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Whole grain phenolics and antioxidant activity of *Triticum* cultivars and wild accessions

DJORDJE MALENČIĆ¹, BILJANA KIPROVSKI^{2*}, VOJISLAVA BURSIĆ¹,
GORICA VUKOVIĆ³, NIKOLA HRISTOV² and ANKICA KONDIĆ-ŠPIKA²

¹Faculty of Agriculture, University of Novi Sad, Trg Dositeja Obradovića 8, 21000 Novi Sad, Serbia, ²Institute of Field and Vegetables Crops, Maksima Gorkog 30, 21000 Novi Sad, Serbia and ³Institute of Public Health of Belgrade, Bulevar Despota Stefana 54, 11000 Belgrade, Serbia

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Abstract: The contents of soluble free phenolics (SP), PVPP-bound tannins (PVPP-P), flavonoids (TF) and proanthocyanidins (PA), as well as the DPPH-radical scavenging capability, of the whole grain of 17 different *Triticum* spp. accessions were analyzed. The contents of SP ranged from 976 to 2927 $\mu\text{g CE g}^{-1}$, of PVPP-P from 335 to 1412 $\mu\text{g CE g}^{-1}$ and of TF from 0.16 to 1.12 $\mu\text{g RE g}^{-1}$ of dry whole grain. The presence of PA in the whole grains was not established. The values for DPPH-radical scavenging activity were rather moderate, under 40 % of neutralized radicals. A positive correlation between DPPH-activity and analyzed phenolics was recorded in twelve of the seventeen genotypes (r from 0.73 to 0.99). *trans*-Cinnamic acid was the major compound among acids and quercetin among flavonoids found in the wheat varieties. The data obtained should enable the selection of the accessions rich in biologically active compounds that could further be processed into functional food with possible health benefits associated with higher antioxidant properties.

Keywords: wheat; polyphenolics; grain; tannins; flavonoids; antioxidants.

INTRODUCTION

Wheat (*Triticum aestivum* L.) is an important agricultural crop and a primary food ingredient worldwide. Its products are essential components of the human diet, mainly because of the energy they provide, due to their high carbohydrate contents. Wheat and wheat-based food ingredients rich in natural antioxidants can serve as a basis for the development of functional foods. Growing evidence indicates that the intake of whole wheat foods may be associated with many health benefits, which are attributed to bioactive factors, such as non-digestible

* Corresponding author. E-mail: bkiprovski@gmail.com
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carbohydrates and phytochemicals with antioxidant properties.¹ Many phenolic classes found in plant tissues (in addition to tocopherols) are potential antioxidants: flavonoids, tannins, proanthocyanidins, anthocyanins and lignin precursors may all act as scavenging compounds for reactive oxygen species (ROS).² Phenolic acids, as well as their associated antioxidant activity, have been widely studied in recent years.³ Along with flavonoids, phenolic acids represent the most common form of phenolic compounds found in whole grains. They are among the major and most complex groups of phytochemicals with a number of types that exist as soluble free compounds, soluble conjugates that are esterified to sugars and other low molecular mass compounds, and insoluble bound forms.⁴ However, the crucial obstacle to the use of these compounds is their bioavailability, which is determined by their bioaccessibility. Mateo Anson *et al.*⁵ reported that only the free and conjugated forms phenolic acids in breads are bio-accessible, due to their solubility.

The aim of this study was to examine the content of phenolics, the antioxidant activity and the composition free phenolic acids of the whole grain of *Triticum* spp. accessions growing in Serbia. The data obtained should enable the selection of the genotypes rich in biologically active compounds that could be further processed as functional food.

