

## Antioxidant Activity, $\beta$ -Glucan and Lipid Contents of Oat Varieties

LUCIA BRINDZOVÁ<sup>1</sup>, MILAN ČERTÍK<sup>2</sup>, PETER RAPTA<sup>3</sup>, MICHAL ZALIBERA<sup>3</sup>,  
ANNA MIKULAJOVÁ<sup>1</sup> and MÁRIA TAKÁCSOVÁ<sup>1</sup>

<sup>1</sup>*Institute of Biochemistry, Nutrition and Health Protection, Department of Nutrition and Food Evaluation, <sup>2</sup>Institute of Biotechnology and Food Science, Department of Biochemical Technology and <sup>3</sup>Institute of Physical Chemistry and Chemical Physics, Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, Slovak Republic*

### Abstract

BRINDZOVÁ L., ČERTÍK M., RAPTA P., ZALIBERA M., MIKULAJOVÁ A., TAKÁCSOVÁ M. (2008): **Antioxidant activity,  $\beta$ -glucan and lipid contents of oat varieties.** Czech J. Food Sci., **26**: 163–173.

The antioxidant activity, total phenolic and  $\beta$ -glucans contents, and the fatty acid profile of total lipids in covered (black and yellow) and naked oats were studied. Oats with black hulls showed a significantly higher antioxidant activity in 2,2'-azino-di-[3-ethylbenzthiazoline sulphonate] (ABTS) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) based tests in comparison to the grains with yellow hulls and those of the naked varieties. Radical scavenging activity of oats determined by electron paramagnetic resonance (EPR)/spin-trapping test did not depend on the colour of the grain hulls, but the naked grains showed a lower ability in scavenging reactive radicals. A positive correlation between the content of  $\beta$ -glucans in covered oat grains and the amount of reactive radicals scavenged was observed. Total phenolic content in the black oats was significantly higher than in the yellow and naked oat varieties. However, no significant differences in the fatty acid profile between the naked and covered oats were found, and the common fatty acids being linoleic, oleic, and palmitic acids.

**Keywords:** oat; antioxidants; phenolic compounds;  $\beta$ -glucans; fatty acids; EPR

Oat (*Avena sativa* L.) is an important crop produced in various regions of Europe and North America. Although it is considered one of the latest domesticated crops, the wild type (*Avena sterilis*) of oat grains was discovered around the human settlements from the Neolithic era, dated back more

than nine thousand years B.C. (WEISS *et al.* 2006). Oats are largely used in cattle breeding and have occurred in human diet for a long time, mainly as oatmeal and rolled oats, but the positive physiological effects of oat products were recognised just rather recently (PIRJO *et al.* 2003). Oats are a

Supported by the Scientific Grant Agency (VEGA) of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences (Grants No. 1/0845/08, 1/3488/06 and 1/2390/05) and by the Slovak Grant Agency of the Ministry of Education of the Slovak Republic (Applied Research Project AV 4/0013/07) and by the Science and Technology Assistance Agency (Grant No. APVT-20-0045/04).

rich source of soluble fiber, well-balanced proteins, several vitamins and minerals essential for the human health (CHARALAMPOPOULOS *et al.* 2002; PETERSON *et al.* 2002; DEMIRBAS 2005; ESPOSITO *et al.* 2005). Oats contain relatively high amounts of lipids compared with other cereal grains, with a substantial level of essential linoleic acid (HARELAND & MANTHEY 2003). Additionally, oats are a source of several natural antioxidants such as tocopherols, alk(en)ylresorcinols, and phenolic acids and their derivatives, and a unique source of avenanthramides (N-cinnamoylanthranilate alkaloids) and avenalumic acids (ethylenic homologues of cinnamic acids), which are not present in other cereal grains (MILLER *et al.* 2000; BRYNGELSSON *et al.* 2002; LIU *et al.* 2004; MATTILA *et al.* 2005). All of these phenolic compounds possess potential health-promoting properties because of their antioxidant activities and/or membrane-modulating effects (alk(en)ylresorcinols). Moreover,  $\beta$ -glucans, which also exhibit an antioxidant capacity (JOHANSSON *et al.* 2004; LYLÝ *et al.* 2004), are included in the soluble dietary fibre fractions of oats that participates in the glucoregulation and causes a decrease in serum cholesterol levels in humans (JOHANSSON *et al.* 2000; TUDORICA *et al.* 2002; DELANEY *et al.* 2003; ZWER 2004; ESPOSITO *et al.* 2005). The consumption of oats is therefore an important component of diet for hypercholesterolemic patients (CZERWIŃSKI *et al.* 2004). In addition to their importance in the diet, oats antioxidants may also contribute to the stability and the taste of food products (PETERSON 2001).

Most of the previous studies in literature reported a good antioxidant capacity of oats (XING & WHITE 1997; PETERSON *et al.* 2001; CHEN *et al.* 2004; MATTILA *et al.* 2005). However, to the best of our knowledge, the correlations between the antioxidant and radical scavenging capacities, determined by EPR/spin trapping, and the contents of biologically active compounds in oats have not been studied. Therefore, the aim of the present study is the investigation of antioxidant and radical scavenging capacities and their relation to the total phenolic and  $\beta$ -glucans contents and fatty acid profile in covered (black and yellow) and naked oats. The deviations in the biosynthetic stabilities of the compounds studied are also discussed. These data may offer additional valuable taxonomic and physiological information for the classification of various cereal varieties.

## MATERIALS AND METHODS

**Oat samples.** Grain samples of nine registered oat cultivars belonging to two different oat species, *Avena sativa* L. – covered black oats (cvs Mesdag, Taiko, Jostrain), yellow oats (cvs Triumph, Lucy, Zvolen), and *Avena sativa nuda* L. – naked oats (cvs Jakub, Detvan, Izak), originating from different countries, were obtained from the Gene bank of the Research Institute of Plant Production (Piešťany, Slovak Republic). The cultivar samples were grown in Víglaš Pstruša (Slovak Republic) in 2003 crop year.

