Changes in the functional components and radical scavenging activity of maize under various roasting conditions

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Received: 15 September 2017 / Revised: 30 October 2017 / Accepted: 8 December 2017 / Published online: 19 December 2017
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Abstract The phenolic compounds and radical scavenging activity of ethanolic extracts from maize at various roasting conditions were evaluated in this research. The free sugar contents in roasted maize significantly decreased with higher roasting temperature and longer roasting time. The total polyphenol and total flavonoid contents in roasted maize significantly increased with higher roasting temperature and longer roasting time. The predominant phenolic acid in the roasted maize was homogentisic acid. The contents of homogentisic acid and myricetin in roasted maize significantly increased with higher roasting temperature and longer roasting time. The DPPH and ABTS radical scavenging activities of roasted maize significantly increased with higher roasting temperature and longer roasting time. DPPH and ABTS radical scavenging activities were positively correlated with phenolic compounds. The activities of these components increased following heat treatments because of the low molecularization effects of the heating process, which resulted in active, low-molecular-weight components that were readily extracted.

Keywords Maize (*Zea mays* L.) · Roasting condition · Polyphenol · Phenolic acid · Radical scavenging activity

Introduction

Maize (*Zea mays* L.) is the world's third largest food crop after rice and wheat, and contains large amounts of nutrients, unique flavors, and vitamins [1]. It has a wide variety of uses including use as a raw material for edible and processed food, in animal feed, and in industrial applications. In many countries, maize grains are transformed into various products. They can be roasted, boiled, fried, or ground and fermented to produce bakery products or alcoholic beverages [2].

Maize grain is 72% starch, with the remainder composed mainly of protein, fat, and fiber, and contains a large amount of linoleic acid, which is an essential fatty acid. Maize grain is rich in molecules with antioxidant characteristics, such as phenol compounds, tocopherols, carotenoids, anthocyanins, and flavonoids [3]. Many studies have measured the content of antioxidant compounds and antioxidant activity in maize grains [4]. Maize has received increased attention from a nutraceutical perspective due to its potential health benefits [5]. Phytochemicals such as phenol compounds, anthocyanins, and carotenoids have been found in maize landraces [6].

Roasting is a heat-processing method that involves the use of dry heat, and results in various physicochemical, nutritional, and phytochemical changes that can be desirable or undesirable [7]. It has been traditionally used in Korea in the processing of maize for the preparation of maize beverages and for ingredients used in the production of different types of food [8]. The roasting of maize grains increased flavors, enhanced antioxidant contents and activity, and improved food quality and safety of intermediate and end products [8]. In addition, the roasting process causes changes in the chemical composition and biological characteristics of the coffee bean, allowing

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additional antioxidant compounds to form [9]. Studies have been performed to determine the effects of roasting on bioactive compounds in soybean [10], wheat [11], barley [12], pistachio nuts [13], cocoa beans [14], coffee beans [15], and wattle seeds [16]. 2006). Roasting can also extend the shelf life of foods and improve the processing efficiency of a subsequent step [8].

Therefore, the purpose of this study was to evaluate the effects of roasting temperature and roasting time on the functional components and radical scavenging activity of maize, so that it may be used as a resource for nutraceutical products or the food industry in the future.

Materials and methods

Chemicals and reagents

Folin–Ciocalteu reagent, sodium carbonate, gallic acid, sodium nitrite (NaNO_2), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), (+)-catechin, sodium carbonate (Na_2CO_3), 2,2-Diphenyl-1-picrylhydrazyl (DPPH), 2,2-azinobis(3-ethylbenothiazoline-6-sulphonic acid) diammonium salt (ABTS), potassium persulfate, trolox, and phenolic acids were purchased from Sigma-Aldrich (St. Louis, MO, USA). HPLC-grade water, acetonitrile, methanol, and acetic acid were purchased from J.T. Baker (Phillipsburg, NJ, USA). The reagents had highest-grade quality.

Sample preparation and extraction

The Kwangpyeongok cultivars of maize (*Zea mays* L.) were grown at the National Institute of Crop Science, Rural Development Administration, Suwon, South Korea (37°26'N and 126°98'W) during the 2015 cropping season and were stored at -20°C . The kernels of the Kwangpyeongok cultivars are dent-type kernels. The roasted maize was manufactured using a far-infrared grain roaster (FEC-006, Biotech Co., Incheon, Korea). The roasting temperature was 200–300 °C, and the roasting time was 20–60 min. The roasted maize was pulverized before analysis using a micro hammer-cutter mill (Type 3, Culatti Ag., Zürich, Switzerland).

Analysis of the free sugar composition

Free sugars (fructose, glucose, sucrose, and maltose) were measured by extracting 5 g homogenized sample in 20 mL water, which was filtered through a 0.45 μm membrane and analyzed by HPLC (Waters e2695; Waters, New Castle, DE, USA). The analysis conditions followed the method used by Woo et al. [17]. Here we used a carbohydrate analysis column (4.6 $\times$ 150 mm; Waters), refractive index

detector (Waters 2414; Waters), and an acetonitrile/water 75:25 (v/v) mobile phase at a flow rate of 1 mL/min.

