	–	15	15
Wholegrain wheat flour	–	–	–	100	70	70
Barley flour	–	15	–	–	15	–
Barley flakes	–	–	15	–	–	15
Yeast	3	3	3	4	4	4
Gluten	2	2	2	4	4	4
Vegetable fat	2	2	2	2	2	2
Salt	2	2	2	2	2	2
Water	57.3	58.3	60.3	67.0	74.0	74.0

Table 2
Chemical composition of hull-less barley-supplemented breads.

	Bread samples	Protein (g/100 g dw)	Fat (g/100 g dw)	Starch (g/100 g dw)	Reducing sugar (g/100 g dw)	Ash (g/100 g dw)	Crude fibre (g/100 g dw)	β-glucan content (g/100 g dw)
White bread	Control	14.28 ± 0.40[a]	2.82 ± 1.64[a]	78.71 ± 1.54[a]	0.31 ± 0.04[a]	1.34 ± 0.10[a]	0.36 ± 0.03[a]	0.26 ± 0.04[a]
	Bread + hull-less barley flour	15.86 ± 1.04[a]	3.26 ± 1.03[a]	75.92 ± 1.04[a]	1.47 ± 0.00[b]	1.64 ± 0.01[b]	0.51 ± 0.03[b]	1.03 ± 0.08[c,d]
	Bread + hull-less barley flakes	15.12 ± 0.74[a]	3.07 ± 1.67[a]	76.98 ± 0.32[a]	1.29 ± 0.32[b]	1.76 ± 0.02[b]	0.71 ± 0.02[b]	0.90 ± 0.09[c]
Wholegrain bread	Control	15.7 ± 1.66[a]	3.43 ± 0.25[a]	66.47 ± 5.91[b]	0.48 ± 0.09[a]	1.92 ± 0.03[c]	1.32 ± 0.32[c]	0.50 ± 0.06[b]
	Bread + hull-less barley flour	16.88 ± 0.32[b]	3.70 ± 1.27[a]	65.70 ± 3.45[b]	1.10 ± 0.26[b]	2.09 ± 0.06[d]	2.23 ± 0.05[d]	1.15 ± 0.09[d]
	Bread + hull-less barley flakes	16.64 ± 0.22[a]	3.65 ± 1.18[a]	65.76 ± 2.48[b]	1.04 ± 0.35[b]	2.18 ± 0.03[d]	2.28 ± 0.03[d]	1.06 ± 0.07[c,d]

[a,b,c,d]Different superscripts in the same column indicate that means were significantly different ($p < 0.05$).

Table 3
Contribution of macronutrient intakes to the relevant DRIs consuming an average portion (300 g) of supplemented breads.

Macronutrient	Gender	DRIs (g/day)	Contribution to DRIs (%)*					
			White breads			Wholegrain breads		
			Control	With hull-less barley flour	With hull-less barley flakes	Control	With hull-less barley flour	With hull-less barley flakes
Proteins	Male	56	53.6	57.9	53.3	57.3	59.2	55.7
	Female	46	65.2	70.4	64.9	69.8	72.0	67.8
Carbohydrates	Adults	130	127.6	121.6	118.8	72.1	100.9	96.4
β-Glucan	Adults	3**	18.0	70.0	59.0	34.0	75.0	66.0

* Dietary Reference Intakes (DRIs) for males/females of 19–70 years of age set by the Food and Nutrition Board of the National Research Council.
** Value recommended by the FDA for recognised health benefits.

DRIs for β-glucan have not been set but, as mentioned above, FDA recommended a daily intake of 3 g barley β-glucan for recognised health benefits but only as a part of a diet low in saturated fats and cholesterol. A 300-gram portion of white or wholegrain bread made with barley flour can meet 70% or 75% of the level proposed by the FDA, respectively. Somewhat lower intakes are anticipated for the breads made with flakes – around 60% (Table 3).

3.2. Mineral composition

Mineral elements must be supplied from food because the body cannot synthesise them. It has been estimated that over 60% of world's population is iron deficient, over 30% is Zn deficient and about 15% is Se deficient (White & Broadley, 2007). Deficiencies of Ca, Mg and Cu are rare but could occur in certain population groups. The problems of dietary malnutrition are usually addressed through supplementation, food fortification or dietary diversification.

