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Phenolic Content, Composition, Antioxidant Activity, and Their Changes during Domestic Cooking of Potatoes

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Potatoes in the diet contribute significantly to antioxidant daily intake worldwide. The influence of different domestic cooking conditions, boiling, microwaving, and baking, on total phenolics (TP), antioxidant capacity, phenolic composition, and tryptophan content was studied using eight commercial potato varieties. The antioxidant capacity was detected by the methods of oxygen radical absorbance capacity assay (ORAC) and the 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH•) assay. The phenolic composition and tryptophan content were determined using high-performance liquid chromatography coupled with a diode array detector (HPLC-DAD), whereas phenolics and tryptophan were identified by means of HPLC−mass spectrometry, HPLC-DAD, and authentic standards. Antioxidant capacity was influenced by potato variety and cooking conditions; however, cooked potatoes retained 68−97% ORAC value depending on cooking procedure and variety. Chlorogenic acid and its isomers dominated the phenolic composition of each variety involved in this study. ORAC and TP were highly and positively correlated ($r = 0.9119$). Norkotah ranked highest in chlorogenic acid content and antioxidant value. Principal component analysis showed different cooking processes did not influence the trend of the antioxidant profile of the eight potato varieties, but specific compounds exert influence on the antioxidant capacity. The results imply that the potato varieties rich in antioxidant components could be good antioxidant sources as activities are not greatly affected by different cooking conditions.

KEYWORDS: Potato; antioxidants; chlorogenic acid; phenolics; tryptophan; cooking; principal component analysis

INTRODUCTION

Extensive research indicates that foods rich in antioxidants have been shown to play an essential role in the prevention of cardiovascular diseases and to lower the risk of a number of chronic diseases, such as atherosclerosis, and cancers (*1, 2*).

It is estimated that one-third of all cancer deaths in the United States could be avoided through appropriate dietary modification (*3*). Consumers have become aware of the benefits of natural antioxidants from edible materials, such as fruits and vegetables, because of their presumed safety and potential nutritional and therapeutic effects (*4*).

Today, potato has become an exceptionally high-yielding carbohydrate-rich crop (*5*); although in general potato is not regarded as a high antioxidant food, one cannot ignore the potato's high daily consumption. A recent study has shown that potatoes, owing to their high daily consumption, contributed to the diet the third highest total phenolic content from fruits and vegetables after orange and apple (*6*). The total antioxidant capacity of fresh potatoes commonly consumed in the United States was reported to be in the range of 10.59−15.55 μmol of TE/g (Trolox equivalent per gram) depending on variety, whereas on

a per serving basis potato has exceptionally high ORAC intake, ranging from 1870 to 4649 μmol of TE (*7*).

Previous research data have shown that the phenolic, carotenoid, and anthocyanin components are important indicators of high total antioxidant capacity (*8−10*), whereas potato variety and different skin and flesh colors affect antioxidant capacity. The measurement of ORAC and ferric reducing ability of plasma assay (FRAP) showed that red- or purple-fleshed potatoes were 2−3 times higher than white-fleshed potato in antioxidant levels (*11, 12*). Phenolic acids such as chlorogenic, caffeic, ferulic, protocatechuic, and *p*-coumaric acid have been identified in potato (*13*). Chlorogenic acid is considered to be the key component because it constitutes up to 90% of total phenolic content of potato tubers (*14*). Other compounds such as tyrosine and tryptophan have also been identified in potato (*15*), with tryptophan shown to exhibit antihydroxyl radical activities (*16*). Although there is considerable research involving antioxidant values of potato including the effect of genotype and breeding on antioxidant components of potatoes, the literature on how cooking methods affect antioxidant activity of potatoes is limited (*17−19*).

Cooking processes may change not only food physical characteristics but also chemical composition (*20, 21*). The

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antioxidant properties of food have been shown to change during thermal processing (*22, 23*). It is reported that processed sweet corn has increased antioxidant activity, which does not support the notion that processed fruits and vegetables have lower nutritional value than fresh produce (*22*). The effects of thermal processing on the antioxidant properties would be useful knowledge because potatoes are consumed in cooked forms. Common methods to cook potato include boiling, microwave processing, and oven baking.

The objectives of this study were (1) to investigate the phenolic content and hydrophilic antioxidant capacities of different potato varieties and their changes during domestic cooking processes and (2) to further understand the relationship between the chemical composition and antioxidant activity. In this study, commercial table potatoes were supplied by the Peak of Market Co., Winnipeg, Manitoba, Canada, which is a grower-owned vegetable supplier in Manitoba that ships produce worldwide.

MATERIALS AND METHODS

Reagents. Folin−Ciocalteu reagent, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH$^\bullet$), 2,2′-azobis(2-methylpropionamide) dihydrochloride (AAPH), D-tyrosine, L-tyrosine, L-tryptophan, and phenolic acid standard compounds were purchased from Sigma-Aldrich (St. Louis, MO). Phenolic acid standard compounds were as follows: gallic acid, ferulic acid, caffeic acid, catechin, 5-*o*-caffeoylquinic acid, *p*-coumaric acid, rutin, and *o*-coumaric acid. Trolox and fluorescein were purchased from Fisher Acros Organics (Fair Lawn, NJ) for oxygen radical absorbance capacity assay (ORAC). Methanol, aectonitrile, and formic acid were of mass grade (Fisher Scientific Co., Ottawa, ON, Canada).

Samples and Processing. Different varieties of table potatoes (approximately 25 kg for each variety) were shipped from Peak of the Market within 2 days after harvest. To ensure highly reproducible results, representative samples were obtained from each variety by selecting six average-sized tubers (each approximately 150 ± 10 g). Whole tubers were thoroughly washed under running water. For raw potatoes, whole potatoes were manually sliced into approximate uniform cubes of 1 cm^3 and flash-frozen with liquid nitrogen before being lyophilized for 24 h in vacuo (Genesis SQ freeze drier, VirTis, Gardiner, NY). The lyophilized potato was milled and sieved (30 mesh size), with the resulting powder stored at −20 °C prior to analyses.