Determination of total polyphenol and flavonoid contents

The pulverized samples were extracted with a shaker (SK-71 Shaker, JEIO Tech, Kimpo, South Korea) using 80% ethanol at room temperature (25 °C) to analyze antioxidant components and radical scavenging activity. Then the extracts were filtered through Adventec No. 2 paper to remove any debris and were used as the sample for analysis. The total polyphenolic contents in the maize according to roasting conditions were determined using the Folin–Ciocalteu method [18] with some modifications, and the results were expressed as mg gallic acid equivalents (GAE) per gram of sample. Standard solution or ethanolic extracts (10 μL) was mixed with 200 μL of 2% sodium carbonate solution and 10 μL of a 50% Folin–Ciocalteu reagent. After incubation at the incubator for 30 min at room temperature (25 °C), the absorbance was measured at 750 nm. Total flavonoid contents in the maize according to roasting conditions were determined by the colorimetric method described by Lee et al. [18] with some modifications, and the results are expressed as μg (+)-catechin equivalents (CE) per gram of sample. Standard solution or ethanolic extracts (50 μL) was mixed with 200 μL distilled water and 15 μL 5% NaNO_2 solution. After 5 min, 30 μL 10% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was added. After 6 min, 100 μL 1 M NaOH was added. The solution was mixed well, and the intensity of pink color was measured at 510 nm. All extracts were analyzed in triplicate.

Determination of some individual phenolic acids

The phenolic acid composition of each extract was determined using an HPLC system according to the method described by Kim et al. [19] with slight modifications. The analytical column was an ODS column (5 μm , 4.6 mm $\times$ 250 mm, Agilent Technologies, Santa Clara, CA, USA). A gradient elution was employed using solvent A (water containing 0.1% (v/v) acetic acid) and solvent B (acetonitrile containing 0.1% (v/v) acetic acid). The gradient program was as follows: 0–2 min, 92 to 90% A in B (gradient); 2–27 min, 90 to 70% A in B (gradient); 27–50 min, 70 to 10% A in B (gradient); 50–51 min, 10 to 0% A in B (gradient); 51–60 min, 0% A in B (isocratic); and 60–70 min, 0 to 92% A in B (gradient). The flow rate was maintained at 1 mL per min, and the injection volume was 20 μL . The UV detector was set at 280 nm. The phenolic acid standard mixture containing gallic acid, homogentisic acid, protocatechuic acid, gentisic acid, chlorogenic acid, (+)-catechin, caffeic acid, phloretic acid,

p-coumaric acid, ferulic acid, veratric acid, naringin, hesperidin, salicylic acid, quercetin, trans-cinnamic acid, naringenin, hesperiten, myricetin, and biochanin A was prepared in HPLC-grade methanol. The phenolic acid concentrations were determined by standard curves obtained by injecting different concentrations of the phenolic acid standard into the HPLC system. Peaks were verified by adding the standard phenolic acids to the samples, and each peak area was calculated in relation to a standard peak area. The total phenolic acid content was calculated by summing the different phenolic acid component amounts.

Measurement of DPPH and ABTS radical scavenging activities

The DPPH radical scavenging activity of the sample extracts was measured according to the methods of Lee et al. [18] with some modifications. A 200 μL aliquot of 0.2 mM DPPH ethanolic solution was mixed with 50 μL ethanolic extracts. The mixture was shaken vigorously and left to stand for 30 min under low light, and then the absorbance was measured at 515 nm. The ABTS cation radical scavenging activity of the extracts was measured according to the methods of Lee et al. [18] with some modifications. The ABTS cation radical was generated by adding 7 mM ABTS to 2.45 mM potassium persulfate solution and leaving the mixture to stand overnight in the dark at room temperature. The ABTS cation radical solution was diluted with methanol to obtain an absorbance of 1.4–1.5 at 735 nm (molar extinction coefficient, $\varepsilon = 3.6 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$). Diluted ABTS cation radical solution (1 mL) was added to 50 mL ethanolic extracts, Trolox standard solution, or distilled water. After 30 min, the absorbance was measured at 735 nm using a spectrophotometer (MultiskanTM GO Microplate Spectrophotometer, Thermo Fisher Scientific, Waltham, MA, USA). The DPPH radical and ABTS cation radical scavenging activities were expressed in terms of trolox equivalent antioxidant capacity (TEAC), as milligrams of trolox equivalents (TEs) per 100 g of sample.

Statistical analysis

All of the data are expressed as mean $\pm$ standard deviation (SD) values. The significance of differences among treatment means was determined by one-way analysis of variance and Duncan's multiple range tests using SAS version 9.2 (SAS Institute, Cary, NC, USA) with a significance level of 0.05. Correlations from regression analyses among the parameters were also investigated.

