Quality Assurance and Safety of Crops & Foods, 2019; 11 (4): 341-349

Wageningen Academic Publishers

A comparison between wheat and different kinds of corn flour based on minerals, free phenolic acid composition and antioxidant activity

N. Nikolić[1*], J. Mitrović[1], I. Karabegović[1], S. Savić[1], S. Petrović[1], M. Lazić[1] and G. Stojanović[2]

[1]University of Niš, Faculty of Technology, Department for Food Technologies and Biotechnology, Bulevar oslobodjenja 124, 16000 Leskovac, Serbia; [2]University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia; nadanikolic64@yahoo.com

Received: 15 August 2018 / Accepted: 6 March 2019

RESEARCH ARTICLE

Abstract

In order to compare different kinds of corn flour (white, yellow and degerminated yellow corn flour) with wheat flour, this paper investigates the content of free phenolics, minerals and phenolic acids composition and antioxidant activity, determined as the DPPH radical scavenging capacity and reducing power. All the samples of corn flour proved to be a better source of phenolic compounds (1,100.51-1,268.26 μg/g) than wheat flour (705.60 μg/g) and had a statistically significant higher antioxidant activity. The yellow and white corn flour had a statistically significant higher content of calcium (1.44-1.84 mg/g), magnesium (1.43-1.45 mg/g), sodium (178.73-183.53 mg/g), potassium (2.59-2.63 mg/g) and zinc (30.11-106.24 μg/g) than the wheat flour (0.26 mg/g, 0.28 mg/g, 47.29 mg/g, 1.41 mg/g and 10.79 μg/g, respectively). The white corn flour was especially stood out from the wheat and other corn flour based on its content of zinc, which is such that 100 g of white corn flour could satisfy 73.1% of an adult man's needs for zinc. Gallic, protocatechuic, chlorogenic, caffeic, coumaric, *trans*-ferulic and syringic acid were detected in the corn flour, while only gallic, protocatechuic and chlorogenic acid were detected in the wheat flour. A higher content of gallic (66.68-70.89 μg/g) and protocatechuic acid (41.89-42.76 μg/g) was detected in the corn flour than in the wheat flour, where the gallic acid content was 28.60 μg/g and protocatechuic acid content, 36.38 μg/g.

Keywords: ICP-OES, HPLC, phenolic compounds

1. Introduction

Corn (*Zea mays* L.) and products made from corn grains (flour, starch, oil, meal, syrup, bourbon, etc.) are widely used in the food industry. By milling up the white or yellow corn grains, white or yellow corn flour, respectively, is obtained. As corn flour is obtained by milling the whole corn grain, flour and food prepared from it can be considered integral and functional food. Corn flour contains protein, carbohydrates, vitamins, minerals (Ragaee *et al.*, 2006), oil and fibre, and does not contain gluten. The oil is located in the corn germ, and it consists of glycerides of unsaturated fatty acids, phytosterols, and liposoluble vitamins A and E, which contribute to the nutritional and medicinal importance of corn oil (Eisaa *et al.*, 2016).

Corn belongs to the group of cereals, and the bioavailability of minerals from cereals can be poor due to the presence of anti-nutritional factors such as phytic acid (Frontela *et al.*, 2011). Luckily, traditional food processes such as soaking and cooking (Karkle and Beleia, 2010), germination (Sokrab *et al.*, 2012) and fermentation (Mohite *et al.*, 2013), activate the enzyme phytase, which substantially reduces the content of phytic acid. Various food technologies for processing corn grains into different corn products have different influences on mineral content. Thus, milling the corn grains into flour causes a decrease in the content of Fe, Mg, Na and Cu, and has no impact on Ca, Mg and Mn (Gwirtz and Garcia-Casal, 2014), while roasting, reduced the contents of Fe and K, and increased the contents of Ca, Na, Mg and Zn in yellow and white corn varieties (Oboh *et al.*, 2010).

Cereal grains contain phenolics, well known for their antioxidant (Van Hung, 2016) and anticancerogenic activity (Rosa *et al.*, 2016), as well as for their beneficial effects on human health. In plant cells, phenolics are mainly located in the pericarp, and exist in free and bound forms (Perez-Jimenez and Torres, 2011). Bound phenolics are covalently bound to the plant matrix, and can be extracted only using alkaline or acid hydrolysis. In corn the highest amount of phenolics (98.9%) are present as bound, and the remainder in free fraction (Adom and Liu, 2002). Phenolics which have been detected in corn include: phenolic acids, such as protocatechuic, p-hydroxybenzoic, vanillic, ferulic, caffeic and p-coumaric acid (Mattila *et al.*, 2005). The investigation of Oboh *et al.* (2010), showed the antioxidant and nutritional properties of yellow and white corn varieties to also be affected by food processing. Therefore, roasting reduced the amount of extractable phenolics and flavonoids content, as well as crude protein and fibre, but caused a significant increase in ferric reducing antioxidant power crude fat and carbohydrates content.

Knowledge of the chemical, mineral and phenolics composition, as well as of the antioxidant activity of food is important for evaluating its nutritional value, potential benefits to health, and assessment of the daily dietary intake. In this paper, the mineral, free phenolic content, free phenolic acid composition, and antioxidant activity of an 80% v/v methanol extract from white, yellow and degerminated yellow corn flour (DGCF) were studied in order to compared them to wheat flour.