All cooking procedures were performed using six tubers for each potato variety.

Baking. Potato tubers, wrapped with aluminum foil, were baked for 40 min in an electric convection oven (Moffat model EC03, Toronto, Canada) preheated to 178 °C.

Boiling. Potato tubers were immersed in 1.8 L of boiling distilled water in a stainless steel pot with a lid and boiled at 100 °C for 15 min.

Microwaving. Potato tubers were cooked at high power for 5 min in a microwave oven (1100 W, Kenmore, 1.6 ft^3).

After cooking and cooling, the whole potatoes were cut into small cubes, lyophilized, ground, and sieved (30 mesh size), and the residue remaining on the screen was remilled until all sample passed through the 30 mesh screen and stored at 4 °C until use.

Sample Extraction. Extraction was performed by an automated Dionex-ASE300 (accelerated solvent extractor) system (Dionex Co., Milano, Italy). Powdered freeze-dried samples (500 mg) were well mixed with diatomaceous earth (2:1, w/w) and loaded into the 66 mL cell on top of Ottawa sand (12 mL). A mixture of methanol/water (80:20) was used as the extraction solvent. The extraction protocol was as follows: pressure, 1500 psi; temperature, 40 °C; static time, 15 min; flush volume, 60%; purge time, 90 s; and static cycles, 3. The total amount of extraction solvent was about 80 mL.

The extraction volume was collected and evaporated to dryness in a rotary evaporator (Hitec, Yamato Scientific America Inc., Sanata Clara, CA). Phenolic compounds were dissolved in 5 mL of 50% methanol and stored at −20 °C in the dark until analysis.

Total Phenolic Analysis. The total phenolic content of the samples was determined according to a modified Folin−Ciocalteu (F-C) colorimetric method (*24*). The sample solution (0.2 mL) was allowed to react with 1.9 mL of freshly diluted 10-fold F-C reagent, followed by the addition of 1.9 mL of sodium carbonate solution (60 g/L), and vortex mixed. The absorbance reading was recorded after 90 min and compared to a prepared blank of distilled water at 725 nm (50Bio UV−visible spectrophotomer, Varian, Australia). Gallic acid was used as an equivalent standard. All analyses were performed in duplicate. The results were expressed as milligram of gallic acid equivalents per gram of freeze-dried weight basis (mg of GAE/g of FDW).

DPPH$^\bullet$ Scavenging Activity. The DPPH method was performed according to the method of Brand-Williams et al. (*25*) and Li et al. (*23*) with minor modification. The method involves the reaction of the antioxidants with the stable DPPH$^\bullet$ in 95% ethanol solution. Briefly, a 60 μmol/L DPPH$^\bullet$ solution was freshly made in 95% ethanol solution. The sample (200 μL) was reacted with 3.8 mL of the DPPH$^\bullet$ solution for 60 min. The absorbance (*A*) at 515 nm was measured at 60 min against a blank of pure 95% ethanol. DPPH tests were all carried out in duplicate. Antioxidant activity was calculated as follows:

$$\% \text{ DPPH}^\bullet \text{ scavenging activity} = \left(1 - \frac{A_{\text{sample},t}}{A_{\text{control},i}}\right) \times 100.$$

Trolox was used as an equivalent standard. The results were expressed as milligrams of Trolox equivalents per gram of freeze-dried weight basis (mg of TE/g of FDW).

Oxygen Radical Absorbance Capacity Assay (ORAC). The ORAC assay was performed by a Precision 2000 automated microplate pipetting system (Bio-Tek Instruments, Inc., Winooski, VT) with some modifications (*23*). Fluorescein (FL) acted as the fluorescent probe, and the antioxidative capacity of samples was measured by the decline in the inhibition of fluorescence induced by AAPH radical. An FL×800 microplate reader (Bio-Tek Instruments, Inc.) equipped with fluorescence filters for an excitation wavelength of 485/20 nm and an emission wavelength of 528/20 nm and controlled by KC4 3.0 software was used. Initially, 120 μL of fluorescence working solution was transferred to each well in a 96-well microplate, then 20 μL of buffer solution (blank), plus either Trolox standard, diluted samples, or 20 μM rutin control, was transferred to designated wells of the 96-well microplate. The 96-well microplate was

Table 1. Total Phenolic Content of Raw and Processed Potato (Milligrams of GAE per Gram of FDW)^a

variety	raw	boiled	baked	microwaved	LSD
Dakota Pearl	0.92 eA	0.80 fB	0.91 fAB	0.87 eAB	0.11
Goldrosh	2.35 bA	2.24 aAB	2.03 bBC	1.90 bC	0.21
Nordonna	2.06 cA	1.73 bB	1.71 dB	1.25 dC	0.20
Norkotah	3.04 aA	1.77 bC	2.12 aB	2.03 aB	0.25
Red Norland	2.09 cA	1.79 bB	1.8 bB	1.82 bB	0.2
Sangre	1.56 dA	1.06 eB	1.42 dA	1.22 dB	0.17
Viking	1.47 dA	1.25 dC	1.39 eAB	1.33 dBC	0.08
Dark Red Norland	2.05 cA	1.52 cC	1.74 cB	1.48 cC	0.21
LSD	0.17	0.15	0.28	0.18	

^{a} Mean values within a column with different lower case letters are significantly different at *P* < 0.05. Mean values within a row with different upper case letters are significantly different at *P* < 0.05.

