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Total phenols and antioxidant capacity of hull-less barley and hull-less oats

Z. Kruma[1,*], L. Tomsone[1], R. Galoburda[1], E. Straumite[1], A. Kronberga[2] and M. Åssveen[3]

[1]Latvia University of Agriculture, Department of Food Technology, Rigas iela 22, LV-3004 Jelgava, Latvia
[2]Institute of Agricultural Resources and Economics, Zinatnes iela 2, LV-4126 Priekuli, Latvia
[3]Norwegian Institute of Bioeconomy Research, Fredrik A. St. Dahls 20, 1432 Ås, Norway
[*]Correspondence: zanda.kruma@llu.lv

Abstract. Grain products are the main source of carbohydrates but they also contain other bioactive substances such as phenolic compounds. Content of phenolic compounds differ among cereal types, varieties, and farming methods. The aim of the current study was to assess total phenolic content and radical scavenging activity in different oats and barley varieties compared to hulled ones. In the experiment hull-less varieties / lines were analysed: three barley (line 'GN 03386', from Norway and 'Kornelija', 'Irbe' from Latvia) and three oats varieties ('Bikini', 'Nudist', from Norway and 'Stendes Emilija,' from Latvia). One hulled variety of barley and oats from each country was included in the experiment for comparison. For the isolation of phenolic compounds ultrasound assisted extraction was used. For all extracts the total phenol content and DPPH, $ABTS^{+}$ radical scavenging activity were determined spectrophotometrically. Overall, the highest content of total phenols was detected in hull-less barley samples. The barley variety with the highest content was line 'GN 03386,' followed by varieties 'Kornelija', 'Irbe,' and hulled Norwegian barley variety 'Tyra'. High DPPH and $ABTS^{+}$ radical scavenging activity was recorded in barley line 'GN 03386'. Generally, there was strong correlation between total phenol content and $ABTS^{\bullet+}$radical scavenging activity and moderate correlation between total phenol content and DPPH radical scavenging activity. In conclusion, the barley varieties had generally higher content of bioactive substances than oats and the barley line 'GN 03386' seems to be one of the best.

Key words: hull-less oats, hull-less barley, total phenols, antioxidant.

INTRODUCTION

Barley (*Hordeum vulgare* L.) is one of the ancient grain cultures, which is widely used as fodder and food, especially in malt production. For many years, pearled grains have been among of the most popular barley products. Researchers have investigated different approaches for using barley in bread industry – sourdough (Mariotti et al., 2014), rye bread (Pejcz et al., 2015), and wheat bread (Rieder et al., 2012) production. Hull-less barley has been confirmed to be a good source of both insoluble and soluble fractions of dietary fibre and other bioactive compounds (Blandino et al., 2015) that

makes beneficial effects on human health (Tong et al., 2015). In Latvia, breeding programs focus on hull-less barley morphological characteristics, agronomical, physical and chemical parameters (Zute et al., 2012; Bleidere et al., 2013a; 2013b; Šterna et al., 2015) and potential use of hull-less barley in beer production (Dabina-Bicka et al., 2011).

Oats (*Avena sativa* L.) is highly recognized for its high energy and nutritional value due to high content of proteins and lipids. Oats are also a good source of soluble fibre, essential amino acids, unsaturated fatty acids, vitamins, minerals, and phytochemicals (Jones, 2003; Arendt & Zannini, 2013; Vilmane et al., 2015). Chen et al. (2015) reported that oats contain abundant antioxidant compounds, including tocols (Shewry et al., 2008), sterols (Peterson, 2001; Shewry et al., 2008), phenolic compounds (Shewry et al., 2008) and phytic acid (Peterson, 2001). All over the world hull-less oats are mainly used for fodder. However, the grain chemical content and nutritional value has aroused interest for their use in human nutrition (Behall & Hallfrisch, 2011; Tiwari & Cummins, 2012; Redaelli et al., 2013; Vilmane et al., 2015). Compared with hulled oats grain, hull-less oats grain contains less fibre, more protein and lipids, and has higher energy value (Givens et al., 2004; Biel et al., 2009).

