

Analysis of Phenolic Compounds by High-Performance Liquid Chromatography and Liquid Chromatography/Mass Spectrometry in Potato Plant Flowers, Leaves, Stems, and Tubers and in Home-Processed Potatoes

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Potato plants synthesize phenolic compounds as protection against bruising and injury from bacteria, fungi, viruses, and insects. Because antioxidative phenolic compounds are also reported to participate in enzymatic browning reactions and to exhibit health-promoting effects in humans, a need exists for accurate methods to measure their content in fresh and processed potatoes. To contribute to our knowledge about the levels of phenolic compounds in potatoes, we validated and used high-performance liquid chromatography and liquid chromatography/mass spectrometry to measure levels of chlorogenic acid, a chlorogenic isomer, and caffeic acid in flowers, leaves, stems, and tubers of the potato plant and in home-processed potatoes. The total phenolic acid content of flowers (626 mg/100 g fresh wt) was 21 and 59 times greater than that of leaves and stems, respectively. For all samples, chlorogenic acid and its isomer contributed 96–98% to the total. Total phenolic acid levels (in g/100 g fresh wt) of peels of five potato varieties grown in Korea ranged from 6.5 to 42.1 and of the flesh (pulp) from 0.5 to 16.5, with peel/pulp ratios ranging from 2.6 to 21.1. The total phenolic acid content for 25 American potatoes ranged from 1.0 to 172. The highest amounts were present in red and purple potatoes. Home processing of pulp with various forms of heat induced reductions in the phenolic content. The described methodology should facilitate future studies on the role of potato phenolic compounds in the plant and the diet.

KEYWORDS: Potatoes; flowers; leaves; chlorogenic acid; caffeic acid; HPLC; LC/MS

INTRODUCTION

Phenolic compounds are secondary plant metabolites found in potatoes and other plants (reviewed in 1 and 2). In the plant, phenolic compounds function beneficially to defend against invading pathogens including bacteria, fungi, and viruses. They also, however, participate in enzyme-catalyzed browning reactions that may adversely affect the color, flavor, and nutritional quality of potatoes. Antioxidative phenolic compounds show promise as health-promoting phytochemicals as they have been shown to exhibit beneficial antimutagenic, anticarcinogenic, antiglycemic, cholesterol-lowering, and antimicrobial properties. These considerations suggest the need for accurate analysis of

phenolic compounds in potato leaves, stems, and tubers and in processed potato products.

Because potatoes are one of our major food plants, the major objective of the present study was to define and validate with the aid of high-performance liquid chromatography (HPLC) and liquid chromatography/mass spectrometry (LC/MS) the content and distribution of antioxidative phenolic compounds in parts of the potato plant, in potato tubers, in the peel and flesh of tubers, in potatoes sold commercially in Korea and the United States, and in home-processed potatoes. **Figure 1** shows the structures of *trans*-cinnamic acid and four cinnamic acid derivatives (phenolic compounds) reported to be present in potatoes.

MATERIALS AND METHODS

Materials. Chlorogenic acid ($\geq 95\%$, catalog no. 3878, lot 27H1006), *p*-coumaric acid (catalog no. 9008, lot 87H3434), and ferulic acid (catalog no. 3500, lot 48H0416) were obtained from Sigma (St. Louis,

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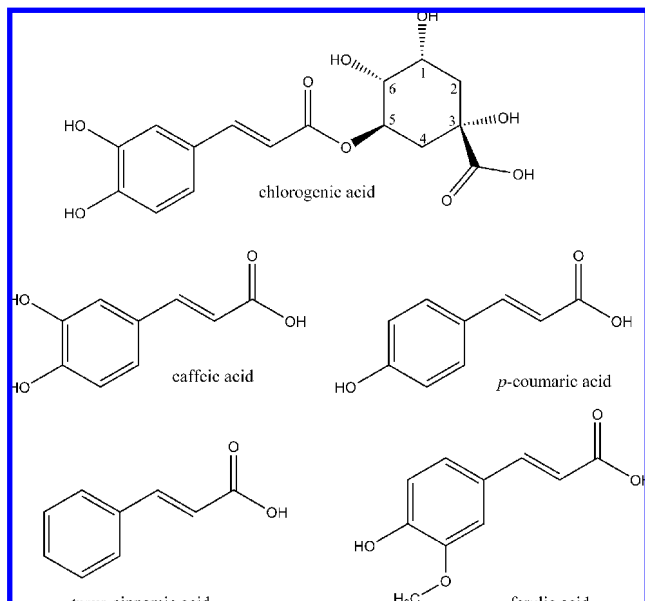