Results and discussion

Free sugar composition of roasted maize

Free sugar content is generally considered an indirect measure of the concentration of the substrate of non-enzymatic browning reactions or of the nutrients remaining after the browning reactions [20]. The changes in free sugar composition of the roasted maize with roasting conditions are shown in Table 1. The fructose, glucose, sucrose, maltose, and total free sugar contents of the non-roasted maize were 3.29 ± 0.61 , 3.69 ± 0.48 , 14.04 ± 1.23 , 2.91 ± 0.03 , and $23.93 \pm 0.28 \text{ mg/g}$ of sample, respectively (Table 1). The fructose, glucose, sucrose, and total free sugar contents of the roasted maize were significantly reduced with higher roasting temperature and longer roasting time. The maltose content of the roasted maize did not show any significant difference. Fructose and glucose were not detected in the roasted maize at 270 °C for 40–60 min and at 300 °C for 30–50 min. Sucrose was not detected at 300 °C for 30–50 min. Maltose was relatively stable in the roasting. Caramelization is the common name for a group of reactions that occurs when carbohydrates are exposed to high temperatures. The reactions often occur during the preparation of traditional sucrose syrups and caramels, which are used extensively in confectionery and pastry products [21]. Woo et al. [22] reported that the fructose content decreased significantly with increasing temperature (from 110 °C to 150 °C) and time (1–5 h) of 20% fructose solution. Also, when 20% sucrose solution was heat-treated, sucrose content decreased, and fructose and glucose content increased in the early stage (at 110–120 °C) but decreased with increasing heat treatment temperature and time [17]. These results suggest that higher temperatures and longer roasting times should not be used when roasting maize to prepare coffee-like beverages because many nutrients, including carbonyl and amino compounds, are degraded in the non-enzymatic browning reactions that occur during the roasting process [23]. It is also suggested that the free sugar contents of roasted maize decrease with increasing roasting temperature and roasting time.

Total polyphenol and flavonoid contents of roasted maize

Polyphenolic compounds are some of the most effective antioxidative constituents in plant foods such as fruits, vegetables, and grains. Therefore, it is important to quantify polyphenolic contents and assess their contribution to antioxidant activity [24]. The total polyphenol and flavonoid contents in the roasted maize significantly increased

Table 1 Amount of free sugar of maize according to roasting conditions

Roasting temp. (°C)	Roasting time (min)	Fructose (mg/g)	Glucose (mg/g)	Sucrose (mg/g)	Maltose (mg/g)	Total (mg/g)
200	30	2.70 ± 0.05 ^{a1}	2.63 ± 0.05 ^a	12.72 ± 0.16 ^a	2.75 ± 0.08 ^a	20.80 ± 0.11 ^a
200	40	2.76 ± 0.09 ^a	2.60 ± 0.02 ^a	11.64 ± 0.25 ^b	2.63 ± 0.08 ^a	19.63 ± 0.26 ^b
200	50	2.75 ± 0.09 ^a	2.62 ± 0.06 ^a	11.22 ± 0.29 ^b	2.63 ± 0.22 ^a	19.22 ± 0.23 ^c
200	60	2.76 ± 0.08 ^a	2.60 ± 0.08 ^a	10.58 ± 0.19 ^c	2.61 ± 0.11 ^a	18.55 ± 0.17 ^d
220	20	2.70 ± 0.03 ^b	2.57 ± 0.06	13.96 ± 0.17 ^a	2.64 ± 0.10 ^{ab}	21.87 ± 0.21 ^a
220	30	2.72 ± 0.05 ^b	2.56 ± 0.06 ^a	11.36 ± 0.09 ^b	2.66 ± 0.08 ^{ab}	19.30 ± 0.05 ^b
220	40	2.87 ± 0.12 ^a	2.68 ± 0.14 ^a	7.49 ± 0.13 ^c	2.77 ± 0.17 ^a	15.81 ± 0.21 ^c
220	50	2.94 ± 0.06 ^a	2.68 ± 0.22 ^a	5.69 ± 0.09 ^d	2.53 ± 0.05 ^b	13.84 ± 0.17 ^d
220	60	2.81 ± 0.06 ^{ab}	2.79 ± 0.03 ^a	4.07 ± 0.02 ^e	2.49 ± 0.00 ^b	12.16 ± 0.05 ^e
250	20	2.75 ± 0.03 ^b	2.60 ± 0.07 ^b	13.37 ± 0.15 ^a	2.72 ± 0.05 ^a	21.44 ± 0.22 ^a
250	30	2.93 ± 0.05 ^a	2.80 ± 0.07 ^a	5.49 ± 0.08 ^b	2.56 ± 0.15 ^a	13.78 ± 0.19 ^b
250	40	2.53 ± 0.02 ^c	2.58 ± 0.03 ^b	2.70 ± 0.00 ^c	2.68 ± 0.17 ^a	10.49 ± 0.15 ^c
250	50	2.43 ± 0.03 ^d	2.51 ± 0.06 ^{bc}	2.38 ± 0.02 ^d	2.76 ± 0.00 ^a	10.08 ± 0.11 ^d
250	60	2.41 ± 0.05 ^d	2.45 ± 0.03 ^c	2.38 ± 0.02 ^d	2.74 ± 0.02 ^a	9.98 ± 0.03 ^d
270	20	2.84 ± 0.02 ^a	2.81 ± 0.02 ^a	5.85 ± 0.05 ^a	2.50 ± 0.10 ^b	14.00 ± 0.12 ^a
270	30	2.45 ± 0.02 ^b	2.54 ± 0.03 ^b	2.51 ± 0.02 ^b	2.57 ± 0.15 ^{ab}	10.07 ± 0.15 ^b
270	40	— ²	—	2.40 ± 0.03 ^c	2.67 ± 0.11 ^{ab}	5.07 ± 0.10 ^c
270	50	—	—	2.35 ± 0.02 ^c	2.70 ± 0.06 ^a	5.05 ± 0.06 ^c
270	60	—	—	1.41 ± 0.03 ^d	1.55 ± 0.03 ^c	2.96 ± 0.06 ^d
300	20	2.65 ± 0.02 ^a	2.71 ± 0.08 ^a	4.00 ± 0.10 ^a	2.61 ± 0.17 ^a	11.97 ± 0.35 ^a
300	30	—	—	—	2.67 ± 0.03 ^a	2.67 ± 0.03 ^b
300	40	—	—	—	2.66 ± 0.03 ^a	2.66 ± 0.03 ^b
300	50	—	—	—	2.51 ± 0.22 ^a	2.51 ± 0.22 ^b
Non-roasted maize		3.29 ± 0.61	3.69 ± 0.48	14.04 ± 1.23	2.91 ± 0.03	23.93 ± 0.28