2. Materials and methods

Samples

Five samples of white corn flour from Serbia (Vega ADM, Čenta; Interkomerc, Rača; Gajčanka, Tabanovac; Moravka, Leskovac; Caltor Kragujevac, all from Serbia), yellow corn flour (Vodenica, Džep; Interkomerc, Rača; Yumis, Niš; Moravka, Leskovac; Interpak, Kraljevo, all from Serbia) wheat flour, type 500 ("Fidelinka", Subotica, Serbia), and degerminated yellow corn flour (DGCF), known as palenta flour (Moravka, Leskovac, Serbia) were studied. Wheat flour type 500, according to the manufacturer's specifications, contained minerals in range of 0.46-0.55%.

The chemical composition

A near infrared grain analyser Inframatic 9500 (Perten Instruments, Hägersten, Sweden) was used to determine the moisture, protein, ash and colour of the studied samples of flour. A flour sample (of approximately 300 g) was placed into a cell, the cell was closed and inserted into the funnel and the 'Analyse' button was pressed. Following analysis, the results were read out from the screen, and the sample box emptied for the next sample. The samples of wheat flour and DGCF were analysed in triplicate.

Extraction of free phenolics

For the extraction of free phenolics, 30 g of the sample were measured; 250 ml of 80% methanol was added, left to rest for 24 h at room temperature and occasionally mixed. The solids were re-extracted with 50 ml of methanol, the filtrates were combined and a volume of 300 ml of the final extract was made with 80% methanol. The phenolics from wheat and DGCF were extracted in triplicate.

To determine phenolic acid composition, the DPPH (1,1-diphenyl-2-picrylhydrazyl) radical scavenging capacity (SC) and the reducing power, 150 ml of each final extract were evaporated in a vacuum at 45 °C until dry, and dissolved in 20 ml of hot methanol (approximately 60 °C). Where necessary, the appropriate dilutions (from 1:1 to1:10 v/v) were made.

Dry matter analysis

The obtained final phenolic extract (3 ml) was dried in the analyser (Scaltec SMO 01, Scaltec instruments, Göttingen, Germany) at 100 °C to a constant mass, the result was read from the display of the apparatus, and calculated to mg of dry matter per ml of extract.

Phenolics and flavonoids content

The phenolic content in the final phenolic extracts was determined using the Folin-Ciocalteu reagent (Singleton and Rossi, 1965). The absorbance was measured at 765 nm by a UV 21000 Spectrophotometer (Cole Parmer Instruments Company, Vernon Hills, IL, USA) and the phenolic content was calculated based on the equation $C = 237.05 \times Ab - 12.69$, obtained with gallic acid (Sigma Aldrich, St. Louis, MO, USA) and covering a range from 10 to 300 mM. The results were expressed as mg of gallic acid per g of flour.

The flavonoids content in the final phenolic extracts was determined via the $AlCl_3$ solution method, by taking 0.1 ml of the final extract and adding 0.2 ml of the 10% $AlCl_3$ solution and 0.05 ml of concentrated hydrochloric acid. Then the solution volume was adjusted to 5 ml with methanol, and after 40 min the absorbance was measured at 415 nm (Eisaa, 2016). A blank test was prepared with 0.1 ml of the extract to which 0.05 ml of concentrated hydrochloric acid was added, and the volume was adjusted to 5 ml with methanol. The flavonoids content was calculated based on the equation $C = 85.47 \times Ab - 1.49$ obtained with quercetin (Sigma Aldrich), and covering a range from 10 to 100 mM. The results were expressed as mg of quercetin per g of dry basis.

DPPH radical scavenging capacity and reducing power

The DPPH radical SC of the phenolic extracts, and the concentration of dry residue of the phenolic extract of up to 8 mg/ml, were determined by the method described by Mensor *et al.* (2001), and the reducing power by the method described by Oyaizu (1986). The IC_{50} value for both methods was calculated by using the Microsoft Excel ed50plus v1.0 software by Mario H. Vargas, Instituto Nacionale de Enfermedades Respiratories, Mexico. The IC_{50} value for the DPPH test represented the concentration of dry residue of the studied extract required for reaching 50% of the DPPH SC, the IC_{50} value for the reducing power, and the concentration of dry residue of the extract required for reaching an absorbance value of 0.5. Butylated hydroxyanisole (BHA) was used as the standard.

Sample decomposition for mineral analysis

The sample (0.1 g) was decomposed by wet digestion using 10 ml of 65% nitric acid (HNO_3) and resting for 24 h at room temperature. Then the sample was heated and portions of 1 ml of 65% HNO_3 were added until a clear vapor and a solution volume of approximately 1 ml were achieved. Then the residue was washed with deionised water to make a final volume of 10 ml, and filtered through Whatman No. 541 tape (Sigma Aldrich. The decompositions of wheat and DGCF were done in triplicate.

Mineral analysis

The mineral composition and content were determined by inductively coupled plasma - optical emission spectrometry (ICP-OES), using the ARCOS FHE12 spectrometer (SPECTRO, Kleve, Germany), according to the manufacturer's instructions. The carrier gas was Argon 5.0 (99.999% purity).