Table 2. Antioxidant Capacity by DPPH Assay of Raw and Processed Potato (Milligrams of TE per Gram of FDW)^a

variety	raw	boiled	baked	microwaved	LSD
Dakota Pearl	1.39 eA	1.25 dA	1.29 cA	1.03 cB	0.29
Goldrosh	2.44 bA	2.21 aB	1.90 bC	2.40 aA	0.12
Nordonna	1.58 eA	1.54 cA	1.51 cA	0.91 dB	0.18
Norkotah	2.83 aA	2.26 aB	2.12 aC	2.38 aB	0.12
Red Norland	2.16 cA	1.75 bB	1.75 bB	1.54 bB	0.13
Sangre	1.90 dA	1.34 dB	1.45 dC	0.91 dD	0.10
Viking	1.46 eA	1.14 eB	1.13 eB	0.63 eC	0.19
Dark Red Norland	1.94 dA	1.67 bB	1.47 cB	1.28 cC	0.22
LSD	0.12	0.11	0.18	0.23	

^{a} Mean values within a column with different lower case letters are significantly different at *P* < 0.05. Mean values within a row with different upper case letters are significantly different at *P* < 0.05.

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incubated at 37 °C for 20 min, and then 60 μL of AAPH solution was transferred to each well of the 96-well microplate. After an adhesive sealing film had been used to cover the plat, the 96-well microplate was immediately transferred to the FL×800 microplate fluorescence reader, and the fluorescence was measured at 1 min intervals for 50 min at 37 °C. All of the reaction mixtures were prepared in the measured plate in

Table 3. Antioxidant Capacity by ORAC Assay of Raw and Processed Potato (Milligrams of TE per Gram of FDW)[a]

variety	raw	boiled	baked	microwaved	LSD
Dakota Pearl	10.1 eA	6.92 fC	7.08 dC	8.36 eB	0.75
Goldrosh	19.52 bA	18.82 aA	18.97 aA	17.03 bB	1.72
Nordonna	15.74 eA	13.79 cB	15.10 bA	12.57 dC	1.45
Norkotah	21.91 aA	17.22 bB	20.02 aA	20.03 aA	2.33
Red Norland	16.98 cA	14.25 cB	14.56 bB	15.76 bA	1.64
Sangre	14.6 eA	10.84 eB	14.48 bA	11.36 dB	1.31
Viking	16.04 cA	12.23 dC	12.61 cC	14.01 cB	1.06
Dark Red Norland	17.02 cA	13.97 cC	15.37 bB	14.08 cB	1.37
LSD	1.29	0.98	1.23	1.52	

[a] Mean values within a column with different lower case letters are significantly different at $P < 0.05$. Mean values within a row with different upper case letters are significantly different at $P < 0.05$.

duplicate, and at least three independent assays were performed for each sample.

Data processing was performed according to previous papers (*26*). The results were expressed as milligrams of Trolox equivalent per gram of freeze-dried weight (mg of TE/g of FDW).

Determination of Phenolic Acid Composition. Analyses were conducted on a HPLC (Waters 2695) system equipped with a photodiode array detector (PDA) (Waters 996), Empower software, and autosampler (Waters 717 plus) (Waters Corp., Milford, MA). The mass of compounds was detected using a Waters Q-TOF mass spectrometer equipped with an ESI.

Phenolic acids were separated on a reverse-phase Luna C18 column (150 mm × 4.6 mm, 5 μm) (Phenomenex, Torrance, CA). The flow rate was 0.7 mL/min, and the injection volume was 10 μL for each sample. Solvent A was 1% acetic acid in water, and solvent B was 100% acetonitrile with 0.1% acetic acid (v/v). The gradient started with 3% B for 7 min, increased to 5−40% B between 7 and 45 min, and reached 100% B at 46 min, was maintained until 51 min, then decreased to 3% B in 6 min. Absorbance was monitored at 280 and 325 nm for the duration of the separation (57 min). The mass spectrometer was operated in negative mode, and the ESI scan was set at m/z 10−1900. The capillary voltage for ESI was 1.2 kV, the cone voltage was 35 V, source temperature was 350 °C, and the collision energy was 10 eV.

Table 4. Aromatic Amino Acid and Phenolic Acid Contents in Raw and Processed Potato (Milligrams per Kilogram)