**Defatting of oat samples.** The oat samples were milled and ground to pass through a 0.5 mm screen. The moisture content was determined and all data were expressed on a dry weight basis. The fine flour (30 g) was transferred to an Erlenmeyer flask, defatted twice with hexane, p.a. (Mikrochem, Slovak Republic) at a 5:1 ratio (v/w) and kept on a mechanical shaker for 1 hour at room temperature. The mixture was filtered through a Büchner funnel after each extraction step.

**Preparation of oat extracts.** One gram of the defatted flour was extracted with 65% ethanol ( $3 \times 15$  ml) at 80°C for one hour. The extracts were filtered and the supernatants were collected, combined, and dried in vacuum at 40°C. The residues containing the extracted antioxidants were dissolved in 5 ml dimethyl sulfoxide (DMSO, Merck, Germany) for both ABTS and EPR tests, and in 5 ml of 96% ethanol for DPPH test and for the determination of total phenolic content.

**ABTS analysis.** The antioxidant activity was measured using a modified version of the RE *et al.* (1999) and ARTS *et al.* (2004) methods. To prepare ABTS cation radical solution, a potassium persulphate ( $K_2S_2O_8$ , p.a., Merck, Germany) aqueous solution (3.3 mg  $K_2S_2O_8$  in 5 ml distilled water) was added to 17.2 mg ABTS (purum > 99%, Fluka, Germany) and the resulting solution was stored in the dark for 14 hours. One ml of the final dark-green radical solution was then diluted with 60 ml distilled water and used in ABTS tests. Here, 50  $\mu$ l of oat extract in DMSO was added to 2 ml of ABTS<sup>•+</sup> solution in 1 cm UV-Vis cell and mixed rigorously. The UV-Vis spectra were read at 1 min intervals for 10 min using UV-Vis Shimadzu 1700 spectrometer (Japan). UV-Vis spectrum of the initial ABTS<sup>•+</sup> solution measured against distilled water was taken as a reference spectrum. The difference in the absorbance in 10<sup>th</sup> min at 730 nm

relative to the reference spectrum ( $\Delta A$ ) was used to calculate the percentage of the scavenged ABTS cation radicals by oat extracts relative to the reference sample (KATALINIC *et al.* 2006). Using the calibration curve of Trolox (Sigma-Aldrich, Germany), the values in % of the scavenged radicals were recalculated to the Trolox equivalents (TEAC – Trolox Equivalent of Antioxidant Capacity) in mg Trolox/g of oat grains dry weight.

**DPPH analysis.** The antioxidant activity determination using free DPPH radical (95%, Aldrich, Germany) was realised according to YEN and CHEN (1995). 3 ml of 96% ethanol and 1 ml of DPPH solution (120 mg DPPH in 100 ml 96% ethanol) were added to 1 ml of the ethanol oat extract (after 1:3 v/v dilution). In the reference sample, 1 ml of ethanol was used instead of the oat extract, and the spectra were measured against ethanol. The changes in the absorption at 517 nm in 10<sup>th</sup> min relative to the reference sample were used to calculate the Trolox equivalents (mg/g on a dry weight) similar to ABTS test.

**EPR/spin-trapping analysis.** The thermal decomposition of  $K_2S_2O_8$  in DMSO at 333 K was used as a source of reactive radicals. For measuring the radical scavenging ability of the oat samples, the EPR/spin trapping method (RAPTA *et al.* 2005) employing the 5,5-dimethylpyrroline-N-oxide (DMPO, Sigma-Aldrich, Germany) spin trap was used (EPR spectrometer, Bruker, Germany). 200  $\mu$ l of DMSO extract (or pure DMSO in reference measurements) was mixed with 25  $\mu$ l of 0.2M DMPO in DMSO and 25  $\mu$ l of 0.01M  $K_2S_2O_{8(aq)}$  and transferred into a EPR flat cell. The time course of EPR spectra of the DMPO spin-adducts was recorded at 333 K in 1 min intervals for 20 min (each spectrum was an accumulation of 3 scans). The EPR intensity (double integral) in the 20<sup>th</sup> min, recorded with the sample solutions, was compared with the reference measurement. The difference between the integral EPR intensities of the reference and the oats samples in 20<sup>th</sup> min characterises the amount of radicals scavenged by the scavengers present in the respective sample. The value for the virtual conditions when all radicals were scavenged was set to 100% of Radical Scavenging Capacity (RSC). The RSC values were calculated as the percentages of the scavenged radicals relative to the reference sample (DMSO). Trolox solutions in DMSO were used to obtain the calibration curve in order to express the RSC in Trolox equivalents similar to the ABTS and DPPH tests.

#### **Determination of total phenolic compounds.**

The total amount of phenolic compounds was determined in the ethanolic oat extract with a standard Folin-Ciocalteu reagent (YU *et al.* 2004). The reaction mixture contained 100  $\mu$ l of the oat extract, and 500  $\mu$ l of the Folin-Ciocalteu reagent (Merck, Germany) and 1.5 ml of 20% sodium carbonate. The sample was then mixed on a vortex mixer and diluted with distilled water to the final volume of 10 ml. After 2 h reaction, the absorbance at 765 nm was determined and used to estimate the phenolic content using the calibration curve made with gallic acid (Sigma-Aldrich, Germany). The total amount of phenolic compounds was expressed in  $\mu$ g gallic acid equivalent (GAE) per g dry weight of oats.

**Determination of  $\beta$ -glucans.** The oat varieties (3 samples each) were analysed for  $\beta$ -glucans.  $\beta$ -Glucan content was evaluated by an enzymatic kit according to the manufacturer's instructions (Megazyme International Ireland Ltd., Co. Wicklow, Ireland). The absorbance was measured at 510 nm.