The ICP-OES was operated under the following conditions: the plasma power was 1,400 W, the auxiliary and coolant gas flow 0.80 and 13 l/min respectively, the nebuliser cross flow rate of 0.95 l/min, and pump speed 30 rpm. In order to estimate the mineral content, the calibration standards were prepared. A multi-standard solution (Merck, Darmstadt, Germany), containing aluminium (Al), silver (Ag), boron (B), barium (Ba), bismuth (Bi), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), mercury (Hg), potassium (K), lithium (Li), indium (In), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), thallium (Tl) and zinc (Zn) at a concentration of 1000 mg/kg, was used for the preparation of the calibration solutions. The elements arsenic (As), mercury (Hg), phosphorus (P), silicon (Si), strontium (Sr) and sulphur (S) (Reagecon, Shannon, Ireland) were determined by using the specific calibration standards (1000 mg/kg), respectively. The preparation of standard solutions was performed by diluting the multistandard to four different concentrations in the range in which concentrations of the studied samples were expected. Distilled water, purified by Fisher Chemical (HPLC grade) (Rockford, IL, USA), was used for the dilution of the samples.

Phenolic acids composition

For the analysis of the phenolic acids composition, the HPLC isocratic method of Amakura *et al.* (2000) was used. The content of phenolic acid was calculated based on the equation obtained for each phenolic acid separately (Nikolić *et al.*, 2016) and expressed as mg of acid per g of flour.

Statistical analysis

The mean value, standard deviation and statistically significant difference ($P<0.01$) were obtained by VassarStats: Website for Statistical Computation, using the One-Way analysis of variance for independent samples (http://www.vassarstats.net/). The dendrograms are obtained by the Statistica-version 10 program, based on their mean, maximal and minimal values, by choosing the option Mult/Exploratory-Cluster analysis, for the appropriate number of variables (Anonymous, 2017).

3. Results and discussion

Chemical composition and antioxidant activity

The results of the studied parameters of the chemical composition (moisture, protein, and ash content, free phenolic content and flavonoid content) in the studied samples are shown in Table 1. In our study, the phenolics were extracted by using 80% methanol, without previous hydrolysis, and the obtained results refer to free phenolics. The free phenolics content among the studied corn flours ranged from 539.01 (in DGCF) to 1,268.26 µg/g (in the white corn flour), while in the wheat flour this content was 705.60 µg/g. The content is lowest in DGCF, probably due to germ removal, as the highest content of soluble phenolics of the corn grain is concentrated in the germ (Cabrera-Soto *et al.*, 2009).

The flavonoid content was highest in the yellow corn flours (about 24 µg quercetin equiv per g, i.e. about 0.08 µmol/g), in the white corn flour there was only half as much, while in the wheat flour it was only 6.06 µg/g. In the literature there are data according to which the phenolics content in different corn varieties ranges from 243.8 to 320.1 mg of gallic acid equiv/100 g of dry weight (De la Parra *et al.*, 2007). In comparison to our results this phenolics content is higher because it includes the content of bound phenolics and represents the content of total phenolics. The content of free phenolics in white corn grain, reported by López-

Table 1. Chemical composition of white and yellow corn, degerminated corn flour (DGCF) and wheat flour.[1,2]

Content/flour sample	Yellow corn	White corn	DGCF	Wheat
Moisture (%)	13.35±0.37[a]	12.55±2.72[a]	10.14±1.27[b]	12.21±1.08[a]
Protein (%)[3]	10.48±1.11[ab]	11.56±0.95[a]	9.09±1.42[b]	12.54±1.21[a]
Ash (%)	1.27±0.17[a]	1.34±0.26[a]	1.35±0.12[a]	0.66±0.11[b]
Colour (*L)	89.52±1.24[a]	88.58±0.56[b]	91.20±0.79[a]	89.1±0.94[b]
Dry residue of phenolics extract (mg/ml)	4.63±0.37[a]	4.56±0.50[a]	2.73±0.42[b]	6.96±0.83[a]
Free phenolics (μg/g)[4]	1,100.51±162.31[a]	1,268.26±125.18[a]	539.01±93.82[b]	705.60±82.78[b]
Flavonoids content (μg/g)[5]	23.37±5.61[a]	10.37±2.65[b]	24.01±1.32[a]	6.06±1.41[b]

[1] Values are mean ± standard deviation, expressed on a dry flour basis.
[2] Values with same superscript in the same row do not differ significantly (P<0.01).
[3] N×6.25 for corn flour; N×5.70 for wheat flour.
[4] μg of gallic acid per g on dry flour basis.
[5] μg of quercetin per g on dry flour basis.

Martínez *et al.* (2009) and De la Parra *et al.* (2007), was 334 and 347 μg gallic acid equiv/g, respectively. In comparison to this result, our sample of white corn flour had nearly three times as many phenolics, but, on the other hand, almost half the content of free phenolics in the white corn genotype (2,480 mg/kg), reported by Del Pozo *et al.* (2006). Xu *et al.* (2010) found out that the free phenolics content in yellow corn grain was only 61.7 μg gallic acid equiv/g. The obtained content of free phenolics in the yellow corn flour in our study investigation of 1,100.51 μg/g is similar to the result of 1,040 μg/g reported by López-Martínez *et al.* (2009). The results for flavonoid content obtained by Adom and Liu (2002) showed that it was approximately 1.68 μmol catechin equiv/g, that over 90% was in bound (1.52 μmol/g) and only a small amount in free form (0.16 μmol/g), and that this content is twice as high as the flavonoid content in our samples.