Most common hulled varieties of barley and oats require mechanical removal of the tenacious hull covering the grain. This process also removes most of the bran layer and germ thus resulting in loss of valuable components. Therefore recently new hull-less barley and hull-less oats varieties have been developed in order to ensure both high productivity level, along with straw strength, disease resistance and increased grain quality (Bleidere et al., 2014).

According to the review of Acosta-Estrada et al. (2014) most of the beneficial properties of grains have been attributed to bioactive non-nutritional chemical compounds commonly named phytochemicals. Among these, phenolic compounds have been extensively studied due to their diverse health benefits as antioxidants, and for preventing chronic inflammation, cardiovascular diseases, cancer and diabetes. This effect seems to be partly due to phytochemicals that combat oxidative stress (Masisi et al., 2016). With increased consumer knowledge on the health benefits provided by soluble dietary fibre and other grain constituents, barley and oats are becoming more attractive for researchers and producers.

Phenolic compounds are considered as a major group in grains that contribute to the antioxidant activity of cereal. These molecules are secondary metabolites of plants possessing possible positive physiological effects (Peng et al., 2015). Dietary antioxidants play a significant role in human health by prevention of radical damage to biomolecules such as DNA, RNA, proteins, and cellular organelles. The antioxidant activity of polyphenols has been mainly related to their redox properties, which can play an important role in neutralizing free radical and quenching oxygen or decomposing peroxides (Kahkonen et al., 1999).

There are various methods suitable for evaluation of phenolic content and antioxidative capacity in plants, foods and ingredients (Moon & Shibamoto, 2009; Kammerer et al., 2011). The initial analytical approach consists of using non-specific methods in order to determine the overall content of phenolic compounds, usually expressed as an index such as gallic acid, chlorogenic acid or catechin equivalent. A more detailed approach using chromatography can specifically quantify certain compounds of interest. Most phenolic compounds in cereal-based matrices are in the insoluble bound forms (Acosta-Estrada et al., 2014). Phenolic compounds in oats and

other grains mainly exist in bound forms and are typical components of complex structures such as lignins, hydrolysable tannins, and organic acids (Alrahmany & Tsopmo, 2012).

Bleidere et al. (2014) found significant differences among cultivars in antioxidant activities and total phenolic contents (TPC). Oats contain tocols, phenolic acids, aventhramides, flavonoids and sterols (Bryngelsson et al., 2002; Dimberg et al., 2005). These groups of compounds are located mainly in the outer layers of the kernel (Pecio et al., 2013). For barley, Dvorakova et al. (2008) reported the phenolic acids such as the hydroxybenzoic (protocatechuic, gallic, vanillic, and syringic) and the hydroxycinnamic acids (caffeic, sinapinic, p-coumaric, and ferulic). Ferulic acid was clearly the most abundant phenolic compound found in the bound form in barley.

Despite the fact that many studies have been conducted on bioactive compounds in hull-less oats and barley, the results are contradictory. Therefore, the aim of the current study was to assess total phenolic content and radical scavenging activity in different hull-less oats and barley varieties comparing to hulled ones.

MATERIALS AND METHODS

Chemical analyses were performed at scientific laboratories of the Latvia University of Agriculture, Faculty of Food Technology. The phenolic compounds, DPPH, and ABTS radical scavenging activity were determined for oats (hulled and hull-less) and barley (hulled and hull-less).

Grain materials

Grain samples were selected from seed material of different cereal cultivars grown in Latvia and Norway.

In the study three hull-less Latvian and Norwegian barley varieties / lines (line 'GN 03386', from Norway and 'Kornelija', 'Irbe' from Latvia) were tested along with hulled barley varieties 'Rubiola' (Latvia) and 'Tyra' (Norway). Similarly, three hull-less oats varieties ('Bikini', 'Nudist', from Norway and 'Stendes Emilija' from Latvia), as well as hulled oat varieties 'Laima' (Latvia) and 'Odal' (Norway) were included in the study. The moisture content of grains at analysing stage was 12.0–12.9%.