¹All values are expressed as the mean ± SD of triplicate determinations. Means with different superscripts within a column (a–e) are significantly different at $p < 0.05$ by a Duncan's multiple range test

²Not detected

with higher roasting temperature and longer roasting time (Table 2). The total polyphenol content in the extracts of row material was 4.02 ± 0.04 mg GAE/g of sample (data not shown), and that in the roasted maize at roasting temperatures of 200 °C, 220 °C, 250 °C, 270 °C, and 300 °C was 2.77–3.10, 2.70–3.98, 3.73–5.36, 4.31–6.78, and 4.21–10.68 mg GAE/g of sample, respectively (Table 2). The total polyphenol content was negatively correlated with the fructose ($r = -0.8378$; $p < 0.001$), glucose ($r = -0.8240$; $p < 0.001$), sucrose ($r = -0.7612$; $p < 0.001$), and total free sugar contents ($r = -0.8569$; $p < 0.001$) (Table 3).

The total flavonoid content in the extracts of row material was 192.70 ± 14.55 µg CE/g of sample (data not shown), and that in the roasted maize at roasting temperatures of 200 °C, 220 °C, 250 °C, 270 °C, and 300 °C was 364.13–922.86, 567.30–1018.10, 684.76–1462.54, 802.22–1646.67, and 929.21–1545.08 µg CE/g of sample, respectively (Table 2). The total flavonoid content was negatively correlated with fructose ($r = -0.7730$; $p < 0.001$), glucose ($r = -0.7465$; $p < 0.001$), sucrose

($r = -0.8486$; $p < 0.001$), maltose ($r = -0.3766$; $p < 0.05$), and total free sugar ($r = -0.8996$; $p < 0.001$), but a significant positive correlation existed with total polyphenol content ($r = 0.8162$; $p < 0.001$) (Table 3). These results suggest that the roasting process may have significantly increased the amount of polyphenolics [18]. Many antioxidant compounds are present in plant materials, mainly covalently bonded with insoluble polymers [25]. Therefore, heat treatment might disrupt cell walls and liberate antioxidant compounds from insoluble portions of maize, thus increasing the pool of bioaccessible antioxidant compounds.

Some individual phenolic acid composition of roasted maize

The phenolic acids compositions of the roasted maize at various roasting conditions are shown in Table 4. The phenolic acids that were detected in the roasted maize are gallic acid, homogentisinic acid, caffeic acid, p-coumaric acid, ferulic acid, naringin, hesperidin, and myricetin. The

Table 2 The total polyphenol, flavonoid contents, DPPH and ABTS radical scavenging activities of the ethanolic extracts of roasted maize according to roasting conditions