| variety	tryptophan	3-CQA	4-CQA	5-CQA	caffeic acid
			Raw		
Dakota Pearl	89.6 ± 13.6	95.4 ± 16.2	21.2 ± 6.3	420.5 ± 73.0	nd[a]
Goldrosh	370.3 ± 19.6	28.6 ± 6.0	33.6 ± 3.7	1845.5 ± 139.2	24.5 ± 1.6
Nordonna	295.1 ± 9.5	70.0 ± 7.5	37.4 ± 1.6	1172.6 ± 50.6	nd
Norkotah	248.7 ± 11.9	299.6 ± 18.5	184.9 ± 5.9	3183.4 ± 85.2	53.4 ± 5.8
Red Norland	292.4 ± 8.2	180.7 ± 20.9	66.9 ± 2.5	1560.0 ± 57.5	15.5 ± 3.3
Sangre	193.6 ± 7.8	nd	12.7 ± 1.0	1166.0 ± 53.7	93.8 ± 13.6
Viking	398.6 ± 6.3	nd	9.1 ± 0.5	628.8 ± 7.7	0.3 ± 5.4
Dark Red Norland	219.6 ± 7.3	116.1 ± 11.8	42.2 ± 4.0	1063.6 ± 47.8	38.8 ± 0.2
			Boiled		
Dakota Pearl	60.5 ± 1.6	28.0 ± 1.6	14.8 ± 0.2	548.5 ± 29.8	1.1 ± 0.1
Goldrosh	483.5 ± 13.4	103.5 ± 2.4	45.6 ± 1.9	1492.1 ± 62.6	8.9 ± 0.2
Nordonna	193.3 ± 12.7	nd	20.4 ± 1.3	1161.6 ± 34.6	66.5 ± 0.8
Norkotah	194.1 ± 4.4	510.8 ± 23.0	135.1 ± 4.6	2113.1 ± 103.8	7.4 ± 1.9
Red Norland	268.5 ± 1.3	184.5 ± 11.3	64.3 ± 2.7	1384.2 ± 62.4	4.4 ± 0.1
Sangre	128.1 ± 1.4	24.0 ± 6.2	12.7 ± 13.9	1148.9 ± 46.8	3.0 ± 0.2
Viking	362.5 ± 2.8	nd	7.03 ± 0.0	483.5 ± 11.3	nd
Dark Red Norland	258.5 ± 13.8	138.1 ± 12.9	50.1 ± 17.1	1176.9 ± 234.5	1.1 ± 3.7
			Baked		
Dakota Pearl	36.2 ± 5.0	4.9 ± 1.9	10.8 ± 0.1	582.9 ± 24.3	14.1 ± 0.1
Goldrosh	369.2 ± 2.1	133.2 ± 12.9	41.5 ± 2.6	1200.3 ± 28.4	12.4 ± 1.5
Nordonna	257.0 ± 4.9	36.8 ± 6.2	32.2 ± 2.5	1139.7 ± 51.9	17.3 ± 0.5
Norkotah	195.3 ± 1.4	564.2 ± 36.3	118.8 ± 12.1	1682.1 ± 50.8	13.2 ± 2.3
Red Norland	197.1 ± 27.4	7.7 ± 1.1	32.9 ± 0.9	1183.2 ± 18.8	30.6 ± 0.5
Sangre	209.1 ± 1.2	45.4 ± 16.1	17.9 ± 10.0	1162.8 ± 23.4	11.7 ± 1.2
Viking	348.2 ± 0.7	nd	0.5 ± 0.4	479.9 ± 3.9	17.1 ± 0.7
Dark Red Norland	350.3 ± 51.4	nd	24.1 ± 0.6	989.8 ± 29.7	17.1 ± 0.7
			Microwaved		
Dakota Pearl	54.4 ± 1.6	4.9 ± 1.1	10.8 ± 0.1	572.5 ± 21.3	14.2 ± 0.1
Goldrosh	314.0 ± 13.0	nd	14.0 ± 0.6	1666.5 ± 55.9	29.3 ± 2.8
Nordonna	179.5 ± 2.2	nd	20.7 ± 0.7	909.1 ± 30.1	31.7 ± 1.0
Norkotah	221.6 ± 6.5	441.8 ± 11.1	158.0 ± 2.0	2625.3 ± 65.8	29.4 ± 0.1
Red Norland	410.1 ± 1.0	62.9 ± 4.3	46.2 ± 0.7	1245.1 ± 28.7	20.8 ± 0.4
Sangre	231.7 ± 2.5	nd	22.7 ± 31.0	569.1 ± 7.9	39.9 ± 6.6
Viking	499.9 ± 4.0	nd	nd	138.3 ± 7.9	9.3 ± 0.1
Dark Red Norland	312.7 ± 2.6	17.2 ± 0.8	30.0 ± 0.2	949.4 ± 5.7	52.1 ± 0.5

[a] nd, not detected.

Identification of the phenolic acids was accomplished by matching the spectra, mass spectrum, and the retention times of peaks in samples with those of the authentic standards. Other caffeoylquinic acids (CQA) such as 3-CQA and 4-CQA were quantified as chlorogenic acid (5-CQA) equivalents. The HPLC analyses were carried out in duplicate.

Statistical Analysis. The effects of variety and raw or cooked state on TP, DPPH, and ORAC were determined by one-way analysis of variance (ANOVA) using SAS version 8.1. Least significant differences (LSD) were detected using Student's *t* test at $P = 0.05$. Pearson correlation coefficients were determined to evaluate relationships between variables. Principal component analysis (PCA) was performed on centered and standardized data to compare the antioxidant profile of the different varieties. Microsoft Excel 2003 was used for the bubble plot.

RESULTS AND DISCUSSION

Effect of Varieties and Processing on Total Phenolics, Antioxidant Capacity. The total phenolic content (TPC) of potatoes is