Chemical analysis

Chemicals

Gallic acid (97.5%), Folin-Ciocalteu phenol reagent, 2,2-diphenyl-1-picrylhydraziyl (DPPH$^{\cdot}$) (99%), 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS$^{\cdot+}$) (98%), (±)-6-Hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) (97%) were purchased from Sigma-Aldrich (Switzerland). All other chemicals used in for analyses were obtained from Acros Organic (USA).

Extraction of phenolic compounds from grains

The homogenized grain samples (2.0 g) were extracted with ethanol/acetone/water (7/7/6 v/v/v) solution in an ultrasonic bath YJ5120-1 (Oubo Dental, USA) at 35 kHz for 10 minutes at 20 ± 1 °C temperature. The extracts were then centrifuged in a centrifuge CM-6MT (Elmi Ltd., Latvia) at 3,500 min^{-1} for 5 min (RCF 2300). Residues were re-extracted using the same procedure. Ratio of sample versus solvent was 1:10. Triplicate extraction process was done.

Determination of total phenolic compounds

The TPC of the grain extracts was determined according to the Folin-Ciocalteu spectrophotometric method (Singleton et al., 1999). To 0.5 mL of extract 2.5 mL of Folin-Ciocalteu reagent (diluted 10 times with water) was added and, after 3 min 2 mL of sodium carbonate water solution (Na_2CO_3) (75 g L^{-1}) was added. Then sample was mixed. The control sample contained all the reaction reagents except the extract. After 30 minutes of incubation at room temperature, the absorbance was measured at 765 nm. The results were calculated using standard curve of gallic acid with the range of the standard of 10 mg to 80 mg GAE L^{-1}. Total phenols were expressed as gallic acid equivalents (GAE) per 100 g dry weight (DW) of the samples.

Determination of DPPH˙ radical scavenging activity

Antioxidant activity of the grain extracts was measured on the basis of scavenging activities of the stable 2.2-diphenyl-1-picrylhydraziyl (DPPH˙) radical as outlined by Yu et al. (2003). The antioxidant reaction was initiated by transferring 0.5 m L of plant extract into a sample cavity containing 3.5 mL of freshly prepared DPPH˙ methanol solution (0.004 g DPPH˙ to 100 mL methanol). The absorbance was measured at 517 nm, after 30 min of incubation in the dark at room temperature. The radical scavenging capacity was expressed as Trolox mM equivalents (TE) 100 g^{-1} DW of the samples. The standard curve was prepared for the concentrations of solutions between 5–10 μM Trolox.

Determination of $ABTS^{\cdot+}$ radical scavenging activity

The radical scavenging capacity of extract was measured also by $ABTS^{\bullet+}$ radical cation assay (Re et al., 1999). Firstly, phosphate buffered saline (PBS) were prepared by dissolving 8.18 g sodium chloride (NaCl), 0.27 g potassium dihydrogen phosphate (KH_2PO_4), 1.42 g sodium phosphate dibasic (Na_2HPO_4), and 0.15 g potassium chloride (KCl) in 1 L of ultra-pure water. A stock solution of ABTS (2 mM) was prepared in 50 mL of PBS. If the pH was lower than 7.4, it was adjusted with sodium hydroxide (NaOH). Ultra-pure water was used to prepare 70 mM solution of potassium persulfate ($K_2S_2O_8$). $ABTS^{\bullet+}$ radical cation was produced by reacting 50 mL of ABTS stock solution with 0.2 mL of $K_2S_2O_8$ solution and allowing the mixture to stand in the dark at room temperature for 15–16 h before use. The radical was stable in this form for more than 2 days when stored in the dark at room temperature. For the assessment of extracts, the $ABTS^{\bullet+}$ solution was diluted with PBS to obtain the absorbance of 0.800 ± 0.030 at 734 nm. Five mL of $ABTS^{\cdot+}$ solution were mixed with 0.05 mL of extract. The absorbance was read at ambient temperature after 10 min. PBS solution was used as a blank sample. The radical scavenging capacity was expressed as Trolox mM equivalents (TE) 100 g^{-1} DW of the samples. The standard curve was prepared for the concentrations of solutions between 2–10 μM Trolox.