Roasting temp. (°C)	Roasting time (min)	Total polyphenol (mg gallic acid equivalents/g sample)	Total flavonoid (µg catechin equivalents/g sample)	Radical scavenging activity (mg trolox equivalents/100 g sample)	
				DPPH radical	ABTS radical
200	30	2.77 ± 0.21 ^{a1}	364.13 ± 33.45 ^d	9.73 ± 0.44 ^c	36.91 ± 0.35 ^d
200	40	2.92 ± 0.13 ^a	665.71 ± 9.52 ^c	11.30 ± 0.70 ^b	38.52 ± 0.60 ^c
200	50	3.04 ± 0.28 ^a	821.27 ± 14.55 ^b	12.28 ± 0.80 ^b	40.13 ± 0.25 ^b
200	60	3.10 ± 0.25 ^a	922.86 ± 16.50 ^a	13.85 ± 0.97 ^a	43.75 ± 0.59 ^a
220	20	2.70 ± 0.09 ^d	567.30 ± 14.55 ^e	10.37 ± 0.17 ^d	35.52 ± 0.60 ^c
220	30	3.32 ± 0.09 ^c	643.49 ± 5.499 ^d	13.27 ± 0.36 ^c	38.63 ± 0.54 ^d
220	40	3.43 ± 0.08 ^c	716.51 ± 19.83 ^c	16.75 ± 0.61 ^b	43.80 ± 0.92 ^c
220	50	3.77 ± 0.11 ^b	878.41 ± 48.87 ^b	17.16 ± 0.17 ^b	46.64 ± 0.35 ^b
220	60	3.98 ± 0.13 ^a	1018.10 ± 28.57 ^a	19.08 ± 0.63 ^a	48.86 ± 0.17 ^a
250	20	3.73 ± 0.04 ^c	684.76 ± 16.50 ^d	10.77 ± 0.96 ^d	33.91 ± 0.82 ^c
250	30	4.21 ± 0.17 ^b	735.56 ± 23.97 ^d	15.13 ± 0.99 ^c	49.03 ± 0.17 ^d
250	40	4.48 ± 0.04 ^b	938.73 ± 19.83 ^c	18.21 ± 0.70 ^b	56.42 ± 0.82 ^c
250	50	5.32 ± 0.17 ^a	1316.51 ± 19.83 ^b	19.37 ± 0.56 ^a	65.48 ± 0.25 ^b
250	60	5.36 ± 0.54 ^a	1462.54 ± 54.15 ^a	20.64 ± 0.35 ^a	68.93 ± 0.54 ^a
270	20	4.31 ± 0.56 ^c	802.22 ± 14.55 ^e	14.55 ± 1.06 ^e	51.97 ± 0.82 ^c
270	30	4.46 ± 0.09 ^c	1110.16 ± 19.83 ^d	16.70 ± 1.16 ^d	58.48 ± 0.63 ^d
270	40	5.89 ± 0.07 ^b	1313.33 ± 28.57 ^c	21.40 ± 0.44 ^c	65.76 ± 0.42 ^c
270	50	7.23 ± 0.37 ^a	1475.24 ± 19.05 ^b	30.52 ± 0.89 ^b	78.88 ± 0.76 ^b
270	60	6.78 ± 0.35 ^a	1646.67 ± 25.20 ^a	34.23 ± 0.46 ^a	85.77 ± 2.92 ^a
300	20	4.21 ± 0.20 ^c	929.21 ± 5.499 ^d	15.13 ± 0.36 ^d	58.81 ± 0.84 ^d
300	30	6.00 ± 0.52 ^b	1218.10 ± 19.05 ^c	25.46 ± 0.56 ^c	74.93 ± 1.01 ^c
300	40	10.32 ± 0.46 ^a	1411.75 ± 33.45 ^b	34.29 ± 0.53 ^b	88.72 ± 0.50 ^b
300	50	10.68 ± 0.44 ^a	1545.08 ± 29.10 ^a	41.43 ± 0.27 ^a	105.39 ± 0.50 ^a
Non-roasted maize		4.02 ± 0.04	192.70 ± 14.55	11.35 ± 0.36	35.19 ± 0.88

¹All values are expressed as mean ± SD of triplicate determinationsMeans with different superscripts within a column (a–e) are significantly different at $p < 0.05$ by Duncan's multiple range test**Table 3** Correlation coefficients among free sugar, total polyphenol, total flavonoid contents, total phenolic acid contents, and radical scavenging activity of roasted maize tea according to roasting conditions

Factor	Glucose	Sucrose	Maltose	Total free sugar	Polyphenol	Flavonoid	Total phenolic acid	DPPH	ABTS
Fructose	0.9972***	0.6503***	0.3124 ^{NS}	0.8427***	− 0.8378***	− 0.7730***	− 0.3462 ^{NS}	− 0.8628***	− 0.8461***
Glucose	1.0000	0.6129**	0.3150 ^{NS}	0.8161***	− 0.8240***	− 0.7465***	− 0.3277 ^{NS}	− 0.8536***	− 0.8219***
Sucrose	—	1.0000	0.2435 ^{NS}	0.9560***	− 0.7612***	− 0.8486***	− 0.7878***	− 0.7906***	− 0.8671***
Maltose	—	—	1.0000	0.3260 ^{NS}	− 0.2117 ^{NS}	− 0.3766*	− 0.2628 ^{NS}	− 0.4012*	− 0.3336 ^{NS}
Total free sugar	—	—	—	1.0000	− 0.8569***	− 0.8996***	− 0.6968***	− 0.8949***	− 0.9383***
Polyphenol	—	—	—	—	1.0000	0.8162***	0.5752**	0.9475***	0.9471***
Flavonoid	—	—	—	—	—	1.0000	0.6241**	0.8723***	0.9105***
Total phenolic acid	—	—	—	—	—	—	1.0000	0.6316**	0.6123**
DPPH	—	—	—	—	—	—	—	1.0000	0.9619***