Based on the obtained results, there are no statistically significant differences between the white and yellow corn flour (P<0.01) and the wheat flour in terms of moisture, protein and dry residue of the phenolics content, but there is a statistically significant difference in the ash and free phenolic content. By comparing the sample of DGCF and wheat flour, a statistically significant difference (P<0.01) was determined for all the studied, except for free phenolic content.

The results for the antioxidant activity of the phenolic extract obtained by using 80% methanol for the extraction of free phenolics from white and yellow corn, DGCF, wheat flour and BHA are shown in Table 2. The results are presented as IC_{50} values and the reciprocal value, $1/IC_{50}$, as a higher $1/IC_{50}$ value indicates a higher antioxidant activity. The results show that the antioxidant activity of both the corn flour and DGCF was higher and statistically significant different (P<0.01) than the activity of the wheat

Table 2. Antioxidant activity in the phenolic extract from white and yellow corn, degerminated corn flour (DGCF) and wheat flour.[1,2]

IC_{50}/Flour sample	Yellow corn	White corn	DGCF	Wheat	Butylated hydroxyanisole
DPPH test					
IC_{50} (mg/ml)[3]	0.76±0.21[a]	0.83±0.20[a]	0.93±0.15[a]	2.48±0.39[b]	0.0046±0.0012
$1/IC_{50}$ (ml/mg)[4]	1.39±0.39	1.26±0.29	1.04±0.26	0.42±0.11	217.39±18.74
Reducing power test					
IC_{50} (mg/ml)[3]	1.62±0.34[a]	1.86±0.61[a]	2.72±0.68[a]	5.12±0.47[b]	0.0305±0.0078
$1/IC_{50}$ (ml/ mg)[4]	0.62±0.13	0.54±0.25	0.37±0.08	0.20±0.06	32.79±2.45

[1] Values are mean ± standard deviation.
[2] Values with same superscript in the same row do not differ significantly (P<0.01).
[3] mg of dry residue per ml of extract.
[4] (mg of dry residue per ml of extract)$^{-1}$.

Table 3. Calibration parameters: λ, nm; R^2; LD (µg/l) and the range of linearity (µg/l).

Element	Detection wavelength (nm)	Correlation coefficient (R^2)	Limit of detection (µg/l)	Linearity range (mg/l)
Al	167.078	0.99985	7.6×10^{-2}	7.6×10^{-5}-2.40
	394.401	0.99998		1.55×10^{-3}-12.00
B	182.641	0.99999	6.43	7.37×10^{-3}-12.00
	249.773	0.99999		6.43×10^{-3}-12.00
Ba	233.527	0.99995	0.183	1.83×10^{-4}-12.00
Ca	183.801	0.99995	2.14	1.6-480.00
	396.847	0.99946		2.14×10^{-3}-2.41
Cr	283.563	0.99998	0.435	4.35×10^{-4}-12.00
Cu	224.700	0.99999	0.259	9.07×10^{-4}-12.00
	324.754	0.99999		2.59×10^{-4}-12.00
Fe	259.941	0.99997	0.118	1.18×10^{-4}-12.00
Ga	417.206	0.99994	1.7	0.0017-12.00
K	404.721	0.99998	0.378	0.798-300.00
	766.491	0.99999		3.78×10^{-4}-1.20
Li	323.261	1.00000	5.75×10^{-2}	7.98×10^{-2}-12.00
	670.780	0.99997		5.75×10^{-5}-1.20
Mg	279.553	0.99997	0.115	1.15×10^{-4}-6.04
	285.213	0.99994		4.03-120.00
Mn	257.611	0.99992	3.57×10^{-2}	3.57×10^{-5}-12.00
Na	330.237	0.99994	4.75	7.98-480.00
	598.592	0.99989		4.75×10^{-3}-12.00
Ni	231.604	0.99994	0.474	4.74×10^{-4}-12.00
P	214.914	0.99992	3.5	3.5×10^{-3}-240
Si	288.158	0.99998	1.6	1.6×10^{-3}-120
Sr	407.771	0.99998	6.23×10^{-3}	6.23×10^{-6}-2.41
Tl	190.864	0.99998	1.72	1.72×10^{-3}-12.00
Zn	213.856	0.99997	8.2×10^{-2}	8.2×10^{-5}-12.00

flour, determined as the DPPH SC and the reducing power. Such results are expected, because the content of phenolics and flavonoids as compounds responsible for antioxidant activity, was also higher in the corn flour samples. The content of phenolics in the DGCF was almost one half of the content of phenolics in the yellow corn flour, and both the DPPH SC and the reducing power were lower, indicating germ removal as the probable cause. On the other hand, DGCF still had a better antioxidant activity than the wheat flour, probably due to the higher content of flavonoids (Table 1). Compare to BHA, the results show the extracts had a 156 to 209 times weaker DPPH SC, and a 52 to 89 times weaker reducing power than BHA.

Mineral composition

The calibration curves, wavelength of detection, correlation coefficient, limit of detection and linearity range obtained for each mineral used to determine of mineral content are presented in Table 3, and the mineral compositions (major, trace, essential trace minerals, nonessential trace minerals and other minerals) of the corn, DGCF and wheat flour are shown in Table 4.