Statistical analysis

Experimental results presented are means of three parallel measurements and were analyzed by Microsoft Excel 2010 and SPSS 17.00. Analysis of variance (ANOVA) and Tukey test were used to determine differences among samples. A linear correlation analysis was performed in order to determine relationship between TPC, antioxidant activity such as DPPH˙, and $ABTS^{\bullet+}$ radical scavenging activity. Differences were considered as significant at $P < 0.05$.

RESULTS AND DISCUSSION

Total phenolic compounds (TPC)

The TPC in oats ranged from 179 to 221 mg GAE g^{-1} DW (Fig. 1A). Difference among varieties was significant and this may indicate variation in genetic background, growing conditions, agrotechnology, and other factors among cultivars. In our study it is difficult to consider which factors have affected TPC content in grains because of the limited information about growing conditions. Chu et al. (2013) reported lower TPC values – in oats ranged from 57 mg to 94 mg 100 g^{-1}. On the other hand total phenolic content in the oats studied by Brindzová et al. (2008) had higher values than in our study and differed significantly between the varieties ranging from 239 to 662 µg GAE g^{-1} DW. Results of our study revealed that the highest TPC content was in oats varieties 'Stendes Emilija', 'Odal,' and 'Laima'. Thus indicating that influence of variety is more significant than grain type – hull-less or hulled. Similar results reported Bleidere et al. who did not find notable difference between hulled and hull-less standard varieties in content of total phenolic compounds in grain (Bleidere et al., 2013a).

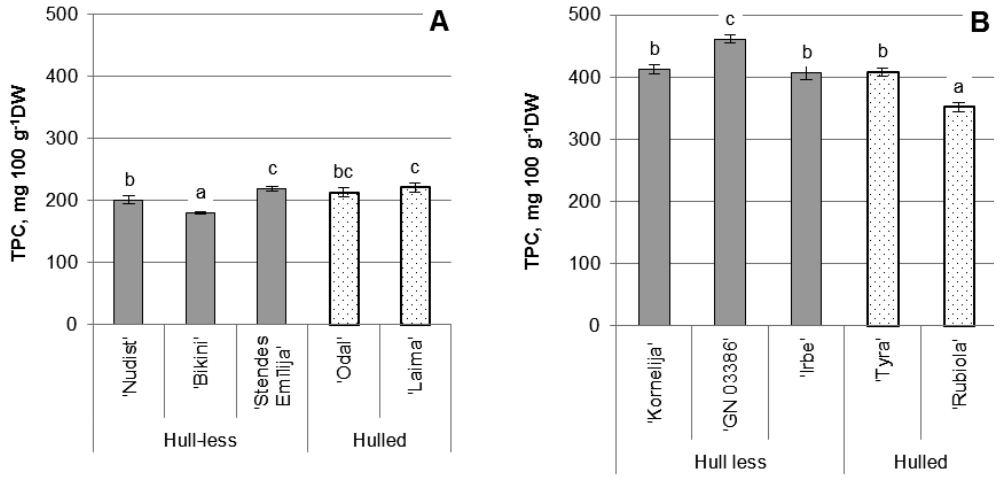

Figure 1. Total phenolic compounds in oats (A) and barley (B) samples. Note: the values marked with different letters for each cereal type represent significant differences between values ($P < 0.05$).

The TPC for barley ranged from 351 to 460 mg GAE 100 g^{-1} DW (Fig. 1B). Bleidere et al. (2013a) reported lower TPC with high variation: from 143.6 to 262.1 mg GAE 100 g^{-1} with coefficient of variation 13.4%. In dehulled highland barley from China phenolic content ranged from 167.9 ± 12.1 to 282.0 ± 5.5 mg 1grain (Zhu et al., 2015). Also for barley, the variety is the most significant factor influencing TPC not the type – hull-less or hulled. Similar results reported Bleidere et al. – that there was also no notable difference between hulled and hull-less standard varieties in content of total phenolic compounds in grain (Bleidere et al., 2013a). In hull-less barley varieties grown in India TPC varied significantly within cultivars and ranged between 278 to

338 mg 100 g^{-1} (Moza & Gujral, 2016). Comparing both cereal types (Fig. 1A and 1B) it can be clearly seen that barley generally has significantly higher TPC.