In the group of supplemented white wheat breads, the contents of selenium and zinc were significantly higher than those found in the control bread: the barley-supplemented breads had about 3 and 2 times higher contents of selenium and zinc, respectively (Table 4). The other investigated minerals in the supplemented breads were slightly higher as compared to the control, although statistically significant differences were not observed.

The group of wholegrain breads had significantly higher contents of minerals than white breads did. The addition of hull-less barley flour or flakes contributed to elevated content of selenium. A threefold increase was determined when compared to the control. The contents of iron, zinc, and copper did not significantly differ from those found in the control, whereas the contents of potassium, calcium and magnesium significantly decreased in the barley-supplemented breads.

Furthermore, considering the differences in the mineral contents within either the white or wholegrain type of supplemented breads, no significant differences were found between the corresponding breads made with barley flakes or barley flour.

According to data displayed in Table 5, a daily portion of barley-supplemented breads would meet approximately 40% of DRIs for selenium in both white and wholegrain types of bread. This observation is interesting because it suggests that hull-less barley products have great potential to become important natural sources of selenium easily available to the general population. Selenium is known to have an important protective role in the prevention and suppression of many disorders, like carcinomas, cardiovascular diseases, fibrosis, etc. It is even considered as an antioxidant and

Table 4
Mineral content of supplemented breads.

Bread samples		Mineral content							
		μg/100 g (dw)	mg/100 g (dw)			g/100 g (dw)			
		Se	Fe	Cu	Zn	K	Ca	Mg	P
White bread	Control	3.6 ± 0.02[a]	1.74 ± 0.19[a]	0.14 ± 0.03[a]	0.41 ± 0.17[a]	0.26 ± 0.02[a]	0.07 ± 0.00[a]	0.01 ± 0.00[a]	0.10 ± 0.01[a]
	Bread + hull-less barley flour	11.5 ± 0.03[d]	2.32 ± 0.29[a]	0.21 ± 0.03[a,b]	0.94 ± 0.11[b]	0.26 ± 0.02[a]	0.07 ± 0.00[a]	0.015 ± 0.00[a,b]	0.12 ± 0.01[a]
	Bread + hull-less barley flakes	11.4 ± 0.04[c,d]	2.19 ± 0.22[a]	0.20 ± 0.08[a,b]	0.90 ± 0.09[b]	0.27 ± 0.01[a]	0.08 ± 0.00[a]	0.03 ± 0.01[b]	0.13 ± 0.01[a]
Wholegrain bread	Control	3.8 ± 0.03[b]	4.75 ± 0.38[b]	0.35 ± 0.06[b]	2.00 ± 0.20[c]	0.69 ± 0.02[c]	0.13 ± 0.00[c]	0.09 ± 0.01[d]	0.29 ± 0.01[b,c]
	Bread + hull-less barley flour	11.3 ± 0.04[c]	4.35 ± 0.56[b]	0.34 ± 0.04[b]	2.02 ± 0.18[c]	0.57 ± 0.03[b]	0.11 ± 0.01[b]	0.06 ± 0.01[c]	0.26 ± 0.02[b]
	Bread + hull-less barley flakes	11.4 ± 0.04[c,d]	4.38 ± 0.41[b]	0.35 ± 0.08[b]	2.05 ± 0.21[c]	0.59 ± 0.03[b]	0.11 ± 0.01[b]	0.08 ± 0.00[d]	0.30 ± 0.01[c]

[a,b,c,d]Different superscripts in the same column indicate that means were significantly different ($p < 0.05$).

Table 5
Contribution of micronutrient intakes to the relevant DRIs consuming an average portion (300 g) of supplemented breads.