**Lipid isolation and fatty acid analysis.** Milled oat samples (1 g) were extracted twice with 50 ml of chloroform/methanol (2:1 v/v, reagents p.a., Mikrochem, Slovak Republic) for one hour. The extracts were filtered, purified with the addition of 1.20 multiple of water, and centrifuged for 10 minutes. The supernatants were dried under vacuum at 40°C. The residues were dissolved in hexane/chloroform (9:1 v/v). Fatty acid composition was determined by gas chromatography according to ČERTÍK *et al.* (1996) after methylation (CHRISTOPHERSON & GLASS 1969). Gas chromatograph (GC-6890 N, Agilent Technologies) was equipped with a capillary column DB-23 (60 m  $\times$  0.25 mm, film thickness 0.25  $\mu$ m, Agilent Technologies) and a FID detector (constant flow, hydrogen 35 ml/min, air 350 ml/min, 250°C). The analyses were carried out under a temperature gradient (130°C for 1 min; 130–170°C at program rate 6.5°C/min; 170–215°C at program rate 2.7°C/min; 21°C for 7 min; 220–240°C at program rate 2°C/min) with hydrogen as a carrier gas (flow 2.1 ml/min, velocity 49 cm/s, pressure 174 kPa) and a split ratio of 1/50 (inlets: heater 230°C, total hydrogen flow 114 ml/min, pressure 174 kPa). The fatty acid methylester peaks were identified by means of authentic standards of  $C_4$ – $C_{24}$  fatty acid methylesters mixture (Supelco, USA) and quantified by an internal standard of heptadecanoic acid (C17:0,

Supelco, USA). The fatty acid concentration was evaluated with ChemStation software 10.2 (Agilent Technologies, USA). The index of fatty acid unsaturation IU ( $\Delta/\text{mol}$ ) was calculated by the following formula (ČERTÍK & SHIMIZU 2000):  $\text{IU} = [1(\sum\% \text{ monoenes}) + 2(\sum\% \text{ dienes}) + 3(\sum\% \text{ trienes}) + 4(\sum\% \text{ tetraenes})]/100$ .

**Statistical analysis.** All tests were carried out in triplicates for the determination of  $\beta$ -glucan, and in duplicates for other methods. Mean values  $\pm$  standard deviations (SD) are presented. The results of the analyses are reported on a dry matter (dm) basis; dm content was determined according ISO 712 method. Student's test for independent samples was used to test for the differences at a  $P \leq 0.05$  significance level where appropriate.

## RESULTS AND DISCUSSION

### Antioxidant and radical scavenging capacity

Significant differences were found in the antioxidant activity among all oat cultivars investigated with three independent tests – ABTS, DPPH and EPR/spin-trapping (Table 1). ABTS and DPPH assays were used for the determination of total antioxidant capacity of our oat extracts. The total antioxidant capacities of oats varied between the naked and covered oats and also between the covered oats with different hull colours, and increased as follows: naked oats < yellow oats < black oats. Black oat cv. Jostrain showed the highest antioxidant activity in both ABTS and

DPPH tests (3.5 mg Trolox/g on a dry weight and 17.8 mg Trolox/g on a dry weight, respectively). A significant correlation was found between the DPPH scavenging activity and ABTS scavenging activity ( $R = 0.911$ ). Not surprisingly, similarly strong correlations ( $R = 0.981$ ) were already reported by other authors (RAGAE *et al.* 2006).

Both the above mentioned standard antioxidant capacity assays are based on the reactions of stable or semi-stable radicals. Although they are widely applied and generally accepted, they are rather artificial in comparison to the free radical chemistry in living systems. Most of the free radical induced damage in living organisms is attributed to the short living reactive species like hydroxyl or superoxide radicals. The total antioxidant capacity of our samples was therefore compared with the radical scavenging capacity (RSC) evaluated by the EPR/spin-trapping method, where the reactive radicals are involved. Figure 1 shows a time course of EPR integral intensities evaluated by the integration of sets of 20 individual EPR spectra of DMPO spin-adducts. The difference between the integral intensities in the reference experiment (with DMSO) and in the experiments with the oat extracts characterises the amount of radicals scavenged by the antioxidants present in the respective sample. The results were calibrated to Trolox to allow a quantitative comparison with the results of ABTS and DPPH assays. The black oat cv. Jostrain showed the best radical scavenging effect also in the EPR/spin-trapping test (13.442 mg Trolox/g on a dry weight). A direct correlation

Table 1. Antioxidant activity of oat cultivars measured by three different tests (mg Trolox/g  $\pm$  SD)

Cultivar	ABTS-test	DPPH-test	EPR/spin-trapping
Detvan	1.107 $\pm$ 0.011	4.618 $\pm$ 0.009	1.431 $\pm$ 0.072
Jakub	1.088 $\pm$ 0.049	3.493 $\pm$ 0.016	1.263 $\pm$ 0.063
Izak	0.825 $\pm$ 0.033	3.437 $\pm$ 0.031	1.069 $\pm$ 0.053
Zvolen	1.654 $\pm$ 0.001	4.654 $\pm$ 0.050	1.203 $\pm$ 0.060
Triumph	2.101 $\pm$ 0.013	4.681 $\pm$ 0.014	3.053 $\pm$ 0.153
Lucy	2.245 $\pm$ 0.038	4.954 $\pm$ 0.007	5.943 $\pm$ 0.297
Jostrain	3.528 $\pm$ 0.007	17.802 $\pm$ 0.022	13.442 $\pm$ 0.672
Taiko	3.269 $\pm$ 0.050	16.022 $\pm$ 0.017	3.253 $\pm$ 0.162
Mesdag	2.720 $\pm$ 0.030	12.819 $\pm$ 0.101	1.114 $\pm$ 0.055

SD – standard deviation; RSD – relative standard deviation

RSD for ABTS-test: 0.22–10.17%; RSD for DPPH-test: 1.13–1.39 %; RSD for EPR-test: 5%