presented in **Table 1** for the eight table varieties. TPC ranged from 0.92 mg of GAE/g of FDW in raw Dakota Pearl to 3.04 mg of GAE/g of FDW in raw Norkotah. As reported previously (*27*), Norkotah ranked highest in TPC compared with other varieties. TPC declined in all varieties after boiling, baking, and microwave cooking. Norkotah processed by baking, boiling, and microwave cooking lost 41.8, 30.3, and 33.3%, respectively, of TPC present in raw tuber. However, corresponding antioxidant values did not decline in the same order, indicating total phenolics (as measured by F-C) may not be the only contributor to antioxidant activity. As shown in **Tables 1–3**, TPC and antioxidant activities of potato were significantly different when varieties were compared. However, when the effects of different cooking procedures for the same variety were compared, no significant difference was found. The effect of different processing on TPC of potato was variety
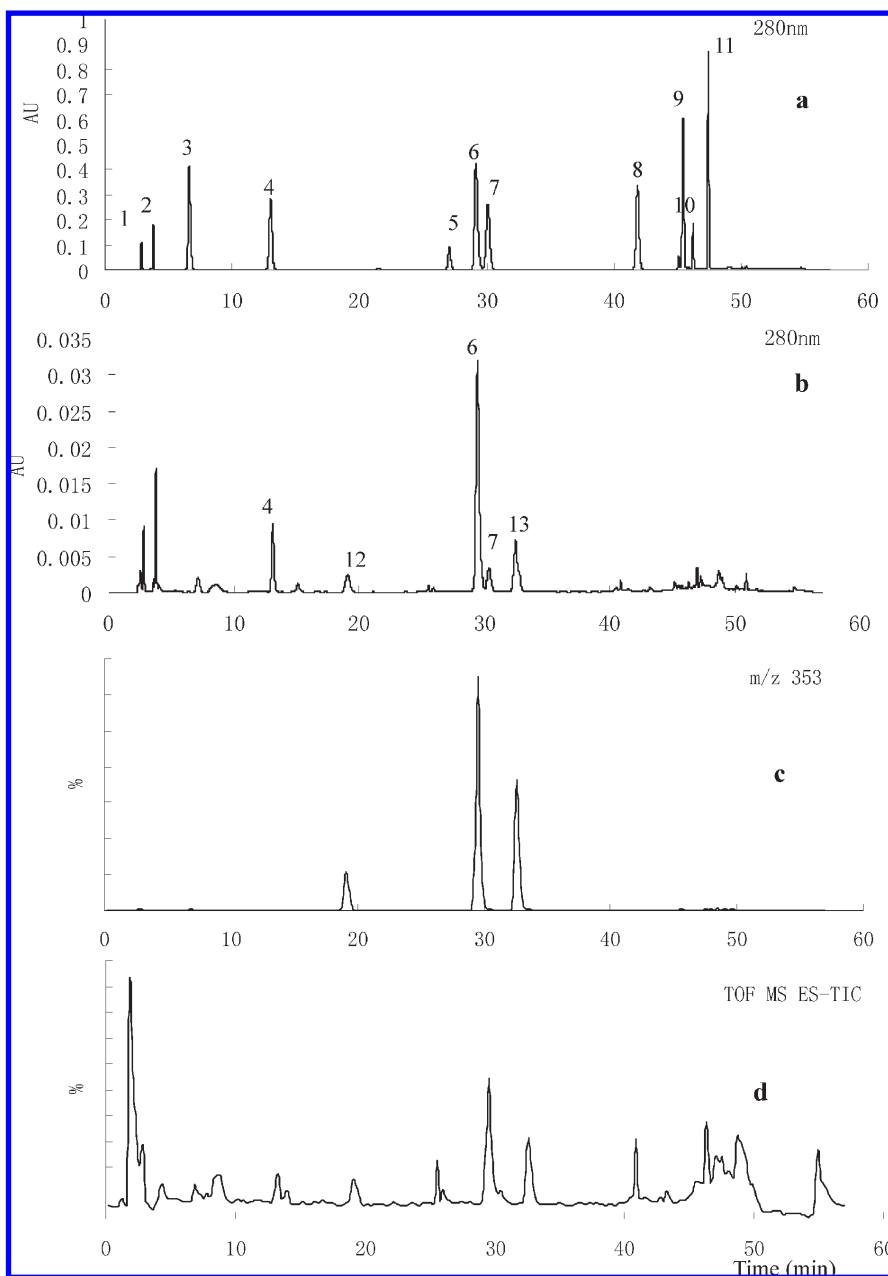
Figure 1. Specimen LC-MS chromatograms: (**a**) UV chromatogram (280 nm) of standards (peaks: 1, D-tyrosine; 2, L-tyrosine; 3, gallic acid; 4, L-tryptophan; 5, catechin; 6, 5-*o*-caffeoylquinic acid; 7, caffeic acid; 8, *p*-coumaric acid; 9, ferulic acid; 10, rutin; 11, *o*-coumaric acid); (**b**) UV chromatogram (280 nm) of the raw Norkotah extract (peaks: 12, 3-*o*-caffeoylquinic acid; 13, 4-*o*-caffeoylquinic acid); (**c**) selected ion chromatogram (*m/z* 353) of the raw Norkotah extract; (**d**) total ion chromatogram of the raw Norkotah extract.

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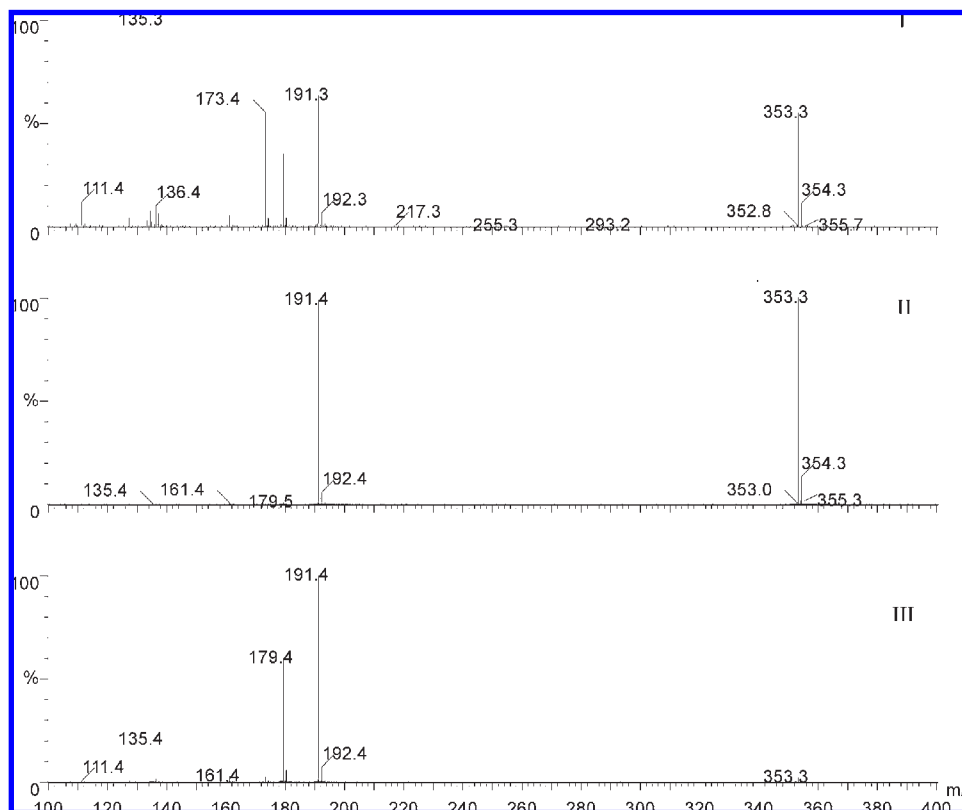
Figure 2. Negative ion MS^2 spectra for 3-CQA (III), 4-CQA (I), and 5-CQA (II).

dependent. For Dakota Pearl, baking and microwave cooking did not significantly affect the levels of TPC; for Red Norland, boiling, baking, and microwave processing were almost at the same level; for Nordonna, baking and microwave processing were significant in affecting TPC level; for Dark Red Norland, boiling and baking were significant cooking processes.