Micro-nutrient	Gender	DRIs (mg/day)	Contribution to DRIs (%)*					
			White breads			Wholegrain breads		
			Control	With hull-less barley flour	With hull-less barley flakes	Control	With hull-less barley flour	With hull-less barley flakes
K	Adults	3500	15.5	15.6	15.5	39.9	31.3	31.4
P	Adults	700	29.7	36.1	35.6	86.2	72.1	72.1
Mg	Male	420	8.1	8.6	13.3	42.5	31.5	35.8
	Female	320	10.6	11.4	17.4	55.8	41.3	47.0
Ca	Adults	1000	14.7	13.7	14.7	26.3	21.0	22.1
Fe	Male	8	45.8	59.2	54.1	121.4	106.7	102.7
	Female	18	20.4	26.3	24.0	54.0	47.4	45.6
Cu	Adults	0.9	33.0	46.52	44.2	78.7	74.5	72.8
Zn	Male	11	7.8	17.4	16.09	37.1	35.9	34.91
	Female	8	10.7	23.9	22.13	51.0	49.4	48.00
Se	Adults	0.055	13.4	42.7	40.7	14.4	40.1	38.8

* Dietary Reference Intakes (DRIs) for males/females of 19–70 years of age set by the Food and Nutrition Board of the National Research Council.

"anti-ageing" micronutrient (Letavayová, Vlčková, & Brozmanová, 2006; Rayman, 2000,2002; Stranges et al., 2006).

Wholegrain breads would provide more adequate intakes of essential and macro elements, as expected. The barley-supplemented white breads can meet around 20% of DRIs for zinc, whereas wholegrain bread types would meet 35% and almost 50% of DRIs for zinc for males and females, respectively.

The above given data on meeting the daily requirements for minerals by consuming a bread portion are estimated on the basis of their contents found in the bread. However, the real contribution to the daily needs for nutrients for the consumer is largely dependent on their bioavailability. Nutrient bioavailability is an important factor in nutrition. It can be defined as that portion of ingested nutrient that, after being absorbed, is incorporated into a biologically active form (Foster, 1995). It depends on combinations of different processes – digestion, absorption, transport, utilisation and elimination of a nutrient which may interact in a complex way (Favier, 1993). Nutrient bioavailability varies for different foods and is influenced by the nutritional state of an individual. It was found that individuals with low calcium and iron status had higher absorption efficiencies for these minerals (King, 2002; Weaver & Heaney, 2006).

Apart from host factors (nutritional state, physiological state and pathological state of individual), many dietary factors affect the bioavailability of minerals as well, such as the intake level of element, its chemical form, presence of promoters or inhibitors, mineral–mineral interactions, mineral–macronutrient interactions and food processing (Young, Nahapetian, & Janghorbani, 1982). Data available from various absorption studies imply the following proportions of absorbed minerals for foods of plant origin: 2–5% for iron from cereal-based diets (Krishnaswamy, 2003), 10–30% for zinc (Abdulla & Chmielnicka, 1990) and 30% for copper (Abdulla & Chmielnicka, 1990). In an *in vitro* study of iron bioavailability from Indian flat bread chapati fortified with iron, an iron bioavailability of 7.9% was reported (Nayak & Nair, 2003). Phytic acid has been known as an important inhibitor of mineral bioavailability in wholegrain food. However, according to the data of Sandström, Arvidsson, Cederblad, and Bjorn-Rasmussen (1980), nearly 50% more zinc was absorbed from a serving of wholewheat bread, compared with a serving of white bread (0.22 mg, compared with 0.15 mg, respectively). Apparently, the higher content of Zn in the wholegrain bread more than compensated for its less efficient absorption. The content of phytic acid in wheat and barley grains has been estimated to amount to around 1.02% on a dry weight basis (Lott, Ockenden, Raboy, & Batten, 2000).

The existence of several organic and inorganic forms of selenium complicates the assessment of its bioavailability (Reeves et al., 2007). Animal studies showed that selenium was highly available from most feedstuffs of plant origin, ranging from 60% to 90% (Cantor, Scott, & Noguchi, 1975). Reeves et al. (2007) reported that selenium from wheat flour (75% extraction) was nearly 100% available but lower availabilities were obtained for selenium from wheat shorts (85%) and wheat bran (60%). However, only scarce data on selenium bioavailability in human subjects exist. In the human absorption study of Stewart, Griffits, Thomson, and Robinson (1978), it was shown that the bioavailability of two selenium forms – selenite and selenomethionine, administered with food, was around 80%.