EXPERIMENTAL

Materials

Thirteen samples of the whole grain of wild relatives of winter wheat from the gene-bank collection of the Institute of Field and Vegetable Crops, Novi Sad were analyzed and compared to four commercially grown winter wheat cultivars, *i.e.*, Pobeda, Simonida, NS 40S (*Triticum aestivum*) and Nirvana (*T. spelta*). The study was realized at the experimental field of the Institute of Field and Vegetable Crops, Novi Sad, Serbia (45°33'N, 19°85'E, 82 m altitude). The location is characterized by semi-arid conditions with dry, hot springs and summers, neutral autumns and moderately cold winters. The soil type was Chernozem Chernic.⁶ The seeds were sown in a randomized complete block design with three replicates. Each plot consisted of 6 rows, 15 cm apart and 2.2 m long (the harvested area was 2 m²). Seedling density was 350 seeds m⁻². All the genotypes were sown in the middle of October (optimum sowing date) and plants reached maturity in late June 2010. Weeds were controlled by hand. The grains of all seventeen genotypes were collected at the full maturity stage for the *in vitro* experiments. The collected plant material was dried in a shaded and well-ventilated place and kept refrigerated (-20 °C) in dark all-glass containers until extracted.

Extraction of soluble free phenolic compounds

Plant material (1 g of whole grain per sample) was ground to a fine powder in a mill and extracted for 20 min under sonication in an ultrasonic bath at ambient temperature (1 g:50 mL). Soluble free phenolics, tannins and proanthocyanidins were determined in 70 % aqueous acetone extracts, and the total flavonoids in MeOH:H₂O:CH₃COOH (volume ratio of 140:50:10) extracts. The DPPH-radical scavenging activity was assayed in absolute EtOH grain extracts. The extracts were rapidly vacuum-filtered through a sintered glass funnel and kept refrigerated until assayed.

Determination of soluble free phenolics, PVPP-bound tannins, flavonoids and proanthocyanidins content

Acetone-soluble phenolics, soluble free phenolics (SP) were determined by the Folin–Ciocalteu procedure.⁷ Aliquots (0.1 mL) of aqueous acetone extracts were transferred into test tubes and their volumes were made up to 0.5 mL with distilled water. After addition of Folin–Ciocalteu reagent (0.25 mL) and 20 % aqueous sodium carbonate solution (1.25 mL), the tubes were vortexed and after 40 min, the absorbance of the resulting blue-colored mixture was recorded at 725 nm against a blank containing only extraction solvent (0.1 mL). The amount of SP was calculated as the catechin equivalent from the calibration curve of catechin standard solutions (covering the concentration range between 0.1 and 1.0 mg mL⁻¹) and expressed as µg catechin equivalents per g dry whole grain (µg CE g⁻¹ d.w.g.).

The content of poly(vinylpyrrolidone)-bound phenolics (PVPP-P) was determined by the Folin–Ciocalteu procedure as above, after removal of tannins by adsorption on an insoluble matrix (PVPP). Insoluble, cross-linked PVPP (Sigma, Germany; 0.1 g) was weighed into test tubes and the aqueous acetone extracts (1 mL) added. After 15 min at 4 °C, the tubes were vortexed and centrifuged for 10 min at 4350g. Aliquots of supernatant (0.1 mL) were transferred into test tubes and non-absorbed phenolics determined as described. The calculated values were subtracted from the SP contents and the PVPP-P content is expressed as µg CE g⁻¹ d.w.g. For the determination of total flavonoids (TF), the extracts (2.5 mL) were transferred into 50 mL volumetric flasks and their volumes made up with water. To each 10 mL of analysis solution, water (2 mL) and AlCl₃ reagent (0.13 g crystalline aluminum chloride and 0.40 g crystalline sodium acetate dissolved in 100 mL of extraction solvent, 5 mL) were added and the absorbances were recorded at 430 nm against a blank (10 mL of analyzed solution plus 5 mL of water). The amount of flavonoids was calculated as the rutin equivalent (RE) from the calibration curve of rutin standard solutions and are expressed as µg RE g⁻¹ d.w.g.⁸

Proanthocyanidins (PA) were determined by a butanol–HCl assay.⁷ In brief, aliquots of prepared extracts (0.5 mL) were transferred into test tubes. After addition of butanol–HCl reagent (volume ratio of 95:5; 3 mL) and 2 % ferric reagent (2 % ferric ammonium sulfate in 2 M HCl, 0.1 mL), the test tubes were vortexed and placed in a boiling water-bath for 60 min. After cooling, the absorbances were recorded at 550 nm against a blank containing solvent (0.5 mL) instead of the extract. Proanthocyanidins are expressed as µg leucoanthocyanidin per g d.w.g., assuming that the specific absorbance of leucoanthocyanidin was at 460 nm.