Two assays were used to estimate antioxidant capacities in this study. DPPH values are shown in **Table 2**, and ORAC values are shown in **Table 3**. The antioxidant value declined for all potato varieties after the various cooking procedures. Both assays gave a comparable rank of antioxidant value for raw varieties; however, the same trend was not observed for cooked samples. For five varieties (Norkotah, Red Norland, Sangre, Viking, and Dark Red Norland), the antioxidant capacity by DPPH assay of cooked potato was significantly different from that of raw; for Nordonna, Dakota Pearl, and Goldrosh microwave processing did not significantly affect their DPPH value; ORAC values showed that the antioxidant capacity of Dakota Pearl, Viking, and Dark Red Norland was significantly lower after being processed, and ORAC value of Goldrosh declined significantly after microwave processing when compared with that of the raw. For baked Nordonna and Sangre, ORAC values were significantly different from raw; for Norkotah, only boiling affected ORAC value; for Red Norland, boiling and baking resulted in significantly lower ORAC. In terms of antioxidant capacity, the three different cooking methods did not show a consistent trend.

Andre et al. (*5*) reported that total phenolic content of 74 native cultivated potato genotypes varied between 1.12 and 12.37 mg of gallic acid equiv/g of DW. The range of hydrophilic ORAC values was 28.25−250.6 μmol of Trolox equiv/g of DW. The levels of TPC in raw potato in this research range from 0.92 to 3.04 mg of gallic acid equiv/g of DW, and ORAC values range from 10.1 to 21.91 mg of Trolox equiv/g of DW, which are

consistent with previously reported results. They are, however, lower than published results. Cooked potatoes retained 68−97% ORAC value depending on cooking procedure and variety. The results imply potatoes can be good sources of daily antioxidant intake as antioxidant capacities are not greatly affected by different cooking conditions.

The ORAC assay is a single quantification method with high specificity that measures the capacity of an antioxidant through combined inhibition time and inhibition degree (*28, 29*), whereas DPPH is a stable radical with the assay providing a convenient, easy, and rapid way to evaluate the antiradical capacities. Both DPPH and ORAC are based on the premise that antioxidants can delay the oxidation of the substrate in the presence of an oxidizable substrate and an oxidizing agent. In ORAC, AAPH is a free radical generating system, measurement is related to AAPH decomposition and formation of peroxyl radicals, and quantification is by combining both the percentage of inhibition and the length of inhibition time (*27*). The DPPH assay evaluates total antioxidant activity by reduction of DPPH•, which is monitored by the decrease in its absorbance at the characteristic wavelength of 515 nm during the reaction.

Brand-Williams et al. (*25*) suggested three hypotheses to explain the antiradical efficiencies of the different monophenolic compounds, with their research showing that interaction of a potential antioxidant with DPPH• depends on its structural conformation. A previous review (*30*) emphasized the difficulty of comparing studies due to the large differences in assays. The ORAC value could be comparable across laboratories due to its automated and largely standardized method (*31*). In addition, for phenolic antioxidants, the ORAC principle is closely related to biological functions of chain-breaking antioxidants (*32*).

Phenolic Acid Compounds and Aromatic Amino Acid. Chlorogenic acid was the main phenolic acid contributing to antioxidant capacity. As shown in **Table 4**, 5-CQA was the predominant

phenolic acid isomer in the potato extract, and tryptophan was also quantified by HPLC. Previous studies reported tyrosine and tryptophan existed in fresh-cut Monalisa potato (*15*). However in this study (shown in **Figure 1**), according to the MS spectrum, only tryptophan identification was supported by both retention time and MS fragment information. As shown in **Table 4**, the tryptophan and phenolic acids contents were affected differently by cooking. It has been reported that oven-baked potatoes contain no chlorogenic acid, and boiled potatoes and microwaved potatoes could retain less than half of the original amount (*33*). However, we have shown chlorogenic acid to still exist in baked potato. In comparison to previous research, potatoes were not peeled in our research before cooking, and the skin appears to act as a barrier preventing losses. In addition to peeling, baking conditions could also explain the different findings. The reported literature work was carried out at 212 °C for 45 min, whereas our cooking was at 178 °C for 40 min. Previous study (*34*) also indicated that the 5-CQA content of boiled potatoes decreased significantly because of its high rate of diffusion in water; however, only trace amounts of 5-CQA were destroyed during oven baking at 40 °C, whereas at oven baking at 100 °C for 60 min, the loss was about 24%. Another study (*34*) also reported that the susceptibility of 5-CQA pure standard at different times and temperatures of heating tests showed that only trace amounts of 5-CQA were left after drastic treatment at 220 °C for 30−60 min, with the pyrolysis reaction causing a loss of 60% of original 5-CQA after heating at 220 °C for 15 min. In our study, for Norkotah, 5-CQA retained 66.4, 52.8, and 82.5% of the original amount after boiling, baking, and microwave cooking. Another possible explanation for the different findings is that in the previous study pure standards were used, whereas in our study the potato component matrix could have affected the results.

The aromatic amino acid tryptophan is reported to contribute to antioxidant capacity (*16*). It has been reported that tryptophan has a higher inhibitory activity than mannitol and dimethyl sulfoxide (DMSO) on the Fenton reaction-induced degradation of 2-deoxy-D-ribose (*35*). Tryptophan stability after cooking conditions in our study is shown in **Table 4**. For some varieties such as Dakota Pearl, Nordonna, and Norkotah, tryptophan decreased after cooking, by 31.5, 34.5, and 22%, respectively; however, other varieties showed a slight increase after cooking. Decomposition of protein during the thermal process is a possible explanation. Further research is needed to investigate the effects of heat processing on aromatic amino acid and the mechanism involved.