The aforementioned facts suggest that the predicted intakes of minerals by bread consumption, calculated from their content in the bread portion are surely overestimated. Thereafter, the more realistic assessment of contribution of the daily portion of white/wholegrain bread made with barley flour to the DRIs derived for adult males would be as follows: 1.19–2.96% and 2.14–5.34% for iron (with bioavailability of 2–5%), 1.74–5.21% and 3.59–10.77% for zinc (with bioavailability of 10–30%), 13.95% and 22.34% for

Table 6
Heavy element content of supplemented breads.

Bread samples		Heavy element content, μg/100 g (dw)			
		Hg	Cd	Pb	As
White bread	Control	$0.30 \pm 0.06^{a,b}$	1.97 ± 0.31^{a}	7.04 ± 0.60^{a}	3.04 ± 1.04^{a}
	Bread + hull-less barley flour	0.26 ± 0.07^{a}	2.94 ± 0.54^{a}	12.5 ± 0.76^{b}	$8.02 \pm 1.52^{b,c}$
	Bread + hull-less barley flakes	0.27 ± 0.05^{a}	2.92 ± 0.68^{a}	12.43 ± 0.82^{b}	$7.90 \pm 1.21^{b,c}$
Wholegrain bread	Control	0.47 ± 0.07^{b}	2.42 ± 0.46^{a}	11.5 ± 0.67^{b}	$4.65 \pm 1.67^{a,b}$
	Bread + hull-less barley flour	$0.37 \pm 0.05^{a,b}$	3.13 ± 0.88^{a}	15.16 ± 1.05^{c}	8.83 ± 1.98^{c}
	Bread + hull-less barley flakes	$0.39 \pm 0.08^{a,b}$	3.21 ± 0.57^{a}	15.54 ± 0.87^{c}	8.99 ± 1.35^{c}

[a,b,c]Different superscripts in the same column indicate that means were significantly different ($p < 0.05$).

copper (with bioavailability of 30%), and 25.60–38.40 i.e. 24.07–39.72% for selenium (with bioavailability of 60–90%), respectively.

3.3. Heavy elements

Content of mercury tended to be lower in the barley-supplemented breads, although significant differences in comparison with the corresponding controls were not observed. Significant variation in the mercury content was determined between the wholegrain control sample and the white supplemented breads. Concentrations of cadmium determined in white and wholegrain breads with barley flour did not significantly vary within the bread samples, although Cd concentrations appeared to be higher in the wholegrain bread types and in white supplemented breads (Table 6). However, the lead concentrations in the barley-supplemented breads and in the wholegrain control were approximately double ($p < 0.05$) that of the white control bread. The arsenic content did not vary significantly between the control breads although 1.5-fold higher As content was determined in the wholegrain control bread. The addition of hull-less barley flour increased 2.6 times the As content in the case of white supplemented breads, whereas it was almost doubled in the case of wholegrain supplemented breads.

When comparing the results only within the group of barley-supplemented breads, the addition of barley flakes and flour contributed similarly to the heavy element content in the corresponding breads.

Daily intakes of heavy elements resulting from consuming a 300-gram daily portion of investigated breads are presented in Table 7. Assuming a 60 kg body weight, the intake of heavy elements corresponding to the daily portion of breads made with barley flour, would amount to 1.3–1.8% (Hg), 10.0–10.3% (Cd), 11.8–13.8% (Pb), and 13.0–13.7% (As) of the Provisional Tolerated Daily Intakes (PTDIs) set by JECFA. Similar and somewhat lower intakes were calculated for the breads made with barley flakes (Table 7). Thus, consumption of bread supplemented with hull-less barley would not cause the average daily intakes to exceed the PTDIs proposed by authorities. Nevertheless, trends towards decrease of these harmful elements in food should be maintained. In addition, the assessed intakes of heavy elements might be viewed with some concern, considering the fact that similar or higher concentrations of these elements are expected to accumulate in food of animal origin (milk, eggs, meat, fish, fat), too. Skibniewska (2003) reported the total daily dietary intake of lead and cadmium in the range 14.5–216 μg/day and 15.1–77.6 μg/day, respectively. Consuming a 300-gram portion of white or wholegrain bread supplemented with hull-less barley flour would contribute to the daily intake of 25.5 or 29.0 μg of lead and 5.98 or 6.16 μg of cadmium, respectively. Thus, the assumed intake of lead by the daily portion of supplemented bread would be much lower than the highest total dietary intake reported by Skibniewska (2003). Satarug, Haswell-Etkins, & Moore (2000) suggested that safe daily levels of Cd should be kept below 30 μg/day per person to ensure normal kidney function.