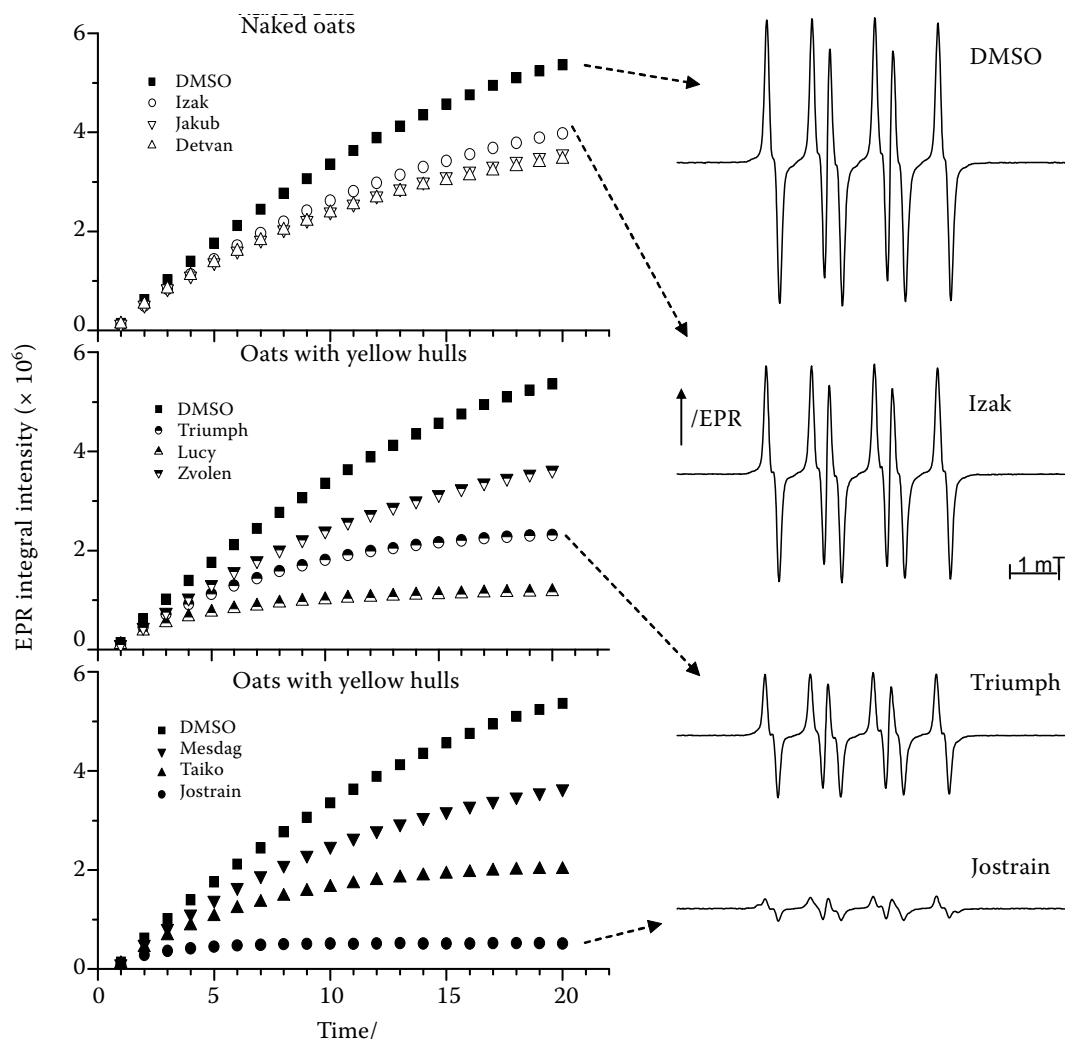


Figure 1. The time course of EPR integral intensities of DMPO spin adducts observed in the reference system (DMSO) and with the extracts of naked oats; oats with yellow hulls and oats with black hulls in the EPR/spin trapping experiments. Representative EPR spectra of spin adducts taken in 20<sup>th</sup> min for selected oat cultivars at identical intensity scale are shown in the right part

between the hull colour and RSC of the oat extract was not observed, but generally the covered oats possessed a higher ability to scavenge oxygen- and carbon-centered reactive radicals generated by the thermal decomposition of  $K_2S_2O_8$ . The radical scavenging capacity of the extracts from different cultivars decreased in the following order: Jostrain > Lucy > Taiko > Triumph > Detvan > Jakub > Zvolen > Mesdag > Izak.

A further comparison of the results of the three different antioxidant capacity methods, expressed in percentages of scavenged radicals, is presented in Figure 2. Under the given experimental conditions, the black oats quenched 74% of the ABTS radicals on average, whereas the yellow oats quenched 48% and naked oats only 26%. All samples also

considerably reduced the concentration of DPPH radicals – 82% (black oats), 53% (yellow oats) and 29% (naked oats), on average. The extract of black oat variety Jostrain quenched 91% of the reactive radicals as measured by the EPR/spin trapping method. Statistical analyses for the DPPH test and ABTS test showed significant differences ( $P \leq 0.05$ ) between the oat genotypes, however, these differences were not so significant in the EPR/spin trapping test.

#### Total phenolic and $\beta$ -glucan content

The total phenolic content in each oat sample was examined, since the phenolics might be the major contributors to the antioxidant activities observed.

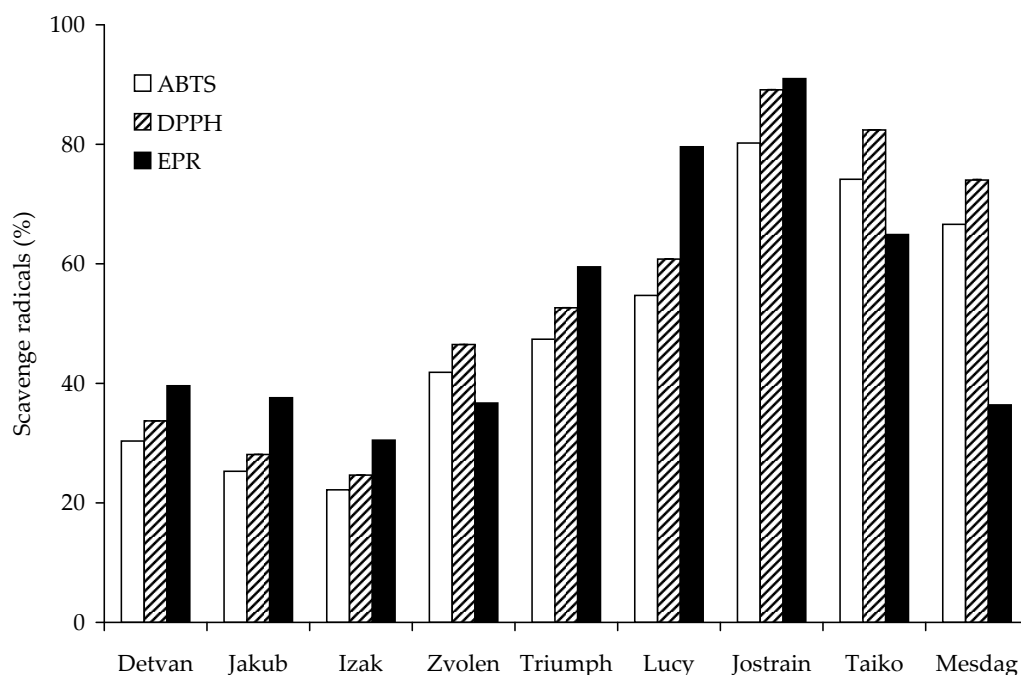


Figure 2. Antioxidant capacity of oat varieties, expressed as the percentage of scavenged radicals relative to the reference sample, determined by ABTS, DPPH, and EPR/spin-trapping method, respectively