Compared to the wheat flour, the studied yellow corn flour samples do not differ in a statistically significant manner ($P<0.01$) in terms of the Fe, Cu, Zn and Mn content, and the white flour does not statistically significantly differ in its Cu, Mn and Li content. When comparing the mineral composition of the yellow corn flour and DGCF, no statistically significant difference in the Ca, Na, Zn and Li content was determined, and between the white corn flour and the DGCF, there is no statistically significant difference in the Na and B content. However, it is necessary to emphasize the presence of a higher content of Mg and K, in the white corn flour compared both to the wheat and DGCF, and especially the content of Zn. The Zn content of 106.24 µg/g in the white corn flour is almost ten times as high as that of the wheat flour (10.79 µg/g) and five times high as the content in the DGCF (18.73 µg/g). The content of Zn in the studied white corn samples can be considered to be high, as in literature there is data that Zn content ranged from 0.25 to 25.2 mg/kg in eighteen different corn

Table 4. Mineral composition and content in white and yellow corn, degerminated corn flour (DGCF) and wheat flour.[1,2]

Minerals/sample	Yellow corn	White corn	DGCF	Wheat
Major minerals				
Ca, mg/g	1.44±0.16^{ab}	1.84±0.46^{a}	0.97±0.15^{b}	0.26±0.08^{c}
Mg, mg/g	1.43±0.21^{a}	1.45±0.23^{a}	0.25±0.04^{b}	0.28±0.12^{b}
Na, µg/g	178.73 ±31.11^{a}	183.53±25.22^{a}	199.14±32.16^{a}	47.29±3.26^{b}
K, mg/g	2.63±0.29^{a}	2.59±0.43^{a}	1.05±0.24^{b}	1.41±0.19^{b}
P, mg/g	7.02±0.64^{a}	6.36±1.43^{a}	1.99±0.34^{b}	nd[3]
Micro minerals				
Fe, µg/g	58.79±5.03^{a}	29.18±3.42^{b}	10.01±1.34^{c}	54.30±5.63^{a}
Cu, µg/g	3.36±2.21^{a}	3.99±1.42^{a}	1.37±0.46^{b}	2.15±0.26^{a}
Cr, µg/g	0.36±0.12^{a}	0.71±0.19^{a}	0.50±0.12^{b}	nd
Zn, µg/g	30.11±6.26^{a}	106.24±14.54^{b}	18.73±2.45^{a}	10.79±2.17^{a}
Mn, µg/g	4.13±1.52^{a}	3.89±0.52^{a}	0.38±0.14^{b}	2.27±0.68^{ab}
Essential trace minerals				
Si, µg/g	88.01±11.65	nd	<8.00	nd
Ni, µg/g	0.08±0.06	nd	nd	nd
Nonessential trace minerals				
Al, µg/g	0.14±0.08^{a}	0.14±0.08^{a}	0.06±0.02^{b}	nd
Sr, µg/g	nd	0.15±0.00	nd	nd
B, µg/g	6.30±1.89^{a}	4.45±1.32^{ab}	3.14±0.61^{b}	0.52±0.15^{c}
Li, µg/g	0.51±0.14^{a}	2.21±0.42^{b}	0.21±0.08^{a}	2.38±0.25^{b}
Other detected minerals				
Ga,µg/g	<0.08	<0.08	<0.08	nd
Ba, µg/g	nd	3.89±0.06^{a}	3.19±0.15^{b}	3.58±0.33^{b}
Tl, µg/g	<0.08	<0.08	<0.08	0

[1] Values are mean ± standard deviation expressed as mg or µg per g on dry flour basis.
[2] Values with same superscript in the same row do not differ significantly (P<0.01).
[3] nd = non detected.

flours from Turkey (Algül and Kara, 2014) and from 0.45 to 2.21 mg/100 g in white, yellow and sweet corn flour (Siyuan *et al.*, 2018). The content of calcium in the yellow corn flour was 1.44, while in the white corn flour it was 1.84 mg/g. Both of these contents are twice as high as the content of calcium, 0.74 mg/g, found in two corn genotypes (genotypes with a high and with a low content of phytate) by Sokrab *et al.* (2012). Pan and Du (2017) found that the antioxidant capacity of lettuce leaves becomes stronger when Zn is added to the nutrient solution, and in the human body, zinc has a wide range of functions (Deshpande *et al.*, 2013). Based on these data, the high content of zinc found in yellow and white corn flour can be considered an important fact. Based on Recommended Dietary Allowance (RDA) for zinc for men which is 14 mg/day (Anonymous, 2018), it has been prove that 100 g of white corn flour could satisfy as much as 73.1% of an adult man's needs, 100 g of yellow corn flour 21.5%, and 100 g of while wheat flour only 7.7%.

Phenolic acid composition

The phenolic acid composition and its content in the phenolic extract from the white and yellow corn, DGCF and wheat flour are all presented in Table 5. The results show various phenolic acid profiles in the flour samples. In the corn flour samples, seven phenolic acids were detected (gallic, protocatechuic, chlorogenic, caffeic, coumaric, *trans*-ferulic and syringic), while only three in the wheat flour (gallic, protocatechuic and chlorogenic acid). In the corn flour samples there were two nonidentified components with a retention time of 7.15 and 7.98 min (NID 7.15 and NID 7.98) and in the wheat flour, only NID 7.98. Among the identified phenolic acids in the yellow and white corn flour, gallic acid was dominant in terms of content of 66.69 and 70.89 µg/g, respectively, in the sample of DGCF, gallic and chlorogenic acid were dominant with contents of approximately 120 µg/g, while in the wheat flour protocatechuic and chlorogenic with a content of 35 µg/g. But if we take into consideration the NID compounds, compound NID 7.15 and NID 7.98 were