Antioxidant activity (DPPH-test)

For this investigation, the total potential antioxidant activity of the investigated whole grain extracts was assessed based on their scavenging of 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radicals.⁹ One mL of the absolute EtOH solution of the sample (1:10, w/v) was mixed with an ethanolic 0.5 mmol DPPH solution (0.5 mL) and 0.1 mol acetate buffer (pH 5.5, 1 mL). After standing for 30 min, the absorbance of the mixture was measured at 517 nm against a blank containing absolute EtOH (0.5 mL) instead of a sample aliquot. The DPPH-radical scavenging activity is expressed as % of the control.

Separation and identification of phenolic acids and flavonoids

All solvents used were of chromatographic grade and were obtained from J. T. Baker (Deventer, Netherlands). The analytical standards used in the research were gallic acid (99.9 %), chlorogenic acid (95.0 %), *trans*-cinnamic acid (99.0 %), *o*-coumaric acid (97.0 %), *p*-coumaric acid (98.0 %), caffeic acid (98.0 %), ferulic acid (99.0 %), (+)-catechin hydrate (96.0 %), quercetin (98.0 %) and kaempferol (97.0 %), all manufactured by Sigma–Aldrich.

Acetic acid was of “pure for analysis” grade from Carl Roth. The basic standard solutions were prepared by dissolving an analytical standard in methanol while the working solution, *i.e.*, a mixture of the studied phenolic compounds, was obtained by mixing and diluting the basic standards with mobile phase resulting in a final mass concentration of 10 µg ml⁻¹. The composite mixtures of all phenol acids at appropriate concentrations were used to spike samples in recovery experiments. The extraction of phenolic compounds was performed from 0.5 g of the sample with the addition of 10 mL of EtOH at a constant 60 °C temperature.^{10,11} The chromatographic separation for phenolic compounds was achieved using an Agilent 1100 (Agilent Technologies, USA) HPLC system with a binary pump and diode array detector (DAD). The phenolic acids were separated on a ZORBAX SB-Aq column (5 µm particle size: 4.6 × 250 mm, Agilent) and the other phenolic compounds on a ZORBAX SB-C18 column (5 µm particle size: 3.0 mm×250 mm, Agilent). The extracts were filtered through 0.45-µm syringe filters and directly injected through a 20 µL fixed loop onto the column. Two methods were used for the separation of the phenolic compounds.

The analysis of phenolic acids was performed in the negative ionization mode. An Agilent 1200 system (Agilent Technologies, USA) with a binary pump was used. This was equipped with a reversed-phase C18 analytical column of 150 mm×4.6 mm and 1.8 µm particle size (Agilent Zorbax Eclipse XDBC18). The mobile phases were 0.1 % formic acid in methanol (solvent A) and 0.1 % formic acid in Milli-Q water (solvent B). The gradient was 0 min (80 % B), 10 min (50 % B), 20 min (5 % B), 24 min (0 % B), and 25 min (80 % B), at a flow rate 0.6 mL min⁻¹. An Agilent 6410 Triple-Quad LC/MS and Agilent MassHunter data acquisition system was applied for the mass spectrometric analysis. Qualitative Analysis and Quantitative Analysis software were used for method development and data acquisition. The linearity and precision values for all the tested phenolic compounds are presented in Table I.