^{NS}Not significantSignificant at * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

Table 4 Phenolic acid contents in ethanolic extracts of roasted maize according to roasting conditions

Roasting temp. (°C)	Roasting time (min)	Gallic acid (µg/g)	Homogentisic acid (µg/g)	Caffeic acid (µg/g)	p-Coumaric acid (µg/g)	Ferulic acid (µg/g)	Naringin (µg/g)	Hesperitin (µg/g)	Myricetin (µg/g)	Total (µg/g)
200	30	23.95 ± 4.42 ^{dl}	97.60 ± 3.95 ^d	48.22 ± 3.90 ^b	42.08 ± 1.22 ^d	58.35 ± 1.46 ^c	4.94 ± 0.83 ^c	53.73 ± 0.76 ^d	35.13 ± 2.30 ^d	363.99 ± 3.65 ^d
200	40	141.81 ± 9.56 ^c	124.29 ± 5.08 ^c	55.10 ± 1.57 ^a	52.05 ± 2.45 ^c	58.86 ± 1.60 ^c	6.31 ± 1.45 ^c	55.87 ± 0.83 ^c	40.31 ± 1.19 ^c	534.60 ± 12.5 ^c
200	50	216.87 ± 4.93 ^b	276.67 ± 16.5 ^b	23.33 ± 1.38 ^c	60.59 ± 1.50 ^b	61.01 ± 0.41 ^b	8.50 ± 0.73 ^b	69.58 ± 1.35 ^b	43.82 ± 1.36 ^b	760.37 ± 14.1 ^b
200	60	275.78 ± 5.88 ^a	317.35 ± 5.34 ^a	20.41 ± 0.27 ^d	79.85 ± 1.33 ^a	74.31 ± 0.35 ^a	22.77 ± 1.17 ^a	76.40 ± 0.71 ^a	72.16 ± 1.37 ^a	929.07 ± 28.1 ^a
220	20	160.23 ± 6.93 ^e	127.67 ± 3.17 ^e	22.95 ± 1.17 ^c	56.42 ± 1.58 ^b	58.20 ± 1.51 ^e	27.26 ± 1.08 ^d	62.69 ± 0.70 ^d	40.42 ± 1.85 ^e	555.83 ± 6.13 ^e
220	30	216.87 ± 4.93 ^d	281.45 ± 14.6 ^d	13.69 ± 1.55 ^d	75.02 ± 1.05 ^a	66.68 ± 0.65 ^d	35.05 ± 1.74 ^c	76.91 ± 1.23 ^c	58.70 ± 1.67 ^d	824.38 ± 8.54 ^d
220	40	240.32 ± 2.27 ^c	1141.03 ± 12.1 ^c	33.14 ± 1.86 ^a	54.79 ± 1.34 ^b	70.96 ± 0.88 ^c	43.57 ± 1.11 ^b	81.35 ± 1.46 ^b	84.15 ± 4.11 ^c	1929.69 ± 41.2 ^c
220	50	537.29 ± 8.43 ^a	1215.57 ± 21.7 ^b	22.85 ± 0.91 ^c	41.69 ± 0.58 ^c	75.04 ± 0.49 ^b	65.20 ± 1.23 ^a	95.78 ± 0.70 ^a	97.93 ± 2.43 ^b	2372.58 ± 14.6 ^b
220	60	504.18 ± 5.28 ^b	1496.06 ± 20.7 ^a	26.90 ± 1.46	36.70 ± 2.54 ^d	80.47 ± 0.90 ^a	45.84 ± 2.54 ^b	75.03 ± 1.53 ^c	110.58 ± 6.14 ^a	2732.09 ± 42.6 ^a
250	20	864.46 ± 8.74 ^a	197.05 ± 13.7 ^e	12.91 ± 0.44 ^c	48.43 ± 0.90 ^a	48.90 ± 3.33 ^c	32.90 ± 1.33 ^d	77.65 ± 4.37 ^c	54.83 ± 2.64 ^c	1293.17 ± 40.4 ^d
250	30	331.58 ± 3.58 ^b	745.20 ± 18.3 ^d	25.58 ± 0.79 ^b	44.32 ± 1.75 ^b	79.56 ± 0.53 ^b	61.96 ± 1.36 ^a	93.87 ± 4.01 ^b	61.81 ± 1.72 ^d	1454.95 ± 11.7 ^c
250	40	59.80 ± 2.39 ^c	1112.42 ± 15.8 ^c	37.18 ± 1.66 ^a	30.80 ± 0.27 ^c	84.19 ± 1.11 ^a	47.91 ± 2.38 ^b	103.09 ± 1.33 ^a	87.58 ± 3.10 ^c	1640.21 ± 38.4 ^b
250	50	43.69 ± 8.73 ^d	1280.31 ± 36.4 ^b	37.64 ± 2.82 ^a	13.84 ± 2.63 ^d	85.87 ± 1.03 ^a	41.69 ± 1.06 ^c	47.39 ± 0.81 ^d	106.53 ± 0.42 ^b	1656.95 ± 40.8 ^b
250	60	18.93 ± 2.92 ^e	1650.05 ± 71.7 ^a	36.32 ± 0.82 ^a	14.60 ± 1.33 ^d	87.06 ± 1.10 ^a	40.78 ± 1.43 ^c	44.24 ± 1.55 ^e	120.70 ± 0.85 ^a	1858.70 ± 23.3 ^a
270	20	592.10 ± 6.95 ^a	788.59 ± 5.99 ^e	29.47 ± 1.24 ^d	51.82 ± 2.98 ^a	51.60 ± 3.39 ^e	48.73 ± 2.36 ^a	84.04 ± 3.50 ^c	73.07 ± 1.81 ^e	1730.47 ± 29.9 ^b
270	30	158.20 ± 6.25 ^b	1072.11 ± 24.9 ^d	57.93 ± 0.90 ^a	31.23 ± 0.36 ^b	91.69 ± 2.39 ^b	32.36 ± 3.81 ^b	108.37 ± 3.36 ^a	101.09 ± 5.10 ^d	1652.98 ± 21.7 ^{bc}
270	40	103.55 ± 1.55 ^c	1323.75 ± 35.6 ^c	36.82 ± 4.36 ^c	3.73 ± 0.39 ^c	108.08 ± 4.16 ^a	26.35 ± 1.15 ^c	94.75 ± 0.66 ^b	111.93 ± 2.12 ^c	1597.64 ± 22.7 ^c
270	50	82.06 ± 5.06 ^d	1443.95 ± 19.5 ^b	36.19 ± 0.59 ^c	–	82.68 ± 1.45 ^c	–	45.63 ± 0.91 ^d	122.39 ± 2.61 ^b	1584.52 ± 23.2 ^c
270	60	53.84 ± 5.51 ^e	1852.29 ± 52.7 ^a	47.07 ± 2.72 ^b	–	71.14 ± 2.20 ^d	–	30.83 ± 0.46 ^e	131.60 ± 2.30 ^a	1984.52 ± 77.6 ^a
300	20	406.04 ± 9.85 ^a	1145.57 ± 29.5 ^d	33.80 ± 2.06 ^b	67.91 ± 1.47 ^a	73.85 ± 2.26 ^c	14.72 ± 1.37 ^a	108.61 ± 1.93 ^a	90.99 ± 2.43 ^d	1933.96 ± 43.5 ^c
300	30	77.75 ± 8.92 ^b	1411.58 ± 24.7 ^c	49.90 ± 2.13 ^a	2.21 ± 0.35 ^b	81.23 ± 1.43 ^b	–	82.78 ± 1.90 ^b	95.16 ± 0.71 ^c	1800.63 ± 37.8 ^d
300	40	– ²	1942.84 ± 76.0 ^b	–	–	88.09 ± 1.56 ^a	–	28.76 ± 0.84 ^c	120.62 ± 1.81 ^b	2180.32 ± 79.4 ^b
300	50	–	2189.49 ± 37.7 ^a	–	–	62.35 ± 1.01 ^d	–	25.27 ± 1.19 ^d	125.70 ± 0.96 ^a	2402.81 ± 39.3 ^a
Non-roasted maize	–	–	39.80 ± 2.76	–	24.65 ± 1.73	12.75 ± 1.52	–	48.70 ± 1.42	3.43 ± 1.22	129.32 ± 4.27