The uptake of heavy elements from foodstuffs certainly has a great impact on the risk evaluation. Most studies dealing with the absorption of cadmium inorganic salts showed that only a small part of ingested Cd is absorbed *via* the small intestine. It was estimated that Cd absorption varied from 3% to 7% in humans and monkeys (Groten & Bladeren van, 1994). Several elements (Zn, Cu, Fe, Ca, P, Mn, Mg and Se) have been shown to interfere with Cd metabolism but none of these reactions has been proven (Groten et al., 1994), although iron and cadmium interaction has been frequently observed in animal absorption studies (Groten et al., 1994). Humans with low iron status often show greater Cd absorptions than those with good iron status. The presence of iron was reported to have a crucial role against the toxicity of Cd in one comparative study on the protective effect of eight minerals (Groten et al., 1994). Furthermore, there is substantial evidence, derived from animal studies, that administration of selenium compounds efficiently counteract the toxicity of cadmium.

There are few investigations of the uptake of lead in the human intestine. The results were found to vary widely. The major causes of variation were physiological factors and dietary habits. It was found that fasting subjects absorbed 40–50% of the ^{203}Pb ingested as chloride (Heard, Chamberlain, & Sherlock, 1983) or 61% ingested as acetate (James, Hilburn, & Blair, 1985). Both studies reported large reduction of lead uptake with meals. Lead uptake ranged from 3% to 7% of the total ingested when it was taken with a meal or with leafy vegetables, which had taken up lead from its root (Heard et al., 1983). James et al. (1985) reported a similar drop in lead uptake (4%) when subjects ate balanced meals.

3.4. Sensory evaluation

Considering its nutritional value, barley is certainly a desirable ingredient in baked products. But, the lack of gluten limits its application in yeast-leavened products. The supplementation of wheat flour with other flours containing no gluten reduces the breadmaking potential of the mixture, as a consequence of gluten dilution, which results in difficulties in dough handling, lower loaf volume and worsening of crumb grain and softness (Wang, Rosell, & De Barber, 2002).

The addition of barley flour and flakes significantly decreased the bread volume for refined bread types but not for wholegrain breads, as compared to the corresponding controls (Table 8). It also affected the bread shape, giving somewhat flatter products, except for wholegrain bread types. Crumb pore uniformity and crumb grain structure were not significantly affected, though in the supplemented breads the crumb quality decreased but only the refined bread type with barley flour differed significantly from the corresponding control. The crumb elasticity significantly worsened with the addition of barley flour only in the case of white breads. In

Table 7
Ratios of average intakes of toxic elements to the PTDI.

Heavy element	PTDI (μg per kg b.w.** /day)	Contribution to PTDI (%)*					
		White breads			Wholegrain breads		
		Control	With hull-less barley flour	With hull-less barley flakes	Control	With hull-less barley flour	With hull-less barley flakes
Cd	1.0	6.9	10.0	9.6	8.25	10.3	10.0
Pb	3.6	6.8	11.8	11.4	10.9	13.8	13.5
As	2.1	5.1	13.0	12.4	7.6	13.7	13.4
Hg	0.7	1.5	1.3	1.3	2.3	1.8	1.8

* Provisional Tolerated Daily Intakes (PTDI) calculated from Provisional Tolerable Weekly Intake (PTWI) set by the JECFA.
** Body weight 60 kg.

Table 8
Sensory and physical characteristics of bread prepared from refined or wholegrain wheat flour and hull-less barley flour/flakes (means ± SD of three independent determinations).