Also DPPH scavenging activity was significantly influenced by variety not the grain type – hull-less or hulled (Fig. 2). Among oats varieties significantly lower DPPH scavenging activity was found only for variety 'Bikini' (Fig. 2A). From barley samples significantly higher activity was in line 'GN 03386,' followed by 'Rubiola' (Fig. 2B). Differences between oats and barley in DPPH scavenging activity were not significant.

The main phenolic classes in oats include phenolic acids, flavonoids and a unique group avenanthramides and several studies showed strong antioxidant capacity of this specific group (Yang et al., 2014), that could explain high DPPH radical scavenging activity, even if TPC is significantly lower, compared to barley. Also opposite results are reported that avenanthramide levels did not correlate with the observed antioxidant capacities, suggesting that other phytochemicals may contribute significantly or synergistically to the wide free radical-scavenging capacities of oats (Chu et al., 2013). Oats contain bioactive peptide lunasin that could also demonstrate antioxidant properties (Nakurte et al., 2013). Tocopherols and tocotrienols found in oats are natural antioxidants, but there was not found correlation between their content and activity (Chu et al., 2013). Oats antioxidant activity could be explained by active components and synergistic effects and interactions among the various antioxidants that give rise to a net antioxidant capacity in different oats varieties (Chu et al., 2013).

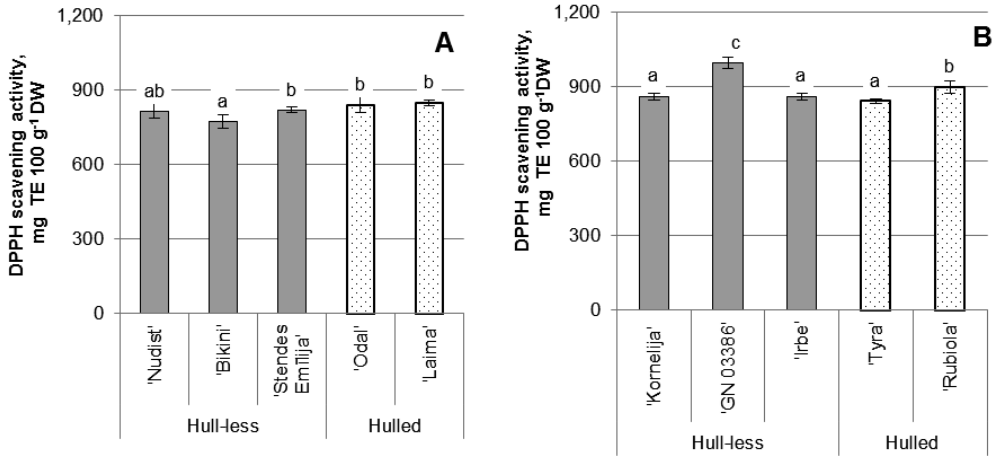

Figure 2. DPPH scavenging activity of oats (A) and barley (B) samples. Note: the values marked with different letters for each cereal type represent significant differences between values ($P < 0.05$).

The abundant content of phenolic compounds in barley reveals that it may serve as an excellent dietary source of natural antioxidants with antiradical and antiproliferative potentials for disease prevention and health promotion (Zhao et al., 2008). Žilić et al. (2011) reported that among the small grain species, hull-less barley had the highest reducing power, contained the most active scavengers of free radicals.