In general, previous studies on the phenolic and aromatic amino acid composition of potatoes have reported the contents of tyrosine, tryptophan, chlorogenic acid, chlorogenic acid isomer, caffeic acid, *p*-coumaric acid, and ferulic acid in the peels and/or flesh of potato tuber cutivars (*9*, *18*). Classically,

chlorogenic acids (CGA) are a family of esters formed between certain *trans*-cinnamic acids and quinic acid [1 L-1(OH),3,4/5-tetrahydroxycyclohexane carboxylic acid (*36*)]. The isomers of caffeoylquinic acid (CQA) are 1-*o*-caffeoylquinic acid (1-CQA), 3-*o*-caffeoylquinic acid (3-CQA), 5-*o*-caffeoylquinic acid (5-CQA), and 4-O*o*-caffeoylquinic acid (4-CQA) according to the IUPAC numbering system with 5-CQA being the only one commercially available. Chlorogenic acid, its isomers, and aromatic amino acids were identified by authentic standard and mass spectrum of the HPLC-MS (shown in **Figure 1**). In a previous paper, discriminating the isomers was difficult because of the unavailability of authentic standards. Now, with the aid of LC-MS^n, the fragmentation behavior of these isomers can be investigated. Although the parent ion of CQA isomers is the same, m/z 353, in negative mode, their fragmentation patterns are not similar to each other. As described in previous research (*37*), for 3-CQA, MS^2 ion has a base peak at m/z 191 and a relatively intense MS^2 ion at m/z 179; for 4-CQA, the MS^2 ion base peak was m/z 173; and for 5-CQA and 1-CQA, the MS^2 base peak m/z was 191, with weak or undetectable MS^2 at m/z 179. 5-CQA and 1-CQA could be distinguished by retention time on reverse phase packing. Our results (shown in **Figure 2**) were strongly supported by previous studies (*37*), and 5-CQA was also identified by the retention time of authentic standard.
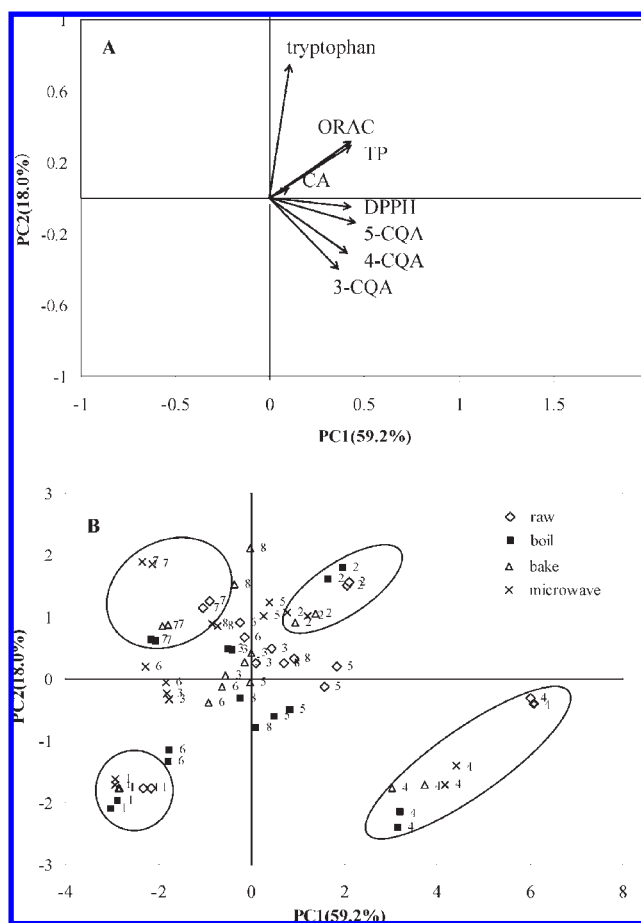
Figure 3. PCA of studied chemical compound contents and antioxidant capacity in eight varieties: (**A**) relationships between variables; (**B**) 64 observations representing each variety including the duplication. Principal component 1 values are on the *x*-axis, and principal component 2 values are on the *y*-axis. Numbers 1−8 correspond to the eight varieties: 1, Dakota Pearl; 2, Goldrosh; 3, Nordonna; 4, Norkotah; 5, Red Norland; 6, Sangre; 7, Viking; 8, Dark Red Norland.

Table 5. Pearson's Correlation Coefficient between Total Phenolic (TP), DPPH, ORAC, and Five Compounds [Tryptophan (Tryp), 3-*o*-Caffeoylquinic Acid (3-CQA), 4-*o*-Caffeoylquinic Acid (4-CQA), 5-*o*-Caffeoylquinic Acid (5-CQA), and Caffeic Acid (CA)]

	DPPH	ORAC	Tryp	3-CQA	5-CQA	CA	4-CQA
TP	0.7905[a]	0.9119[a]	0.4412[a]	0.4578[a]	0.7802[a]	0.2490[a]	0.6366[a]
DPPH		0.7630[a]	0.0777	0.5872[a]	0.8772[a]	0.2146	0.6974[a]
ORAC			0.5328[a]	0.5529[a]	0.7581[a]	0.1903	0.6444[a]
Tryp				−0.1054	0.0398	−0.0908	−0.0496
3-CQA					0.6799[a]	−0.0997	0.8839[a]
5-CQA						0.2581[a]	0.8672[a]
CA							0.1024
4-CQA							

[a] Significant (*p* < 0.01).

Correlation Coefficients among Different Parameters. Pearson correlation coefficient results were observed among DPPH, TP, ORAC, tryptophan (Tryp), 3-CQA, 5-CQA, CA, and 4-CQA (**Table 5**). As previous literature reported (*38*, *39*), significant correlations were observed between TP and all other variables. The isomers of cholorgenic acid had significant correlations with TP, DPPH, and ORAC and also showed significant correlations between one another. Tryptophan had significant correlations with TP and ORAC but did not correlate well with DPPH. Tryptophan also did not exhibit any correlation with chlorogenic acid isomers and caffeic acid, but showed significant correlation with TP.