TABLE I. Phenolic compounds analyzed by LC–MS/MS and some of their MS and analytical performance characteristics; *Rt* – retention time, Frag – fragmentor, *CE* – collision energy, *LOQ* – limits of quantification, *R*² – linearity, *RSD* – relative standard deviation

Phenolic compound	<i>Rt</i> min	Precursor→product ion	Frag V	<i>CE</i> V	<i>LOQ</i> µg mL ⁻¹	<i>R</i> ²	<i>RSD</i> %
Galic acid	1.65	169→125	110	10	0.1	0.9969	11.13
Chlorogenic acid	4.01	353→190	100	10	0.1	0.9945	8.65
<i>trans</i> -Cinamic acid	13.27	147→147	100	10	0.1	0.9816	10.79
<i>o</i> -Coumaric acid	7.25	163→117	100	25	0.1	0.9954	12.29
		163→119	100	10			
<i>p</i> -Coumaric acid	9.05	163→93	100	10	0.1	0.9941	15.6
		163→119	100	10			
Caffeic acid	5.15	179→135	100	10	0.1	0.9918	11.62
Ferulic acid	10.16	193→134	100	10	0.1	0.9972	12.10
		193→177.5	100	10			
(+)-Catechin	3.32	289→205	135	10	0.1	0.9941	9.94
		289→245	120	10			
Quercetin	11.62	301→151	135	10	0.1	0.9944	11.79
		301→179	100	10			
Kaempferol	14.89	285→169	100	25	0.1	0.9920	6.79
		285→257	100	15			

Statistical analyses

Values of the biochemical parameters are expressed as means \pm standard error of determinations made in triplicates. The correlations between antioxidant activity and investigated phenolics contents are expressed as correlation coefficients (r) and tested for significance by the t -test ($P < 0.05$). To discover natural groupings of the samples, cluster analysis was performed with unweighted pair-group average analysis using the Euclidean distance. All statistical analyses were performed using Statistica for Windows version 11.0.

RESULTS AND DISCUSSION

The content of SP ranged from 976 to 2927 $\mu\text{g CE g}^{-1}$ d.w.g. The highest levels of all phenolic classes investigated were recorded in the whole grain of wild *Triticum* accessions (genotype No. 17 (*Triticum* L. var. Vulga I), followed by genotype No. 15 (*T. dicoccum* var. Inerne D), 16 (*T. dicoccum* Sherik var. lig) and 6 (*T. macha* 1)), while the SP contents in the wheat cultivars (particularly genotype No. 3) were significantly lower (Table II). In other samples, the SP levels were lower and rather uniform being close to 1300 $\mu\text{g CE g}^{-1}$ d.w.g., on average.

TABLE II. The content of soluble free (SP) and PVPP-bound (PVPP-P) phenolics, flavonoids (TF) and DPPH scavenging activity in wheat cultivars and wild accessions ($\bar{X} \pm SEM$)