¹All values are expressed as the mean ± SD of triplicate determinations. Means with different superscripts within a column (a–e) are significantly different at $p < 0.05$ by a Duncan's multiple range test

²Not detected

phenolic acids composition of the non-roasted maize was homogentisic acid (39.80 µg/g of sample), *p*-coumaric acid (24.65 µg/g of sample), ferulic acid (12.75 µg/g of sample), hesperidin (48.70 µg/g of sample), and myricetin (3.43 µg/g of sample). The total phenolic acid compound content of the non-roasted maize was 129.32 µg/g of sample. The predominant phenolic acid in the roasted maize was homogentisic acid, and its contents in the roasted maize at the roasting temperatures of 200, 220, 250, 270, and 300 °C were 97.60–317.35, 127.67–1496.06, 197.05–1650.05, 788.59–1852.29, and 1145.57–2189.49 µg/g of sample, respectively (Table 4). The homogentisic acid and myricetin contents in the roasted maize significantly increased with higher roasting temperature and longer roasting time. The gallic acid, caffeic acid, *p*-coumaric acid, and naringin increased at low roasting temperature and short roasting time, but decreased at high roasting temperature and long roasting time. The other phenolic acids differed according to roasting temperature and roasting time. Higher temperature (> 100 °C) treatment might destroy the flavonoid compounds of citrus peel [26]. However, Lou et al. [27] reported that the phenolic compositions of hot water extract from peel of immature calamondin after heating at 150 °C for 1.5 h were increased. In particular, the heating also enhances the release of some phenolic compounds from the immature calamondin peel, i.e., naringin, tangeretin, ferulic acid, *p*-coumaric acid, and gallic acid [27]. Total phenolic acid content was negatively correlated with sucrose ($r = -0.7878$; $p < 0.001$) and total free sugar contents ($r = -0.6968$; $p < 0.001$), but significant positive correlations existed with total polyphenol ($r = 0.5752$; $p < 0.01$) and flavonoid contents ($r = 0.6241$; $p < 0.01$) (Table 3). Wang et al. [28] reported that the predominant phenolic acids in maize are ferulic acid, *p*-coumaric acid, caffeic acid, and syringic acid. Kim et al. [29] reported that the phenolic compound contents of small black soybean of chlorogenic acid, ferulic acid, caffeic acid, and cinnamic acid increased after roasting. This study suggests that the phenolic acid contents of homogentisic acid and myricetin of roasted maize increase with higher roasting temperature and longer roasting time.