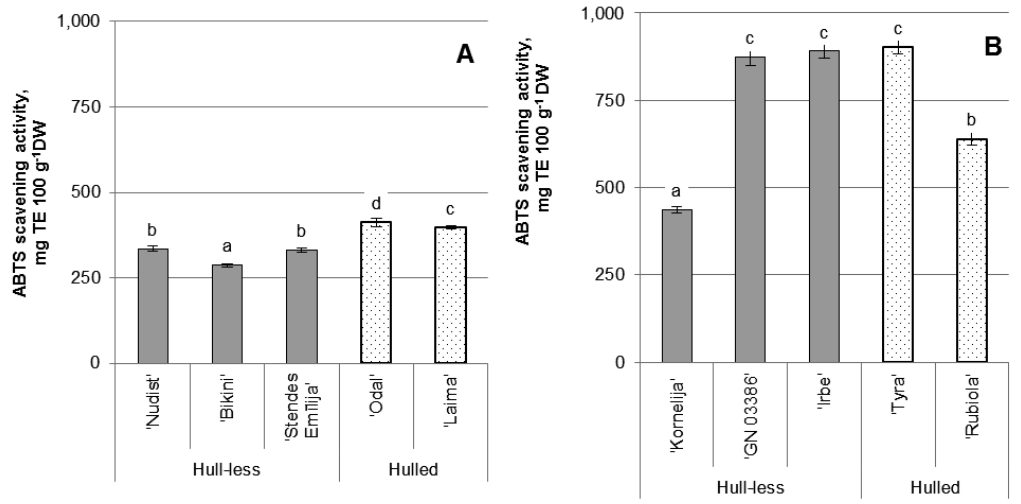

Figure 3. ABTS scavenging activity of oats (A) and barley (B) samples.Note: the values marked with different letters for each cereal type represent significant differences between values ($P < 0.05$).

In oats the highest ABTS scavenging activity was in variety 'Odal', and generally both hulled oats species demonstrated significantly higher activity (Fig. 3A). In barley the highest activity was in varieties 'Irbe', 'Tyra,' and in line GN 00386 (Fig. 3B). The ABTS scavenging activity also depends on variety and not of grain type. Differences between oats and barley in ABTS scavenging activity were significant, with the highest values for barley. Results showed that ABTS assay is more specific for analysed samples and it is possible to see differences between them, comparing to DPPH radical assay. Different ABTS results from the DPPH could be explained with different reaction mechanism. ABTS + radical is stable and is much more active than DPPH˙ radical. ABTS radical cation reactions with antioxidant is faster than the millisecond (Naik et al., 2003). ABTS reacts with most of the antioxidants, it does not affected by the ionic strength and is used to determine both hydrophilic and hydrophobic antioxidant activity (Martysiak-Żurowska & Wenta, 2012). Also the results of a variety of foods suggest that ABTS assay better reflects the antioxidant contents than DPPH assay and the correlation between antioxidant capacities detected by ABTS and DPPH assays was strong in fruits and beverages, but lower in vegetables. Most vegetables analyzed showed much lower antioxidant capacities as measured by DPPH assay relative to ABTS assay (Floegel et al., 2011).

Relationship between phenolic compounds and antioxidant capacity

Phenolic compounds are one of the compounds group posing radical scavenging activity. Pearson's coefficient between TPC and DPPH scavenging activity was strong ($r = 0.74$) but between TPC and ABTS scavenging activity it was very strong ($r = 0.86$). Dordevic et al. (2010) did not find correlation between TPC and DPPH scavenging activity in the grains. Also Brand-Williams et al. (1995) reported similar results. In contrast, significant ($P < 0.05$) positive correlation between radical scavenging activity

and total phenolic content (r = 0.519) was obtained by Bleidere et al. (2013a) and Zhao et al. (2008) in spring barley.

Very strong correlation between TPC and ABTS scavenging activity (r = 0.971) was reported for commercial canola meal (Hassas-Roudsari et al., 2009) and durum (r = 0.950) (Žilić et al., 2012). Whereas Italian researchers analysing whole grain durum wheat (*T. durum* Desf.) determined strong correlation (r = 0.663) (Laus et al., 2012).

CONCLUSIONS

The present study determined TPC and antioxidant activity in grains of five oats and five barley varieties from Latvia and Norway. For oats and for barley, TPC and antioxidant activity was significantly influenced by cultivar variety. The type of grain-hull-less or hulled had no effect on analysed compounds.

All barley varieties had higher TPC and ABTS scavenging activity comparing to the oats varieties. The highest activity was detected in hull-less barley line 'GN 03386'. Impossible was to select the best oats variety with the highest parameters, but significantly lower TPC and antioxidant activity was found in hull-less oats variety 'Bikini'. Bioactive compounds should be taken into consideration developing new functional products.

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