Figure 1. Structures of cinnamic acid derivatives.

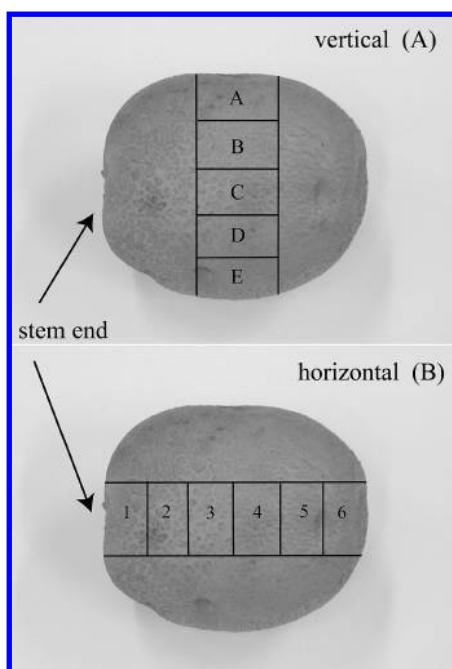


Figure 2. Photomicrographs of the surface of the Superior potato tuber showing vertical (A) and horizontal (B) cuts of slices (sticks) used for analysis of phenolic compounds.

MO). *trans*-Cinnamic acid (catalog no. 8085-7, lot 17420JS) was purchased from Aldrich (St. Louis, MO). Caffeic acid was obtained from Sigma and recrystallized from water. Acetonitrile (LC/MS grade) was obtained from Burdick & Jackson (Muskegon, MI), analytical grade formic acid was from DC Chemical Co. (Seoul, Korea), and ethanol was from Samchun Pure Chemicals (Pyungtack, Korea). The solvents were filtered through a 0.45 μ m membrane filter (Millipore, Bedford, MA) and degassed with an ultrasonic bath before use. The oil used for frying, trade-named Haipyo, was produced by the Shindongbang Corp. of Korea.

The plants of Superior (Korean name, Sumi) potato variety were a gift from a farmer in Gyeonju City, Korea. The tubers of five potato varieties (Jasim, Atlantic, Jowon, Superior, and Jopung) were obtained from the Youngyang Potato Experimental Station (Gyeongsangbuk, Korea). American potatoes of unknown history were obtained from Berkeley Bowl (Berkeley, California).