	Bread samples	Specific volume, ml/g	Crust colour	Porosity	Crumb grain uniformity	Crumb grain structure	Crumb elasticity	Penetrometer number	Flavor
White bread	Control	5.63 ± 0.57[a]	3.40 ± 1.44[a]	6	1.67 ± 1.15[a]	3.33 ± 0.42[a]	4.67 ± 0.42[a]	125.2 ± 2.9[a]	3.07 ± 0.12[a]
	Bread + hull-less barley flour	4.33 ± 0.12[b,c]	4.27 ± 0.46[a]	7	3.00 ± 2.00[a]	2.60 ± 0.53[b]	2.67 ± 0.58[b]	118.6 ± 3.7[a]	3.93 ± 0.12[b]
	Bread + hull-less barley flakes	4.71 ± 0.18[b]	3.53 ± 0.20[a]	6	1.00 ± 0.00[a]	3.60 ± 0.53[a]	4.33 ± 0.42[a]	118.7 ± 2.8[a]	4.06 ± 0.11[b]
Wholegrain bread	Control	3.62 ± 0.09[c]	4.00 ± 0.00[a]	7	2.33 ± 1.15[a]	2.60 ± 0.35[b]	3.00 ± 0.00[b]	68.1 ± 14.6[b]	4.00 ± 0.00[b]
	Bread + hull-less barley flour	3.64 ± 0.46[c]	4.00 ± 1.00[a]	8	1.67 ± 1.15[a]	1.87 ± 0.58[b]	2.67 ± 0.61[b]	63.1 ± 2.6[b]	4.13 ± 0.12[b]
	Bread + hull-less barley flakes	3.24 ± 0.17[c]	3.00 ± 1.00[a]	7	2.33 ± 1.15[a]	1.73 ± 1.10[b]	2.67 ± 0.42[b]	53.0 ± 7.5[b]	4.33 ± 0.58[b]

[a,b,c]Different superscripts in the same column indicate that means were significantly different ($p < 0.05$).

other cases no significant differences were observed in comparison to corresponding controls. No significant difference was observed in the crust colour of the breads. The refined control bread was scored significantly lower in flavour. The other bread types had higher flavour ratings which did not significantly vary within the groups.

4. Conclusions

The results show that the breads supplemented with barley are more nutritious and provide elevated intake of important nutrients such as fibres, zinc and selenium. The consumption of 300 g of supplemented breads can meet up to 40% of DRIs for selenium and 70–75% of recommended daily value for β-glucan. As expected, the incorporation of barley flour and flakes to wheat flour worsened some sensory parameters (volume). However, it was illustrated that crumb elasticity was minimally affected, whereas crumb structure and uniformity were rated similarly to the original formulations containing 100% wheat flour. The barley-supplemented breads were rated higher by taste.

Consumption of barley enriched breads will allow consumers to increase their intake of selenium and soluble fibre, β-glucan, which are of great importance in maintaining good health. In addition, these products would not contribute to the excessive intake of heavy elements.

Acknowledgements

The authors acknowledge that this study is a part of project No. 152001, Sources identification and correlations amongst the elements and organic compounds in abiotic and biotic matrices: risk analysis and a contribution to the monitoring and improvement of the environmental status, coordinated by Prof. B. Škrbić and financially supported by the Ministry of Science and Technological Development of the Republic of Serbia.

References

Abdulla, M., & Chmielnicka, J. (1990). New aspects on the distribution and metabolism of essential trace elements after dietary exposure to toxic metals. *Biological Trace Element Research, 23*, 25–53.

AOAC, H. (2000). In W. Horwitz (Ed.), Official methods of analysis of AOAC international, (17th edition). Maryland, USA.

Behall, K. M., Schofield, D. J., & Hallfrisch, J. (2004a). Lipids significantly reduced by diets containing barley in moderately hypercholesterolemic men. *Journal of the Americal College of Nutrition, 23*, 55–62.

Behall, K. M., Schofield, D. J., & Hallfrisch (2004b). Diets containing barley significantly reduce lipids in mildly hypercholesterolemic men and women. *American Journal of Clinical Nutrition, 80*, 1185–1193.