Total phenolic content in the oats studied differed significantly between the varieties with values of 239–662  $\mu\text{g GAE/g}$  of dry weight (Figure 3). Generally, the phenolic content in black oats was 1.3 times higher than in the yellow varieties and 2.3 times higher than in the naked oats. The highest phenolic content was found in the cv. Jostrain (662  $\mu\text{g GAE/g}$ ) while cv. Izak was characterised by the lowest phenolic values (239  $\mu\text{g GAE/g}$ ). The amounts of total phenolics in naked oats used in our study were similar to five oat cultivars (238 to 278  $\mu\text{g GAE/g}$ ) tested by EMMONS and PETERSON (1999), oat grains (300  $\mu\text{g GAE/g}$ ) and oat groats (400  $\mu\text{g GAE/g}$ ) as observed by KÄHKÖNEN *et al.* (1999), and oat groats (651  $\mu\text{g GAE/g}$ ) as reported by MATTILA *et al.* (2005). An exceptionally high concentration of phenols (1138  $\mu\text{g GAE/g}$ ) was found by HOLASOVÁ *et al.* (2002) in a not defined oat cultivar.

Table 2 shows the variation coefficients (CV) of the phenolic contents in our oat groups, which characterise the variability of the data set studied. Interestingly, quite a low variation coefficient was observed with the black oat cultivars which indicates a high degree of stability of phenolic compounds biosynthesis in these crops.

Table 2. Standard errors (S.E.) and variation coefficients (CV) calculated for phenolics and  $\beta$ -glucans present in oats

Samples		Phenolics	$\beta$ -glucans
Naked oats	S.E.	0.0308	0.4986
	CV (%)	11.26	7.82
Oats with yellow hulls	S.E.	0.0733	0.6503
	CV (%)	15.29	17.22
Oats with black hulls	S.E.	0.0285	0.7702
	CV (%)	4.50	19.94

The total phenolic contents in the oat samples studied and their antioxidant activities evaluated by the ABTS and DPPH assays are highly correlated ( $R = 0.976$  and  $R = 0.924$ , respectively) as shown in Figure 4. This correlation provides strong evidence that the predominant source of the antioxidant activity derives from the phenolic compounds and is in good agreement with the results provided by other groups (ADOM & LIU 2002; BRYNGELSSON *et al.* 2002). The phenolic compounds in oats may be therefore able to cap-

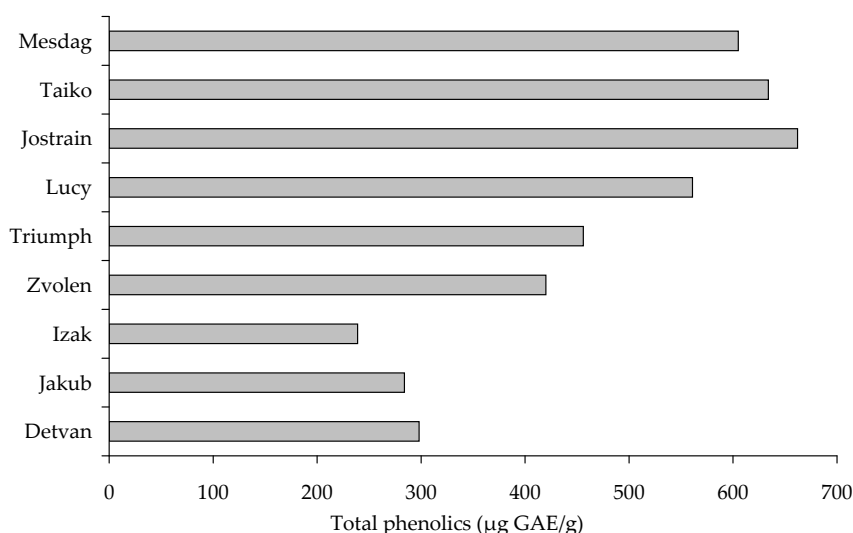


Figure 3. Amounts of total phenolics in oat cultivars

ture the free radicals formed in the human body, if their consumption is supported. However, the antioxidant activity of non-phenolic compounds should be also taken into account (PILARSKI *et al.* 2006) as these may also considerably contribute to the total hydrogen-donating capacity of the oat extracts (BRYNGELSSON *et al.* 2002).

The additional protective effect of oats is ascribed to the dietary fibres and especially to the soluble  $\beta$ -glucans. The  $\beta$ -glucan content in each variety was therefore studied and is presented in Figure 5. The  $\beta$ -glucan contents in covered oats varied between 3.1 and 4.7% (w/w) and in naked oats ranged between 5.8 and 6.8% (w/w), respectively. Slightly lower  $\beta$ -glucan contents were observed among oats from Greece (2.1 to 3.9%) by PAPAGEORGIOUS *et al.* (2005). The  $\beta$ -glucan

contents of covered oats cultivars decreased in the order Jostrain > Lucy > Taiko > Triumph > Zvolen > Mesdag. This trend likely corresponds to the variations in the radical scavenging activity investigated by the EPR/spin trapping method (Figure 6). Moreover, there are several reports that the  $\beta$ -glucan contents of oats are highly influenced by genotypic and environmental factors (LIM *et al.* 1992; JOHANSSON *et al.* 2000). From this point of view, it is interesting that the variation coefficients of  $\beta$ -glucan content were much lower in the naked varieties (7.8%) than in the covered ones (17.2–19.9%). Such a high stability of  $\beta$ -glucan formation in naked oats (expressed by low CV) and wide variability of  $\beta$ -glucans in covered oats might be used as one of taxonomic markers for these two groups of oats.