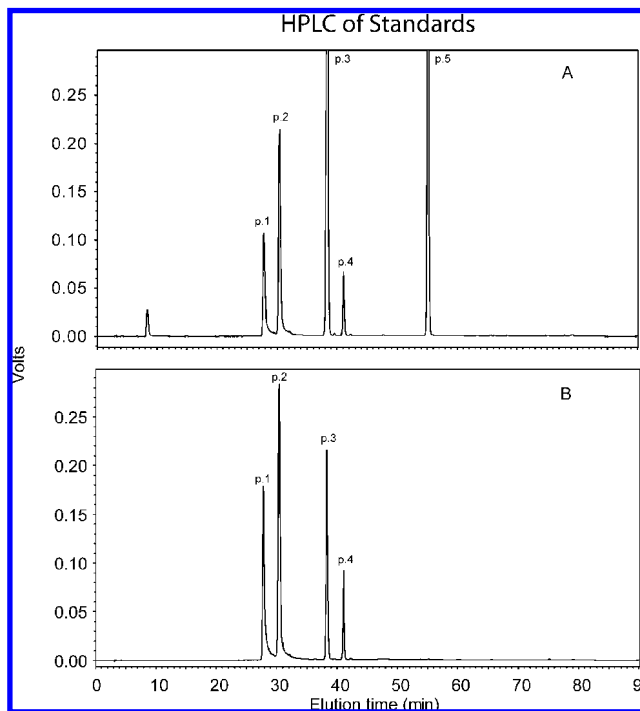


Figure 3. HPLC chromatograms of standard chlorogenic acid (peak 1), caffeic acid (peak 2), *p*-coumaric (peak 3), ferulic acid (peak 4), and *trans*-cinnamic acid (peak 5). Column, Inertsil ODS-3 v (5 μ m, 4.0 mm \times 250 mm); flow rate, 1.0 mL/min; column temperature, 20 $^{\circ}$ C; mobile phase, acetonitrile:0.5% formic acid (gradient mode); and detector, UV at 280 nm (A) and 340 nm (B).

Preparation of Freeze-Dried Unpeeled Potatoes from Fresh Potatoes Sold in the United States. The following method was used to freeze dry (lyophilize) whole tubers of 25 potato varieties obtained at local stores in Berkeley, California. Potatoes were rinsed in cool water and dried. They were then diced, weighed, and quickly cooled with liquid nitrogen to a nearly frozen state. The samples were transferred to a subzero freezer at -35 $^{\circ}$ C where they were frozen solid overnight. Samples were lyophilized over a period of 5 days, after which they were then removed from the lyophilizer, weighed, and immediately transferred to a zip-lock plastic bag to prevent the absorption of moisture. They were ground batchwise in a Waring blender (Waring Laboratory, Torrington, CT) and sieved through a 0.5 mm screen. Pieces, which would not pass through the screen, were ground in a mortar and pestle and passed through the sieve. Samples were then double-bagged and stored in the freezer at -35 $^{\circ}$ C. The freeze-dried powders from potatoes grown in the United States (American potatoes) were then sent to Korea for analysis.

Preparations of Samples for Analysis. *Potato Plants.* Flowers, leaves, and stems were collected during blooming of Superior potato plants. Each sample (0.5–1.0 g; $n = 3$) was macerated in a glass mortar with 10 mL of 80% ethanol and then centrifuged at 12000g for 10 min at 10 $^{\circ}$ C. The residue was re-extracted three times with 80% ethanol and centrifuged. The combined alcoholic solution was adjusted with 80% ethanol to 50 mL. The supernatant (20 μ L) was used for HPLC.

Potato Peel and Pulp from Five Potato Varieties. The peel and pulp of five potato varieties (Jasim, Atlantic, Jowon, Superior, and Jopung) were used for analysis of phenolic acids. Fresh potatoes from each of three uniform-sized tubers (Jasim: weight, 266–330 g; length, 108–113 mm; and height, 65–73 mm; Atlantic: weight, 208–254 g; length, 81–95 mm; and height, 69–75 mm; Jowon: weight, 252–304 g; length, 86–91 mm; and height, 79–89 mm; Superior: weight, 218–256 g; length, 86–95 mm; and height, 69–71 mm; and Jopung: weight, 272–312 g; length, 100–114 mm; and height, 69–73 mm) were chosen for analysis.

Potatoes by Size. Three to four peel and pulp samples from the following four sizes of Superior potato tubers were used for analysis