DPPH and ABTS radical scavenging activities of roasted maize

The stable DPPH radical, which has maximum absorption at 515 nm, is used widely to evaluate the free radical scavenging activity of hydrogen-donating antioxidants in many plant extracts [18]. The ABTS method is employed extensively to measure the relative radical scavenging activity of hydrogen-donating and chain-breaking antioxidants in many plant extracts [24]. The DPPH and ABTS

radical scavenging activities of the extracts of roasted maize expressed as mg TE per 100 g sample are shown in Table 2. The DPPH and ABTS radical scavenging activities in the roasted maize significantly increased with higher roasting temperature and longer roasting time. The DPPH radical scavenging activity in the extracts of row material was 11.35 ± 0.36 mg TE/100 g sample (data not shown), and that in the roasted maize at roasting temperatures of 200, 220, 250, 270, and 300 °C was 9.73–13.85, 10.37–19.08, 10.77–20.64, 14.55–34.23, and 15.13–41.43 mg TE/100 g sample, respectively (Table 2). The DPPH radical scavenging activity was negatively correlated with the fructose ($r = -0.8628$; $p < 0.001$), glucose ($r = -0.8536$; $p < 0.001$), sucrose ($r = -0.7906$; $p < 0.001$), maltose ($r = -0.4012$; $p < 0.05$), and total free sugar contents ($r = -0.8949$; $p < 0.001$), but it was significantly positively correlated with total polyphenol ($r = 0.9475$; $p < 0.001$), flavonoid ($r = 0.8723$; $p < 0.001$), and total phenolic acid ($r = 0.6316$; $p < 0.01$) (Table 3).

The ABTS radical scavenging activity in the extracts of row material was 35.19 ± 0.88 mg TE/100 g sample (data not shown), and that in the roasted maize at roasting temperatures of 200, 220, 250, 270, and 300 °C was 36.91–43.75, 35.52–48.86, 33.91–68.93, 51.97–85.77, and 58.81–105.39 mg TE/100 g sample, respectively (Table 2). The high radical scavenging activity of roasted maize extracts showed high contents of homogentisic acid, myricetin and ferulic acid. The ABTS radical scavenging activity was negatively correlated with fructose ($r = -0.8461$; $p < 0.001$), glucose ($r = -0.8219$; $p < 0.001$), sucrose ($r = -0.8671$; $p < 0.001$), and total free sugar contents ($r = -0.9383$; $p < 0.001$), but it was significantly positively correlated with total polyphenol ($r = 0.9471$; $p < 0.001$), flavonoid ($r = 0.9105$; $p < 0.001$), and total phenolic acid contents ($r = 0.6123$; $p < 0.01$), and with DPPH radical scavenging activity ($r = 0.9619$; $p < 0.001$) (Table 3). The results confirmed that polyphenolic compounds may be responsible for the majority of the antioxidant activity of roasted maize. Many previous studies have reported a significant correlation between polyphenolics and antioxidant activities in food [18, 24].

In this study, non-enzymatic browning reaction products may have been formed during prolonged heat treatment with improvement in antioxidant activity [28]. Recently, a study on tomato and coffee found that prolonged heat treatment enhanced the antioxidant activity of these food items [30]. In the last decade, many studies examined antioxidant activity after heat treatment and showed that heated products exhibit chain-breaking and oxygen-scavenging activities [31]. Velioglu et al. [32] reported strong relationships between antioxidant activity and total

phenolic content in several fruits, vegetables, and grain products. Other research indicates that heating causes enhanced antioxidant activity in fruits and vegetables because of the enhancement of the antioxidant properties of naturally occurring compounds or the formation of novel compounds such as Maillard reaction products that have antioxidant activity [33, 34]. Therefore, it is possible that the release of phenolic compounds from maize after heat treatment could increase its antioxidant activity.

Acknowledgements This study was performed with the support of the “Cooperative Research Program for Agriculture Science and Technology Development (Project No. PJ01117201)” Rural Development Administration, Republic of Korea.

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