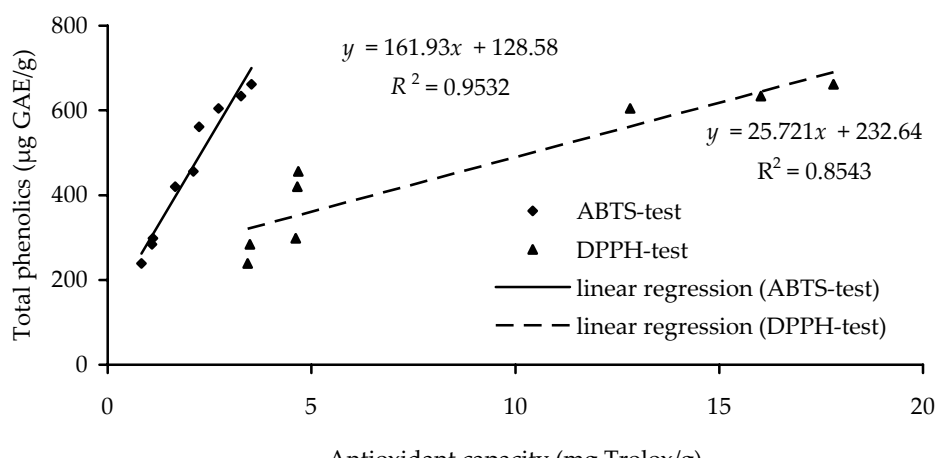


Figure 4. The correlation between the total phenolics and the antioxidant capacity of eight oat varieties expressed in TEAC, determined by ABTS and DPPH assays

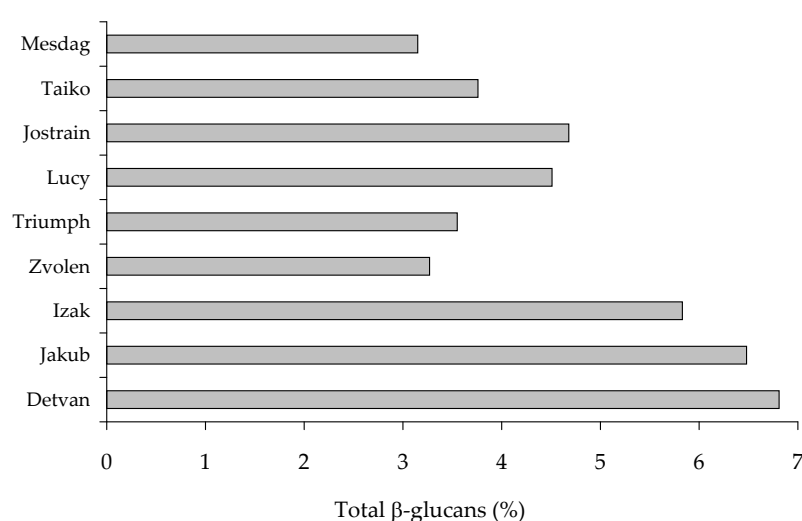


Figure 5. Amounts of β-glucans (% w/w) in oat cultivars

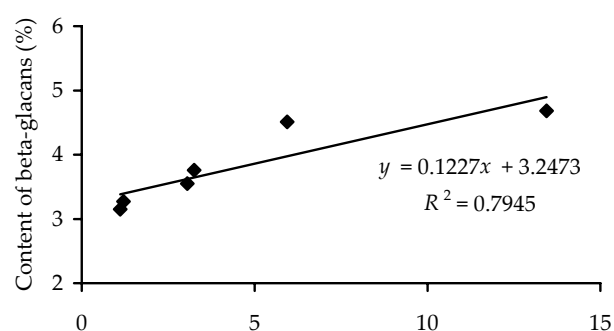


Figure 6. The correlation between TEAC determined in EPR spin-trapping experiments and the β-glucans content of six covered oats

### Lipids profile

Lipids in foods are an important nutritional factor and their profile may play a crucial role as

concerns the stability of cereal products. In addition to the detailed studies of the antioxidant content in grains, a precise mapping of alternations in lipid structures and fatty acid levels in grain varieties attract much attention. Fatty acids that contain two or more unsaturated bonds are normally unstable and oxidise readily in air or when exposed to light and high temperature. Therefore, fatty acid compositions of the investigated oat varieties were further determined. Lipids in the oat varieties studied were about 75% unsaturated, consisting of nearly equal amounts of oleic and linoleic acids, and 1–2% linolenic acid (Table 3). This results in quite a high degree of fatty acid unsaturation (1.13–1.27) in oat lipids. Palmitic acid (14–17%) was the main saturated fatty acid. The present study revealed that an increase in linoleic acid level was accompanied by a reduction of oleic acid

Table 3. Fatty acid composition of oat cultivars

Cultivar	Fatty acids (%)									IU
	14:0	16:0	16:1	18:0	18:1–9c	18:1–11c	18:2	18:3	20:1	
Detvan	0.3	17.2	0.2	1.9	38.2	1.0	36.8	1.2	0.8	1.17
Jakub	0.2	15.5	0.2	2.1	42.2	0.8	35.4	1.3	0.8	1.19
Izak	0.3	16.2	0.2	1.6	38.7	1.0	38.1	1.3	0.8	1.21
Zvolen	0.3	15.9	0.3	1.3	33.4	1.1	42.7	1.9	0.9	1.27
Triumph	0.4	16.6	0.2	2.1	35.6	0.9	37.3	1.2	0.8	1.16
Lucy	0.3	15.7	0.2	2.2	37.9	0.8	35.1	1.2	0.8	1.13
Jostrain	0.3	15.6	0.2	2.2	39.6	0.9	34.4	1.1	0.8	1.14
Taiko	0.3	17.3	0.3	1.4	34.9	1.3	40.2	1.3	0.9	1.22
Mesdag	0.3	13.8	0.2	1.9	41.8	1.0	34.6	1.2	1.0	1.17



content. Similar varietal alterations in fatty acids composition of oat lipids were also reported previously (DE LA ROCHE *et al.* 1977; SAASTAMOINEN *et al.* 1989). However, no significant differences in the fatty acid profile between naked and covered oats were found. Because the covered oat types are characterised by a high capacity to scavenge reactive radicals, these results might indicate that unsaturated fatty acids are protected from the undesired oxidation by phenolic compounds found in large quantities in the investigated oats.