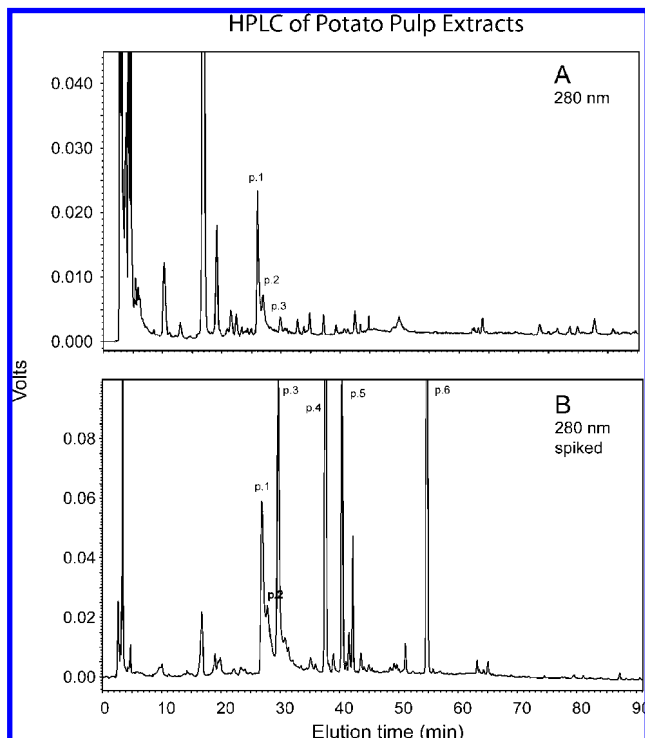


Figure 4. HPLC chromatogram of the extract from Superior potato pulp (A) and of the same extract spiked with standards (B). Identification; p.1, chlorogenic acid; p.2, chlorogenic acid isomer; p.3, caffeic acid; p.4, *p*-coumaric acid; p.5, ferulic acid; and p.6, *t*-cinnamic acid. Chromatographic conditions are the same as in Figure 3.

of phenolic acids: [large (L), 150–210 g; medium (M), 95–110 g; small (S), 56–65 g; and very small (VS), 19–25 g].

Extraction of Phenolic Compounds from Peels and Pulps of Potato Tubers. The potato tubers were each peeled to a depth of 2–3 mm with a clasp knife. Fresh peel weights amounted to 21.1–23.9% of the total weight of the potatoes. Fresh peel and pulp were then cut with a knife into 4 mm thick slices. Samples (10 g) of peel and pulp from each potato tuber were then placed into a 250 mL flask with a reflux condenser to which was added 50 mL of 80% ethanol, followed by heating at 80 °C for 10 min. After homogenization in a Waring blender, the mixture was again transferred to a flask for re-extraction, followed by centrifugation at 12000g for 15 min at 5 °C. The residue was extracted twice with 20 mL of 80% ethanol and centrifuged. The combined extracts were made up to 100 mL with 80% ethanol. This solution (10 mL) was evaporated under reduced pressure at 20 °C, and the residue was dissolved in 80% ethanol (1 mL) and centrifuged. The supernatant (20 μ L) was used for HPLC.

Distribution of Phenolic Acids Across the Potato Flesh. Superior potatoes (weight, 95–110 g; length, 58–60 mm; and height, 59–61 mm) were used for analysis of the distribution of phenolic acids throughout the body (flesh) of the potato. Two cutting methods were adopted for this purpose (Figure 2). In the first, the potato tubers were penetrated with a cork borer (i.d. 1.5 cm) horizontally from the stem end to the opposite end. The obtained plugs were cut with a clasp knife into six equal 1 cm long sticks. In the second, the potato tubers were penetrated vertically with a cork borer from the upper to lower surfaces and divided into five equal plugs. Each plug was weighed and then extracted for phenolic acid determination by the same method described earlier for the five potato varieties.