Table 5. Phenolic acid content in free phenolics extract from white and yellow corn, degerminated corn flour (DGCF) and wheat flour.[1,2]

Acid/content (µg/g)[3]	Yellow corn	White corn	DGCF	Wheat
Gallic	66.68±11.08[a]	70.89±9.21[a]	121.69±3.24[b]	28.60±4.18[c]
Protocatechuic	42.76±3.03[a]	41.89±1.38[a]	33.13±4.62[b]	36.38±2.12[b]
Chlorogenic	39.52±3.41[a]	38.06±6.53[a]	128.33±17.45[b]	35.21±3.58[a]
Caffeic	39.14±7.71[a]	24.12±4.11[b]	14.10±1.04[b]	nd[5]
Coumaric	35.44±3.61[a]	38.61±5.81[a]	25.31±4.25[b]	nd
trans-ferulic	8.48 ±4.24[a]	7.39±2.70[b]	2.28±0.87[b]	nd
Syringic	5.87±2.19[a]	5.27±1.53[ab]	1.17±0.31[b]	nd
NID 7.15 min[4]	82.27±9.34[a]	53.84±18.66[ab]	25.72±1.89[b]	nd
NID 7.98 min[4]	174.53±30.91[a]	166.16±11.86[a]	56.19±6.02[b]	10.96±1.14[b]

[1] Values are mean ± standard deviation.
[2] Values with same superscript in the same row do not differ significantly (P<0.01).
[3] Expressed as µg acid per g on dry flour basis; NID = nonidentified component.
[4] Expressed as µg coumaric acid per g on dry flour basis.
[5] nd = non detected.

the most abundant in the yellow corn flour, with a content of 82.27 and 174.53 µg/g (expressed as coumaric acid), respectively. Compared to the wheat flour, the corn flour samples had a statistically significantly higher content of gallic and protocatechuic acid.

Del Pozo *et al.* (2006), reported that in the white corn genotype, six derivatives of ferulic acid (88.8-816 mg/kg), *p*-coumaric acid (6.6 mg/kg), two protocatechuic acid derivatives (4.2 and 14.2 mg/kg), and gallic acid (3.9 mg/kg) were identified as free phenolic acids, so the content of *p*-coumaric, protocatechuic and gallic acid of 38.61, 41.89 and 70.89 µg/g respectively, was much higher in the white corn flour sample studied in our paper. The study of Žilić *et al.* (2013) showed that the content of ferulic and *p*-coumaric acids determined in the extract of total phenolics, which besides the free included the bound form of these acids, was much higher (4,153.43 and 624.46 µg/g dry basis, respectively). Bakan *et al.* (2003) reported that caffeic, coumaric and ferulic acids are present in the germ. Our results agree with those of Bakan *et al.* (2003) study, as the content of these acids was lower in the corn flour from which the germ had been removed (DGCF) than in the other studied corn flour.

Statistical analysis

The dendrograms for minerals in the yellow corn, white corn and wheat flour are presented in Figure 1 (A and B). In the wheat flour, the minerals are classified into two well-distinguished clusters: one containing Na and Fe, and the second one containing the rest of the minerals.

The mineral Zn is fused at a distance that is close to the distance of the minerals of the second cluster (about 15), and can be classified as belonging to this cluster. The dendrogram for the minerals in the corn flour shows that the minerals Ca, Mg, Cr, Al, K, Cu, Mn, P and B are at a close distance in the cluster (up to 5), while Fe, Zn and Na are fused at a distance of nearly 100, 185 and 290, respectively. Due to the large distance from the minerals connected to the cluster, at a distance of up to 5, Fe, Zn and Na can be classified as belonging to the same cluster. As these minerals make a special cluster in the wheat flour, it can be concluded that the minerals in the yellow and white corn flour are classified into the same clusters as the minerals in the wheat flour, i.e. their relationships are the same, but their content is much higher in the corn than in the wheat flour.

The dendrogram for phenolic acids and undetected components with a retention time of 7.15 (NID 7.15) and 7.98 min (NID 7.98) in the yellow and white corn flour and wheat flour is presented in Figure 1 (C and D). In the yellow and white corn, the acids are classified into three clusters: the first with gallic acid and the NID 7.15 component, the second with protocatechuic, chlorogenic, coumaric and caffeic acid, and the third with *trans*-ferulic and syringic acid. These clusters are joined together at a distance of about 55, and the component NID 7.98 is fused at a longer distance of about 210. The dendrogram for phenolic acids and undetected components in the wheat flour shows a similarity to the dendrogram for the yellow and white corn flour, as protocatechuic and chlorogenic acid are in the same cluster, the gallic acid is branched (similar to the first cluster for acids in the corn flour), and component NID