Principal Component Analysis (PCA). PCA is a multivariate technique for examining relationships among several quantitative variables. PCA was done to determine the deviation of total phenolic (TP), DPPH, ORAC, and compounds Tryp, 3-CQA, 4-CQA, 5-CQA, and CA on eight table potato varieties under raw and three cooking treatments. The results shown in **Figure 3** indicate principal component 1 (PC 1) (59.2%) and principal component 2 (PC2) (18.0%) account for 77.2% of the total variance. The variables showed similar vector directions, indicating a strong relationship between these attributes. As can be seen on the loading plot (**Figure 3A**), the different isomers of chlorogenic acid, 5-CQA, 4-CQA, and 3-CQA, of similar molecular structure, showed similar vector directions, implying a high degree of relationship between them. On the contrary, tryptophan distinguishes itself on a different vector direction due to its different molecular structure. For this study, caffeic acid was not taken into account in the PCA because it had a short vector length.

The directions of the vectors suggest that PC1 explains the variability in the quantity of antioxidant capacity, whereas PC2 explains the differences in mechanism of determining antioxidant activities. From the results obtained in our study (**Figure 3A**), as

the vector direction of tryptophan was different from those of phenolic acids, the difference in its biosynthetic pathway could give a reasonable explanation.

As indicated in **Figure 3B**, three different processing treatments were scattered and four different groups were observed. Different cooking processes did not influence the trend of the antioxidant profile of eight potato varieties; however, some varieties such as Dakota Pearl, Goldrosh, Norkotah, and Viking form a group or cluster by their varieties rather than different cooking processes. PC1 mainly discriminates Goldrosh and Norkotah from Dakota Pearl and Viking, whereas PC2 mainly discriminates Goldrosh and Viking from Dakota Pearl and Norkotah. Norkotah and Goldrosh ranked first and second in antioxidant capacity of potatoes involved in this research, whereas Dakota Pearl ranked last and Viking, second from last. The variability in specific components and antioxidant capacity among the eight varieties under three different cooking processes was graphically emphasized using bubble plots (**Figure 4**). The area of the bubble is proportional to the concentration of the variables concerned. Goldrosh and Viking were identified for their relatively high tryptophan content compared with those of Dakota Pearl and Norkotah. There is strong evidence to support our opinion that PC2 provides an explanation of different mechanisms in antioxidant activities.

The results imply that specific compounds affect potato antioxidant capacity. Goldrosh has a similarly high antioxidant capacity as Norkotah; however, the determined factors of their antioxidant profile are different. For different varieties, different cooking methods affected their antioxidant capacities due to the influence of component content. Specific compounds influence antioxidant capacity to different extents. Norkotah, which was high in phenolic acid compounds, and Goldrosh, which has high tryptophan content, exhibited high antioxidant capacities.
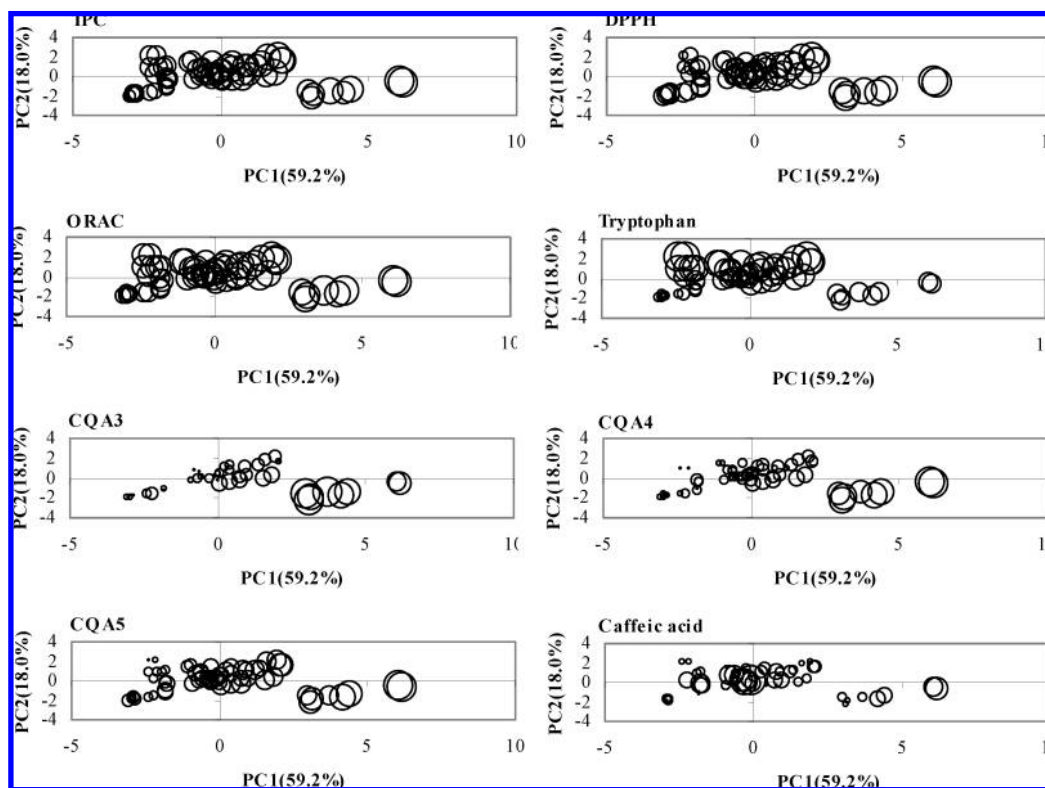
Figure 4. Bubble plots of the PCA performed on the eight varieties, emphasizing quantitative variability in chemical compound content and antioxidant capacity.

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