Sample Preparation for Home Processing. Superior potatoes were used to analyze changes in phenolic acid content induced by the different “cooking” methods. Three fresh potatoes (weight, 174–208 g; length, 73–86 mm; and height, 60–73 mm) were rinsed with water and patted dry with a paper towel. Potato plugs were obtained by penetration with a cork borer from the stem to the opposite end and then cut with a clasp knife. The plugs of the central part (length, 2 cm)

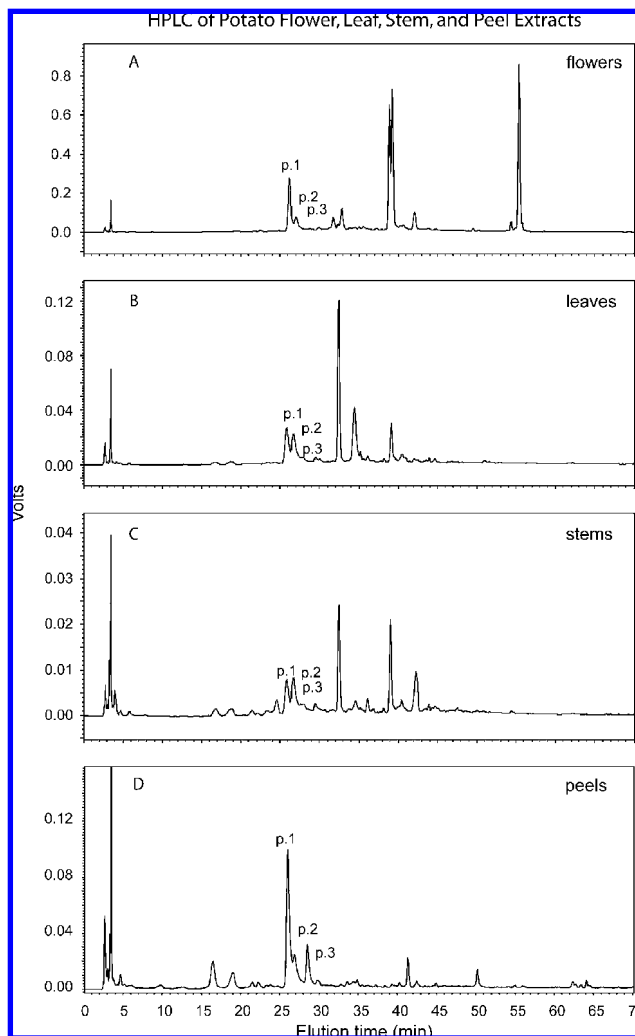


Figure 5. HPLC chromatograms of extracts from flowers (A), leaves (B), stems (C), and peels (D) of Superior potato plants. Identification: p.1, chlorogenic acid; p.2, chlorogenic isomer; and p.3, caffeic acid. Chromatographic conditions are the same as in Figure 3.

were divided with a clasp knife into two 1 cm long plugs. One plug was used as the untreated control, and the other was used for determination of the effect of the following home-processing conditions used in Korea on the phenolic acid content of the potato pulps.

Baking. The samples wrapped with aluminum foil were baked for 10 min in a gas oven range (Dongyang Magic Co., Korea) preheated to 200 °C.

Boiling. Distilled water (100 mL) was placed into an aluminum cook pot and boiled at 100 °C. When the water started boiling, the sample (one plug) was put into the pot and boiled for 10 min. For boiling with salt (NaCl), each plug was boiled for 10 min in distilled water containing 1 or 3% salt.

Frying. Distilled water (500 mL) in a pot was heated to the boiling point. Samples were added to the pot and then parboiled for 7 min. The moisture was then removed from the cooled samples with a paper towel. The samples (2 g) were then fried submerged in the oil (300 mL) for 30 s on a frying pan heated at 170 °C. They were held for 5 min at room temperature and then fried for an additional 30 s.

Microwaving. Samples were placed onto the middle of china plate and cooked at high heat for 1 min in a microwave oven (Mistubishi-RO-D52, Japan).

Steam Cooking. Potato samples were placed on a steamer at room temperature, containing 500 mL of distilled water. They were cooked at high heat for 10 min.