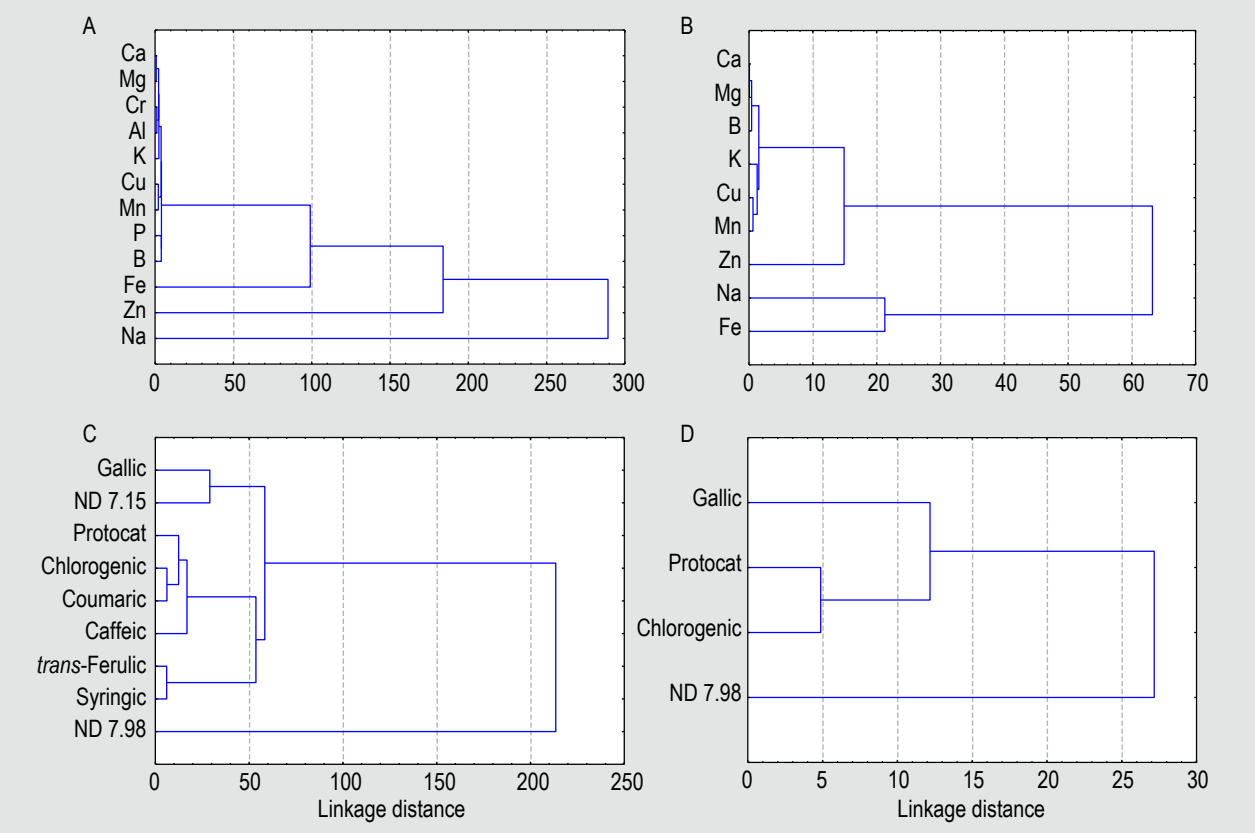

Figure 1. Dendrograms for minerals in the corn flour (A) and wheat flour (B); for phenolic acids in the corn flour (C) and wheat flour (D).

7.98 is fused at the longest distance, at about 27, due to its content being the lowest in the wheat flour.

4. Conclusions

A comparison of the content of minerals, phenolics, flavonoids, and the composition of free phenolic acids and antioxidant activity in wheat and different corn flour samples was carried out. The studied yellow and white corn flour differed significantly from the wheat flour in terms of ash, free phenolics, Ca, Mg, Na and K content. The white corn flour especially stands out based on its content of Zn (106.24 μg/g) which is ten times higher than the content in the wheat flour, so 100 g of studied white corn flour can satisfy over 70% of an adult man's RDA for zinc. The studied samples of corn flour contained gallic, protocatechuic, chlorogenic, caffeic, coumaric, *trans*-ferulic and syringic acid, while the wheat flour contained only gallic, protocatechuic and chlorogenic acid. All of the samples of corn flour had a statistically significantly higher content of gallic and protocatechuic acid and a stronger antioxidant activity than the wheat flour. Compared to BHA, the DPPH SC of the studied phenolic extracts from the corn flour was up to 209 times weaker, and the reducing power up to 89 times weaker.

Acknowledgements

This work is supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, under the project OI 172047.

References

Adom, K. and Liu, H., 2002. Antioxidant activity of grains. Journal of Agricultural and Food Chemistry 50:6182-6127.

Algül, I. and Kara, D., 2014. Determination and chemometric evaluation of total aflatoxin, aflatoxin B1, ochratoxin A and heavy metals content in corn flours from Turkey. Food Chemistry 157: 70-76.

Amakura, Y., Okada, M., Tsuji, S. and Tonogai, Y., 2000. Determination of phenolic acids in fruit juices by isocratic column liquid chromatography. Journal of Chromatography A891: 183-188.

Anonymous, 2017. NCSS Statistical Software 2017. Hierarchical clustering/dendrograms. Available at: http://tinyurl.com/y6c3wrs5

Anonymous, 2018. Nutrient reference values for zinc. Available at: https://www.nrv.gov.au/nutrients/zinc

Bakan, B., Bily, A.C., Melcion, D., Cahagnier, B., Regnault-Roger, C., Philogene, B.J.R. and Richard-Molard, D., 2003. Possible role of plant phenolics in the production of trichothecenes by *Fusarium graminearum* strains on different fractions of maize kernels. Journal of Agriculture and Food Chemistry 51: 2826-2831.

Cabrera-Soto, M.L., Salinas-Moreno, Y., Velázquez-Cardelas, G.A. and Trujillo, E., 2009. Content of soluble and insoluble phenols in the structures of corn grain and their relationship with physical properties. Agrociencia (Montecillo) 43: 827-839.