Genotype No.	Genotype	SP ^a	PVPP-P ^a	TF ^b	DPPH ^c
1	Pobeda (<i>T. aestivum</i>)	1368.8 \pm 105.0	480.5 \pm 140.4	0.16 \pm 0.04	31.5 \pm 4.0
2	Simonida (<i>T. aestivum</i>)	1150.4 \pm 38.5	334.9 \pm 14.5	0.60 \pm 0.11	31.4 \pm 2.2
3	NS 40S (<i>T. aestivum</i>)	975.6 \pm 38.5	364.0 \pm 14.5	0.81 \pm 0.04	29.5 \pm 4.0
4	Nirvana (<i>T. spelta</i>)	1397.9 \pm 151.3	946.5 \pm 162.1	0.28 \pm 0.01	31.8 \pm 1.5
5	<i>T. zhuhovsky</i>	1427.1 \pm 52.5	1033.9 \pm 145.6	0.53 \pm 0.01	37.2 \pm 2.5
6	<i>T. macha</i> 1	1995.0 \pm 267.3	1106.7 \pm 317.3	0.47 \pm 0.01	39.9 \pm 2.3
7	<i>T. macha</i> 2	1237.8 \pm 95.5	800.9 \pm 58.2	0.56 \pm 0.01	31.6 \pm 4.0
8	<i>T. dicoccoides</i> 1	1296.0 \pm 52.5	815.5 \pm 95.5	1.12 \pm 0.01	29.2 \pm 3.4
9	<i>T. dicoccoides</i> 2	1368.8 \pm 124.4	815.5 \pm 20.4	0.37 \pm 0.01	33.6 \pm 5.8
10	<i>T. turgidum</i> var. <i>nigrobarbatum</i>	1310.6 \pm 133.5	655.3 \pm 151.3	0.58 \pm 0.01	31.9 \pm 0.2
11	<i>T. araraticum</i>	1033.9 \pm 138.9	902.8 \pm 177.1	0.67 \pm 0.01	33.1 \pm 0.5
12	<i>T. durum</i> var. <i>caerulescens</i>	1689.2 \pm 58.2	1412.5 \pm 177.1	0.79 \pm 0.01	31.3 \pm 2.5
13	<i>T. polonicum</i> var. <i>levissimum</i>	1397.9 \pm 50.4	1092.1 \pm 50.4	0.74 \pm 0.01	31.2 \pm 1.2
14	<i>T. dicoccum</i> var. <i>farum</i> Ja	1397.9 \pm 90.9	1092.1 \pm 115.5	1.00 \pm 0.02	33.8 \pm 2.4
15	<i>T. dicoccum</i> var. <i>inerne</i> D	2839.6 \pm 87.4	1135.8 \pm 87.4	0.67 \pm 0.01	32.2 \pm 1.3
16	<i>T. dicoccum</i> Sherik var. <i>lig</i>	2009.6 \pm 115.5	640.7 \pm 52.5	0.60 \pm 0.01	29.0 \pm 1.6
17	<i>Triticum</i> L. var. Vulga I	2927.0 \pm 248.4	1310.6 \pm 341.2	0.33 \pm 0.01	38.5 \pm 1.5

^aExpressed as $\mu\text{g catechin g}^{-1}$ dry whole grain; ^bexpressed as $\mu\text{g rutin g}^{-1}$ dry whole grain; ^cexpressed as % of neutralized DPPH free radicals

The affinity of PVPP is proportional to the number of phenolic hydroxyl groups, since the adsorption of polyphenols by PVPP is through hydrogen bonding between the proton donor from the polyphenol and the carbonyl group from

PVPP.¹² The content of PVPP-P ranged from 335 to 1413 $\mu\text{g CE g}^{-1}$ d.w.g. (Table II). The lowest amount was recorded in the wheat cultivars (genotypes No. 1–3), which also showed low SP contents. The highest PVPP-P content was detected in *T. durum* var. *caerulescens*. According to Makkar *et al.*,⁷ PVPP strongly binds with tannins. Contrary to phenolic acids, flavanols (epicatechin and catechin) and flavonols (quercetin and kaempferol) have higher affinities toward PVPP, especially at lower pH value and in the aglycone form.¹³ This implies that PVPP-bound phenolics in the present research could belong to these groups of phenolics (flavanols and flavonols). The presence of PA in the whole grain of the specimens examined in this study was not established, which is in agreement with the results of Žilić *et al.*¹⁴ for bread and durum wheat.

Compared to some other cultivated plants, such as maize and soybean,^{15,16} the wheat whole grains were poor in flavonoids. The TF content ranged from 0.16 to 1.12 $\mu\text{g RE g}^{-1}$ d.w.g. The highest content was recorded in the genotype No. 8 (*T. dicoccoides* 1), followed by the genotype No. 14 (*T. dicoccum* var. *farum Ja*, Table II).