Berglund, P. T., Fastnaught, C. E., & Holm, E. T. (1992). Food uses of waxy hull-less barley. *Cereal Foods World, 37*(9), 707–714.

Bhatty, R. S. (1986). Physicochemical and functional (breadmaking) properties of hull-less barley fractions. *Cereal Chemistry, 63*, 31–35.

Bojat, S., Vukobratović, R., & Kiš, M. (1994). Ječmene instant pahuljice kao sirovina u izradi hleba i peciva (instantinized barley flakes as an ingredient in the production of bread and other bakery commodities). *Cereal-Bread, 21*, 117–126.

Cantor, A. H., Scott, M. L., & Noguchi, T. (1975). Biological availability of selenium in feedstuffs and selenium compounds for restoring blood plasma glutathione peroxidase activity in selenium-depleted chicks. *Journal of Nutrition, 105*, 96–105.

Dallmann, H. (1958). Porentabelle. Detmold, Germany: Hermann Bösmann GmbH (pp. 4–5).

Favier, A. E. (1993). Nutritional, chemical and food processing implications of nutrient bioavailability. *Proceedings of bioavailability '93 (Part 1)*. Ettlingen, Karlsruhe: Bundesfoschunganstalt für Ernährung.

Food and Drug Administration (2003). Food labelling; health claims; soluble dietary fibre from certain foods and coronary heart disease. Final rule. *Federal Register, 68*(144), 44207–44209.

Foster, L. H. (1995). Selenium in the environment, food and health. *Nutrition and Food Science, 95*(5), 17–23.

Groten, J. P., & Bladeren van, J. (1994). Cadmium bioavailability and health risk in food. *Trends in Food Science and Technology, 5*, 50–55.

Heard, M. J., Chamberlain, A. C., & Sherlock, J. C. (1983). Uptake of lead by humans and effect of minerals and food. *Science of the Total Environment, 30*, 245–253.

ICC Standard No. 123/1. (1994). Determination of starch content by hydrochloric acid dissolution.

James, H. M., Hilburn, M. E., & Blair, J. A. (1985). Effects of meals and meal times on uptake of lead from the gastrointestinal tract in humans. *Human Toxicology, 4*, 401–407.

King, J. (2002). Evaluating the impact of plant biofortification on human nutrition. *The Journal of Nutrition, 132*(3), 511S–513S.

Krishnaswamy, K. (2003). Anaemia – A matter of serious concern and threat to human development. In I. Elmadfa, E. Anklam, & J. S. König (Eds.). *Modern aspects of nutrition, present knowledge and future perspectives* (Vol. 56, pp. 53–56). Basel, Karger: Forum Nutr.

Letavayová, L., Vlčková, V., & Brozmanová, J. (2006). Selenium: From cancer prevention to DNA damage. *Toxicology, 227*(1–2), 1–14.

Lott, J. N. A., Ockenden, I., Raboy, V., & Batten, G. D. (2000). Phytic acid and phosphorous in rope seeds and fruits: A global estimate. *Seed Science Research, 10*, 11–33.

McCleary, B. V., & Mugford, D. C. (1992). Interlaboratory evaluation of β-glucan analysis methods. In *Proceedings of the Fourth International Oat Conference "The changing role of oats in human and animal nutrition*". Adelaide, Australia, Oct 19–23.

McCleary, B. V., & Codd, R. (1991). Measurement of (1–3)(1–4)-β-D-glucan in barley and oats: A streamlined enzymic procedure. *Journal of the Science of Food and Agriculture, 55*, 303–312.

McCleary, B. V., & Glennie-Holmes, M. (1985). Enzymatic quantification of (1–3)-(1–4)-β-D-glucan in barley and malt. *The Journal Institute of Brewing, 91*, 285–295.

McCleary, B. V., & Nurthen, E. J. (1986). Measurement of (1–3)(1–4)-β-glucan in malt, wort and beer. *The Journal Institute of Brewing, 92*, 168–173.