De la Parra, C., Saldivar, S.O. and Liu, R.H., 2007. Effect of processing on the phytochemical profiles and antioxidant activity of corn for production of masa, tortillasand tortilla chips. Journal of Agriculture and Food Chemistry 55: 4177-4183.

Del Pozo-Insfran, D., Brenes, C.H., SernaSaldivor, S.O. and Talcott, S.T., 2006. Polyphenolic and antioxidant content of white and blue corn (*Zea mays* L.) products. Food Research International 39: 696-703.

Deshpande, D., Joshi, M. and Giri, A., 2013. Zinc: the trace element of major importance in human nutrition and health. International Journal of Medical Science and Public Health 2: 1-6.

Eisaa, M., El-Refaib, H. and Aminc, M., 2016. Single step biotransformation of corn oil phytosterols to boldenone by a newly isolated *Pseudomonas*a eruginosa. Biotechnology Reports 11: 36-43.

Frontela, C., Ros, G. and Martínez, C., 2011. Phytic acid content and '*in vitro*' iron, calcium and zinc bioavailability in bakery products: the effect of processing. Journal of Cereal Science 54: 173-179.

Gwirtz, J. and Garcia-Casal, N., 2014. Processing maize flour and corn meal food products. Annals of the New York Academy of Sciences 1312: 66-75.

Karkle, E.N.E. and Beleia, A., 2010. Effect of soaking and cooking on phytate concentration, minerals, and texture of food-type soybeans. Food Science and Technology 30: 1056-1060.

López-Martínez, L.X., Oliart-Ros, R.M., Valerio-Alfaro, G., Lee, C.H., Parkin, K.L. and García, H.S., 2009. Antioxidant activity, phenolic compounds and anthocyanins content of eighteen strains of Mexican maize. LWT – Food Science and Technology 42: 1187-1192.

Mattila, P., Pihlava, M. and 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.

Mensor, L., Menezes, F., Leitão, G., Reis, A., Dos Santos, T., Coube, C. and Leitão, S., 2001. Sreening of Brazilian plant extracts for antioxidant capacity by the use of DPPH free radical method. Phototherapy Research 15: 127-130.

Mohite, V., Chaudhari, A., Ingale, S. and Mahajan, N., 2013. Effect of fermentation and processing on *in vitro* mineral estimation of selected fermented foods. International Food Research Journal 20: 1373-1377.

Nikolić, N., Stojanović, J., Mitrović, J., Lazić, M., Karabegović, I. and Stojanović, G., 2016. The antioxidant activity and the composition of free and bound phenolic acids in dough of wheat flour enriched by *Bletus edulis* after mixing and thermal processing. International Journal of Food Science and Technology 51: 2019-2025.

Oboh, G., Ademiluyi, A. and Akindahuns, A., 2010. The effect of roasting on the nutritional and antioxidant properties of yellow and white maize varieties. International Journal of Food Science and Technology 45: 1236-1242.

Oyaizu, M., 1986. Studies on product of browning reaction prepared from glucose amine. Japanese Journal of Nutrition 44: 307-315.

Pan, C. and Du, X., 2017. Effects of the best combination of copper, zinc, iron, and manganese on the relationship of lettuce resistance to Botrytis cinerea and its antioxidant system. Emirates Journal of Food and Agriculture 29: 330-338.

Perez-Jimenez, J. and Torres, J., 2011. Analysis of nonextractable phenolic compounds in foods: the current state of the art. Journal of Agriculture and Food Chemistry 59: 12713-12724.

Ragaee, S., Abdel-Aal, E-S. and Noaman, M., 2006. Antioxidant activity and nutrient composition of selected cereals for food use. Food Chemistry 98: 32-38.

Rosa, L.S., Silva, N.J.A., Soares, N.C.P., Monteiro, M.C. and Teodoro, A.J., 2016. Anticancer properties of phenolic acids in colon cancer – a review. Journal of Nutrition and Food Science 6: 2-7.

Singleton, L. and Rossi, J., 1965. Colorimetry of total phenolics with phosphomolybdate-phosphotungestic acid reagents. American Journal of Viticulture and Anology 16: 144-158.

Siyuan, S., Tong, L. and Rui, H.L., 2018. Corn phytochemicals and their health benefits. Food Science and Human Wellness 7: 185-195.

Sokrab, A., Mohamed Ahmed, I. and Babiker, E., 2012. Effect of germination on antinutritional factors, total, and extractable minerals of high and low phytate corn (*Zea mays* L.) genotypes. Journal of the Saudi Society of Agricultural Sciences 11: 123-128.

Van Hung, P., 2016. Phenolic compounds of cereals and their antioxidant capacity. Critical Reviews in Food Science and Nutrition 56: 25-35.

Xu, J.G., Hu, Q.P., Wang, X.D., Luo, J.Y., Liu, Y. and Tian, C.R., 2010. Changes in the main nutrients, phytochemicals, and antioxidant activity in yellow corn grain during maturation. Journal of Agriculture and Food Chemistry 58: 5751-5756.

Žilić, S., Mogol, B.A., Akıllıoğlu, G., Serpen, A., Babić M. and Gökmen, V., 2013. Effects of infrared heating on phenolic compounds and Maillard reaction products in maize flour. Journal of Cereal Science 58: 1-7.