The structure of phenolic compounds is the key determinant of their antioxidant activity, since antioxidant activity of phenolic acids and their ester derivatives depends on the number of hydroxyl groups in the molecule that are affected by steric hindrance from their carboxylate group.¹⁷ The DPPH-radical scavenging activity is a measure of the non-enzymatic antioxidant activity. The DPPH values for the investigated extracts varied in the range between 29.0 % (*T. dicoccum* Sherik var. *lig*) and 39.9 % (*T. macha* 1). Having a high content of all the investigated phenolic classes, the whole grain of samples *T. macha* 1, *Triticum* L. var. *Vulga* and *T. dicoccum* var. *inerne D* expressed the highest DPPH-radical scavenging activity among the tested genotypes. Interest in grain phenolics has increased in recent years because of their activity as antioxidants. As the total phenolic content and antioxidant activity were shown to be highly correlated,¹⁸ the correlation between the results of the antioxidant activity test and the contents of phenolics was tested in this study. Positive correlations between the DPPH values and SP contents were established in the genotypes No. 1, 3, 4, 6, 9, 11 and 14 (r from 0.85 to 0.99) and it was significant in the *T. macha* 1 genotype ($r = 0.99$). The genotypes No. 1, 3, 4, 6, 11 and 14 exhibited positive correlations between the DPPH values and the contents of PVPP-P (r from 0.77 to 0.95), while the genotypes No. 3–6, 9, 12 and 17 showed a positive correlation between the DPPH values and TF content (r from 0.73 to 0.99). Significant correlations between the DPPH values and the PVPP-P and TF contents were recorded only in Nirvana (*T. spelta*, $r = 0.99$) and NS 40S (*T. aestivum*, $r = 0.99$).

A tendency towards grouping of the genotypes in accordance with phenolic contents and antioxidant activity is graphically presented by the dendrogram in Fig. 1. The first, phenolics-high group, includes the genotypes with SP contents

above 2000 $\mu\text{g CE g}^{-1}$ d.w.g. (*Triticum* L. var. *vulga* I and *T. dicoccum* var. *inerne* D), which were clearly separated from the other genotypes. The second, the intermediate one, includes those with SP content between 1000 and 2000 $\mu\text{g CE g}^{-1}$ d.w.g. Finally, the phenolics-low group includes the genotypes that contain less than 1000 $\mu\text{g CE g}^{-1}$ d.w.g. of SP (samples No. 2, 3 and 11). The grouping based on the SP content was made to contribute to a better classification. Despite the difference in the SP contents, it could be clearly distinguished that the cultivars (sample Nos. 1–3) were separated from the rest of the investigated genotypes and sample No. 11 with a low SP content was connected with the intermediate group.

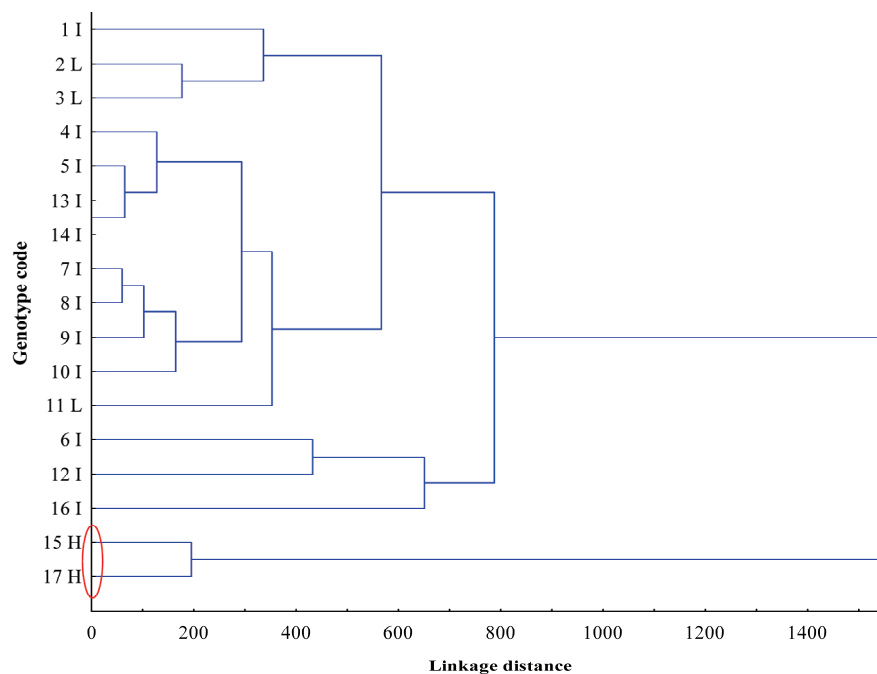


Fig. 1. Dendrogram of the results of a cluster analysis using the content of phenolics and antioxidant activity as variables in the estimated *Triticum* spp. genotypes. For the genotype codes see Table II (L – low, I – intermediate, H – high (eclipse) content of phenolics).