McIntosh, G. H., Whyte, J., McArthur, R., & Nestel, P. J. (1991). Barley and wheat foods: Influence on plasma cholesterol concentrations in hypercholesterolemic men. *American Journal of Clinical Nutrition, 53*, 1205–1209.

Nayak, B., & Nair, K. M. (2003). In vitro bioavailability of iron from wheat flour fortified with ascorbic acid, EDTA and sodium hexametaphosphate, with or without iron. *Food Chemistry, 80*, 545–550.

NRC (National Research Council) (2001). Dietary Reference Intakes table – The complete set http://www.iom.edu/?id=21381.

Rayman, M. P. (2000). The importance of selenium to human health. *Lancet, 356*, 233–241.

Rayman, M. P. (2002). The argument for increasing selenium intake. *Proceedings of the Nutrition Society, 61*, 203–215.

Reeves, P. G., Gregorie, B. R., Garvin, D. F., Hareland, G. A., Lindlauf, J. E., Johnson, L. K., et al. (2007). Determination of selenium bioavailabilty from wheat mill fractions in rats by using the slope-ratio assay and modified torula yeast-based diet. *Journal of Agriculture and Food Chemistry, 55*, 516–522.

Sandström, B., Arvidsson, B., Cederblad, A., & Bjorn-Rasmussen, E. (1980). Zinc adsorption from composite meals, I: The significance of wheat extraction rate, zinc, calcium, and protein content in meals based on bread. *American Journal of Clinical Nutrition, 33*, 739–745.

Satarug, S., Haswell-Etkins, M. R., & Moore, M. R. (2000). Safe levels of cadmium intake to prevent renal toxicity in human subjects. *British Journal of Nutrition, 84*, 791–802.

Skibniewska, K. A. (2003). Diet monitoring for assessment of human exposure to environmental pollutants. *Environment International, 28*, 703–709.

Škrbić, B., & Čupić, S. (2005). Toxic and essential elements in soft wheat grain cultivated in Serbia. *European Food Research and Technology, 221*, 361–366.

Škrbić, B., & Filipčev, B. (2008). Nutritional and sensory evaluation of wheat breads supplemented with oleic-rich sunflower seed. *Food Chemistry, 108*(1), 119–129.

Soares, R. M. D., De Francisco, A., Rayas-Duarte, P., & Soldi, V. (2007). Brazilian hull-less and malting barley genotypes: I. Chemical composition and partial characterisation. *Journal of Food Quality, 30*, 357–371.

Stewart, R. D. H., Griffits, N. M., Thomson, C. D., & Robinson, M. F. (1978). Quantitative selenium metabolism in normal New Zealand women. *British Journal of Nutrition, 40*, 45–54.

Stranges, S., Marshall, J. R., Trevisan, M., Natarajan, R., Donahue, R. P., Combs, G. F., et al. (2006). Effects of selenium supplementation on cardiovascular disease incidence and mortality: Secondary analyses in a randomized clinical trial. *American Journal of Epidemiology, 163*, 649–699.

Swanson, R. B., & Penfield, M. P. (1988). Barley flour level and salt level selection for a wholegrain bread formula. *Journal of Food Science, 53*, 896–901.

Wang, J., Rosell, C. M., & De Barber, C. B. (2002). Effect of the addition of different fibres on wheat dough performance and bread quality. *Food Chemistry, 79*, 221–226.

Weaver, C., & Heaney, R.P. (2006). Food sources, supplements, and bioavailability. In C.M. Weaver, & R.P. Heaney (Eds.), Calcium in human health (pp. 129–131). Towota, NJ: Humana Press.

White, P., & Broadley, M. (2007). Genetic aspects of mineral biofortification. *Comparative Biochemistry and Physiology-Part A: Molecular and Integrative Physiology, 146*(4), 246 (Suppl. 1).

Young, V. R., Nahapetian, A., & Janghorbani, M. (1982). Selenium bioavailability with reference to human nutrition. *The American Journal of Clinical Nutrition, 35*, 1076–1088.

Zhang, G., Junmei, W., & Jinxin, C. (2002). Analyis of β-glucan content in barley cultivars from different locations in China. *Food Chemistry, 79*, 251–254.