### CONCLUSIONS

This study was designed to determine the total phenolic compounds,  $\beta$ -glucans, and lipids in nine oat varieties and their relationships and contributions to the total antioxidant activities. Two standard spectroscopic assays based on ABTS and DPPH reagents were applied in order to characterise the antioxidant capacity of oat extracts. The best antioxidant capacity was found with the black oats (74% and 82% of scavenged radicals on average in ABTS and DPPH tests, respectively). Our data show for the first time that the colour of oat hulls plays a significant role in their antioxidant activity. The EPR/spin-trapping method revealed that the antioxidants present in hull oats, namely in cvs Jostrain, Lucy and Taiko, show a higher ability to scavenge reactive radicals than those from the rest of the oats followed.

Significant variations were found in the total phenolic compounds, total lipid and  $\beta$ -glucan contents of flours from the oat varieties as well as in their total antioxidant and radical scavenging activities. The antioxidant activity investigated by ABTS and DPPH assays and total phenolics were highly correlated. In addition, there were significant differences in total phenolics,  $\beta$ -glucans, and antioxidants between naked and covered oats and also between oats with black and yellow hulls used in this study.

The largest part of the oat production for food industry in the Slovak Republic is covered by the yellow oat cv. Zvolen and the naked cv. Detvan. Black oats are planted on a much smaller scale and are almost exclusively used for horse breeding. However, our results indicate that the black oats are a rich source of antioxidant compounds and should be used for processing, nutrition, and stabilisation of fat containing food. The black hull cv. Jostrain, with its outstanding properties, is the

best candidate for a more extensive cultivation in the future.

**Acknowledgement.** The authors thank SCPV, VÚRV Piešťany, VŠS Víglaš-Pstruša for providing the oats for this research project.

### References

- ADOM K.K., LIU R.H. (2002): Antioxidant activity of grains. *Journal of Agricultural and Food Chemistry*, **50**: 6182–6187.
- ARTS M.J.T.J., HAENEN G.R.M.M., VOSS H.-P., BAST A. (2004): Antioxidant capacity of reaction products limits the applicability of the Trolox Equivalent Antioxidant Capacity (TEAC) assay. *Food and Chemical Toxicology*, **42**: 45–49.
- BRYNGELSSON S., MANNERSTEDT-FOGELFORS B., KAMAL-ELDIN A. (2002): Lipids and antioxidants in groats and hulls of Swedish oats (*Avena sativa* L.). *Journal of the Science of Food and Agriculture*, **82**: 606–614.
- ČERTÍK M., ANDRÁŠI P., ŠAJBIDOR J. (1996): Effect of extraction methods on lipid yield and fatty acid composition of lipid classes containing gamma-linolenic acid extracted from fungi. *Journal of the American Oil Chemists' Society*, **73**: 357–365.
- ČERTÍK M., SHIMIZU S. (2000): Kinetic analysis of oil biosynthesis by arachidonic acid-producing fungus, *Mortierella alpina* 1S-4. *Applied Microbiology and Biotechnology*, **54**: 224–230.
- CHARALAMPOPOULOS D., WANG R., PANDIELLA S.S., WEBB C. (2002): Application of cereals and cereal components in functional foods: a review. *International Journal of Food Microbiology*, **79**: 131–141.
- CHEN CH.-Y., MILBURY P.E., KWAK H.-K., COLLINS F.W., SAMUEL P., BLUMBERG J.B. (2004): Avenanthramides and phenolic acids from oats are bioavailable and act synergistically with vitamin C to enhance hamster and human LDL resistance to oxidation. *Journal of Nutrition*, **134**: 1459–1466.
- CHRISTOPHERSON S.W., GLASS R.L. (1969): Preparation of milk fat methyl esters by alcoholysis in an essentially nonalcoholic solution. *Journal of Dairy Science*, **52**: 1289–1290.
- CZERWIŃSKI J., BARTNIKOWSKA E., LEONTOWICZ H. (2004): Oat (*Avena sativa* L.) and amaranth (*Amaranthus hypochondriacus*) meals positively affect plasma lipid profile in rats fed cholesterol-containing diets. *Journal of Nutritional Biochemistry*, **15**: 622–629.
- DELANEY B., NICOLOSI R.J., WILSON T.A., CARLSON T., FRAZER S., ZHENG G.-H., HESS R., OSTERGREN K., HAWORTH J., KNUTSON N. (2003): B-glucan fractions