The free phenolic acids and flavonoid composition of the extracts from the wheat whole grain preparations identified by HPLC are given in Table III. The major free acids in the extracts of the cultivars and wild accessions were *trans*-cinnamic and gallic acid (3,4,5-trihydroxybenzoic acid). Żuchowski *et al.*,¹⁹ reported that ferulic acid (3-methoxy-4-hydroxycinnamic acid) was the predominant phenolic acid in the grain of the wheat varieties they tested. In addition, they detected, in low amounts, other phenolic acids, *i.e.*, sinapic acid (4-hydroxy-3,5-dimethoxycinnamic acid), *p*-coumaric acid (4-hydroxycinnamic acid), vanil-

lic acid (4-hydroxy-3-methoxybenzoic acid) and *p*-hydroxybenzoic acid. Cinnamic acid derivatives, such as *p*-coumaric and ferulic acids, are known to be important components of cell walls of cereals, where they dominantly occur in bound form to polymers of the wall.^{20–23} Contrary to this, the contents of *p*-hydroxybenzoic and sinapic acids were comparable in the inner and outer aleurone layers, as they are mainly located in the aleurone intracellular compartment, and are mostly found in conjugated form.^{18,22} For the whole grain flour samples, the flavonoids catechin and apigenin (red sorghum), apigenin (white sorghum) and quercetin occurred in higher quantities compared with the other identified flavonoids. Overall, most of the flavonoids identified in whole grain flour were not detected in the cell wall preparation. The present results also confirmed presence of quercetin in one of *T. aestivum* cultivars (NS 40S), as well as in all the investigated *T. dicoccum* accessions (Table III). If the results from the individual and group phenolics are compared, it could be proposed that the antioxidant capacity of the *T. dicoccum* accessions mostly depended on and correlates with the flavonols content, since the contents of phenolic acids were quite low compared to those of the other accessions (Tables II and III).

TABLE III. Contents of free monomeric compounds in the whole grain of the wheat cultivars and their wild relatives ($\bar{X} \pm SEM$, expressed as $\mu\text{g g}^{-1}$ dry whole grain, nd – not detected)

Genotype	Gallic acid	<i>trans</i> -Cinnamic acid	<i>o</i> -Coumaric acid	<i>p</i> -Coumaric acid	Quercetin
Pobeda (<i>T. aestivum</i>)	nd	1.27±0.00	nd	0.59±0.01	nd
Simonida (<i>T. aestivum</i>)	2.05±0.02	1.59±0.00	nd	0.44±0.01	nd
NS 40S (<i>T. aestivum</i>)	2.23±0.02	0.64±0.00	nd	nd	4.0±0.05
Nirvana (<i>T. spelta</i>)	2.77±0.01	3.5±0.05	nd	nd	nd
<i>T. zhuhovky</i>	2.82±0.00	3.82±0.01	1.23±0.00	nd	nd
<i>T. macha</i> 1	3.40±0.05	5.09±0.03	1.49±0.00	nd	nd
<i>T. macha</i> 2	2.57±0.01	2.86±0.01	nd	0.79±0.00	nd
<i>T. dicoccoides</i> 1	3.52±0.01	6.36±0.01	nd	nd	nd
<i>T. dicoccoides</i> 2	2.94±0.01	4.13±0.02	nd	nd	nd
<i>T. turgidum</i> var. <i>nigrobarbatum</i>	2.67±0.01	0.32±0.02	nd	nd	nd
<i>T. araraticum</i>	3.03±0.04	3.18±0.03	nd	nd	nd
<i>T. durum</i> var. <i>caerulescens</i>	2.29±0.06	0.64±0.00	nd	0.91±0.01	nd
<i>T. polonicum</i> var. <i>levissimum</i>	3.54±0.04	nd	nd	nd	nd
<i>T. dicoccum</i> var. <i>farum</i> Ja	nd	1.59±0.00	nd	nd	2.87±0.01
<i>T. dicoccum</i> var. <i>inerne</i> D	3.07±0.04	4.77±0.01	nd	nd	1.44±0.02
<i>T. dicoccum</i> Sherik var. <i>lig</i>	nd	nd	nd	0.72±0.00	0.70±0.02
<i>Triticum</i> L. var. <i>Vulga</i> I	3.39±0.03	1.53±0.01	nd	nd	nd

Many studies have been devoted to the evaluation of the total antioxidant capacity of foods, its correlation with the phenolic content, and the evaluation of

the changes with cultivation and processing factors. However, recent evidence has indicated that the effects of antioxidants are less relevant than expected, as the antioxidant phenolics are poorly absorbed and extensively metabolized to non-antioxidant metabolites. In addition, many of these compounds have a very low bioavailability and never reach the tissues where they have to exert their antioxidant action in sufficient amounts. According to Adam *et al.*,²³ phenolic compounds bound to endosperm arabinoxylans might be more easily released with respect to phenolics linked to the pericarp or the outer aleurone layer. Moreover, Zaupa *et al.*²⁴ explained that hydroxybenzoic acids presented the highest bioaccessibility in all wheat fractions, likely because of their predominant free form in the undigested fractions. In the previous paper, the authors suggested the isolation and use of wheat fractions in the formulation of new cereal-based products could be a strategy for improving the offer of whole grain products.

According to the results, it seems that capability to accumulate all investigated classes of phenols varies within the cultivated wheat genotypes, as well as within the wild accessions. However, there is a great and significant similarity in the phenolic contents between them, which points to the fact that there is a considerable gene pool to be explored for enhancing the quality of wheat whole grain in future selection work. The whole grain of phenolics-rich genotypes (cultivars and wild accessions) may become potentially attractive, inexpensive and readily available on a large-scale raw material for food with higher antioxidant properties.

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ИЗВОД

САДРЖАЈ ФЕНОЛА И АНТИОКСИДАТИВНА АКТИВНОСТ СЕМЕНА ГАЈЕНИХ И ДИВЉИХ ВРСТА *RODA Triticum*

БОРЂЕ МАЛЕНЧИЋ¹, БИЉАНА КИПРОВСКИ², ВОЈИСЛАВА БУРСИЋ¹, ГОРИЦА ВУКОВИЋ³,
НИКОЛА ХРИСТОВ² и АНКИЦА КОНДИЋ-ШПИКА²

¹Пољопривредни факултет, Универзитет у Новом Саду, Трп Досићеја Обрадовића 8, 21000 Нови Сад,

²Институт за рајшарство и површарство, Максима Горког 30, 21000 Нови Сад и ³Градски Завод за јавно здравље Београд, Булевар десетог Септембра 54, 11000 Београд

У екстрактима семена 17 различитих гајених и дивљих *Triticum* spp. одређен је садржај растворљивих фенола (976–2927 μg катехина g^{-1} суве масе), PVPP-везујућих танина (335–1412 μg катехина g^{-1} суве масе), флавоноида (0,16 до 1,12 μg рутина g^{-1} суве масе) и проантоцијанидина, као и антиоксидативна способност датог екстракта (% неутрализације DPPH радикала). Присуство проантоцијанидина у екстрактима целог семена испитиваних врста није потврђено. Антиоксидативна способност екстракта била је умерена (до 40 % неутралисаних DPPH радикала), а позитивна корелација између датог параметра и анализираних фенолних једињења утврђена је за 12 од 17 генотипова (r , 0,73–0,99). Доминантна киселина је била *trans*-циметна, док је кверцетин био најдо-

минантнији међу флавоноидима. Добијени резултати представљају значајан допринос селекцији генотипова са повећаним садржајем биолошки активних компоненти као извора потенцијалне функционалне хране.

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