- from barley and oats are similarly anthiatherogenic in hypercholesterolemic Syrian golden hamsters. *American Society of Nutrition Science*, **22**: 468–475.
- DE LA ROCHE I.A., BURROWS V.D., MCKENZIE R.I.H. (1977): Variation in lipid composition among strains of oats (*Avena sativa* L.). *Cereal Chemistry*, **72**: 335–340.
- DEMIRBAS A. (2005):  $\beta$ -glukan and mineral nutrient contents of cereals grown in Turkey. *Food Chemistry*, **90**: 773–777.
- EMMONS CH.-L., PETERSON D.M. (1999): Antioxidant activity and phenolic content of oat as affected by cultivar and location. *Crop Science*, **41**: 1676–1681.
- ESPOSITO F., ARLOTTI G., BONIFATI A.M. (2005): Antioxidant activity and dietary fibre in durum wheat bran by-products. *Food Research International*, **38**: 1167–1173.
- HARELAND G.A., MANTHEY F.A. (2003): Oats. In: *Encyclopedia of Food Sciences and Nutrition*. 7. 1<sup>st</sup> Ed. Elsevier Academic Press, Oxford: 4213–4220.
- HOLASOVÁ M., FIEDLEROVÁ V., SMRCINOVÁ H., ORSAK M., LACHMAN J., VAVREINOVA S. (2002): Buckwheat – the source of antioxidant activity in functional foods. *Food Research International*, **35**: 207–211.
- JOHANSSON L., VIRKKI L., MAUNU S., LEHTO M., EKHOLM P., VARO P. (2000): Structural characterization of water soluble  $\beta$ -glucan of oat bran. *Carbohydrate Polymers*, **42**: 143–148.
- JOHANSSON L., TUOMAINENE P., YLINEN M., EKHOLM P., VIRKKI L. (2004): Structural analysis of water-soluble and -insoluble  $\beta$ -glucans of whole-grain oats and barley. *Carbohydrate Polymers*, **58**: 267–274.
- KÄHKÖNEN M.P., HOPIA A.I., VOURELA H.J., RAUHA J.-P., PIHLAJA K., KUJALA T.S., HEINOMEN M. (1999): Antioxidant activity of plant extracts containing phenolic compounds. *Journal of Agricultural and Food Chemistry*, **47**: 3954–3962.
- KATALINIC V., MILOS M., KULISIC T., JUKIC M. (2006): Screening of 70 medical plant extracts for antioxidant capacity and total phenols. *Food Chemistry*, **94**: 550–557.
- LIM H.S., WHITE P.J., FRY K.J. (1992): Genotypic effects on  $\beta$ -glucan content of oat lines grown in two consecutive years. *Cereal Chemistry*, **69**: 262–265.
- LIU L., ZUBIK L., COLLINS W., MARKO M., MEYDANI M. (2004): The antiatherogenic potential of oat phenolic compounds. *Atherosclerosis*, **175**: 39–49.
- LYLY M., SALMENKALLIO-MARTTILA M., SUORTTI T., AUTIO K., POUTANEN K., LÄHTEENMÄKI L. (2004): The sensory characteristics and rheological properties of soups containing oat and barley  $\beta$ -glucan before and after freezing. *Lebensmittel-Wissenschaft und -Technologie*, **37**: 749–761.
- MATTILA P., PIHLAVA J.-M., HELLSTRÖM J. (2005): Contents of phenolic acids, alkyl- and alkenylresorcinols, and avenanthramides in commercial grain products. *Journal of Agricultural and Food Chemistry*, **53**: 8290–8295.
- MILLER H.E., RIGELHOF F., MARQUART L., PRAKASH A., KANTER M. (2000): Antioxidant content of whole grain breakfast cereals, fruits and vegetables. *Journal of the American College of Nutrition*, **19**: 312–319.
- PAPAGEORGIOU M., LAKHDARA N., LAZARIDOU A., BILIADERIS C.G., IZYDORCZYK M.S. (2005): Water extractable (1–3, 1–4)- $\beta$ -D-glucans from barley and oats: An intervarietal study on their structural features and rheological behaviour. *Journal of Cereal Science*, **42**: 213–224.
- PETERSON D.M. (2001): Oat antioxidants. *Journal of Cereal Science*, **33**: 115–129.
- PETERSON D.M., EMMONS CH.L., HIBBS A.H. (2001): Phenolic antioxidants and antioxidant activity in pearling fractions of oat groats. *Journal of Cereal Science*, **33**: 97–103.
- PETERSON D.M., HAHN M.J., EMMONS CH.L. (2002): Oat avenanthramides exhibit activities *in vitro*. *Food Chemistry*, **79**: 473–478.
- PILARSKI R., ZIELIŃSKI H., CIESIOŁKA D., GULEWICZ K. (2006): Antioxidant activity of ethanolic and aqueous extracts of *Uncaria tomentosa* (Willd.) DC. *Journal of Ethnopharmacology*, **104**: 18–23.
- PIRJO M., JARKKO H., PILHAV J.-M. (2003): The content of phenolic acid in some grain products. In: *Abstract Books 1<sup>st</sup> International Conference on Polyphenols and Health*, Institut National de la Recherche Agronomique, Clermont-Ferrand: 207.
- RAGAE S., ABDEL-AAL EL-S.M., NOAMAN M. (2006): Antioxidant activity and nutrient composition of selected cereals for food use. *Food Chemistry*, **98**: 32–38.
- RAPTA P., POLOVKA M., ZALIBERA M., BREIEROVA E., ZITNANOVA I., MAROVA I., CERTIK M. (2005): Scavenging and antioxidant properties of compounds synthesized by carotenogenic yeasts stressed by heavy metals – EPR spin trapping study. *Biophysical Chemistry*, **116**: 1–9.
- RE R., PELLEGRINI N., PROTEGGENTE A., PANNALA A., YANG M., RICE-EVANS C. (1999): Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radical Biology & Medicine*, **26**: 1231–1237.
- SAASTAMOINEN M., KUMPULAINEN J., NUMMELA S. (1989): Genetic and environmental variation in oil content and fatty acid composition of oats. *Cereal Chemistry*, **66**: 296–300.
- TUDORICA C.M., KURI V., BRENNAN C.S. (2002): Nutritional and physicochemical characteristics of dietary

- fiber enriched pasta. *Journal of Agricultural and Food Chemistry*, **50**: 347–356.
- WEISS E., KISLEV M.E., HARTMANN A. (2006): Autonomous cultivation before domestication. *Science*, **312**: 1608–1610.
- XING Y., WHITE P.J. (1997): Identification and function of antioxidants from oat groats and hulls. *Journal of the American Oil Chemists' Society*, **74**: 303–307.
- YEN G.CH., CHEN H.Y. (1995): Antioxidant activity of various tea extracts in relation to their mutagenicity. *Journal of Agricultural and Food Chemistry*, **43**: 27–32.
- YU L., HALEY S., PERRET J., HARRIS M. (2004): Comparison of wheat flours grown at different locations for their antioxidant properties. *Food Chemistry*, **86**: 11–16.
- ZWER P.K. (2004): Oats. In: *Encyclopedia of Grain Science*. Vol. 2, 1<sup>st</sup> Ed. Elsevier Academic Press, Oxford: 365–368.

Received for publication May 25, 2007

Accepted after corrections February 19, 2008

---

*Corresponding author:*

Ing. LUCIA BRINDZOVÁ, Slovenská technická univerzita, Fakulta chemickej a potravinárskej technológie, Ústav biotechnológie a potravinárstva, Oddelenie výživy a hodnotenia potravín, Radlinského 9, 812 37 Bratislava, Slovenská republika  
tel.: + 421 259 325 761, fax: + 421 252 967 085, e-mail: lucia.brindzova@stuba.sk

---