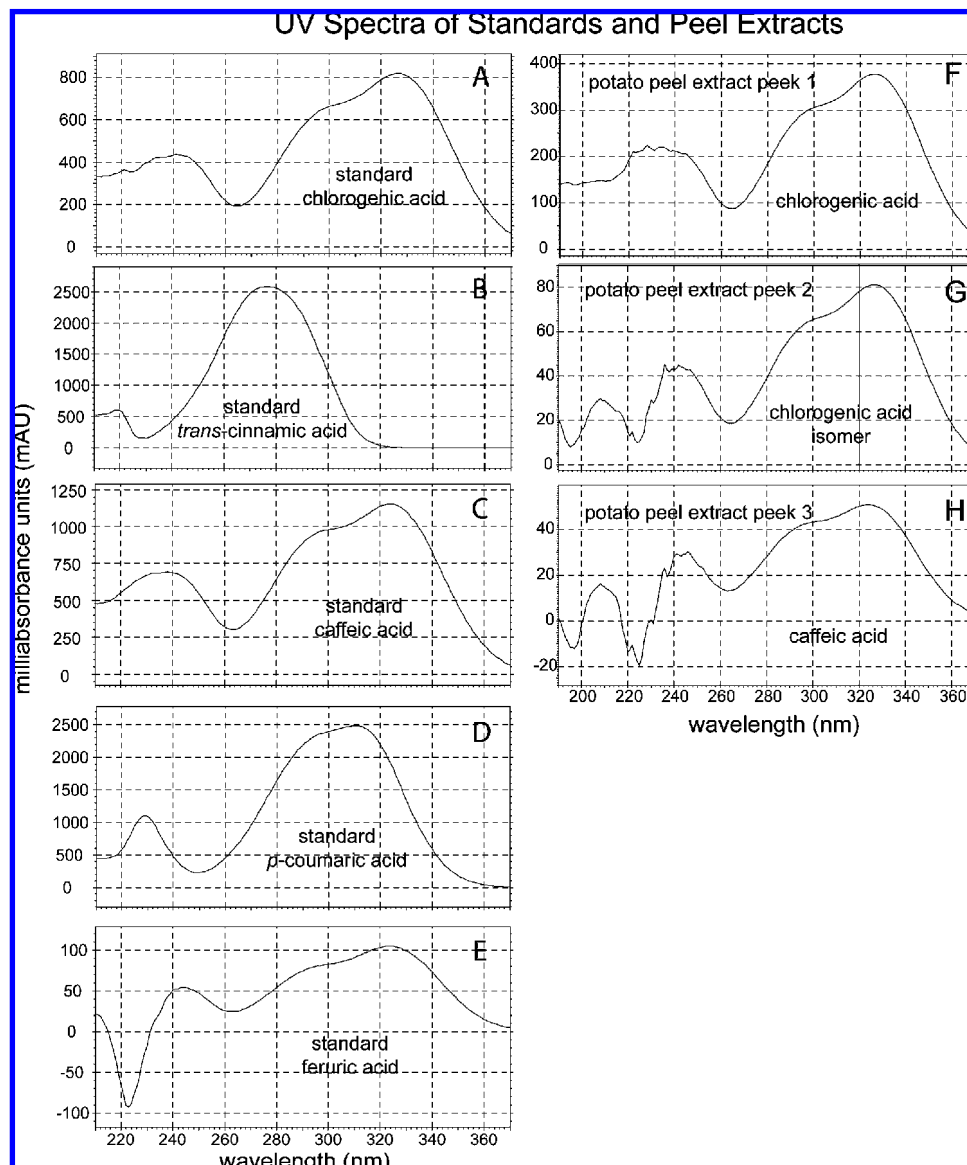


Figure 6. UV spectra of standard chlorogenic acid (A), *trans*-cinnamic acid (B), caffeic acid (C), *p*-coumaric acid (D), and ferulic acid (E). The spectra of peak 1 (chlorogenic acid) (F), peak 2 (chlorogenic acid isomer) (G), and peak 3 (caffeic acid) (H) were determined with HPLC fractions isolated from extracts of Superior potato peel.

Sautéing. Each sample was chopped into pieces (0.3 cm wide and 0.5 cm long) and stir-fried in a pan for 3 min with 5 mL of oil without salt.

Freeze-Dried Potato Samples. Each powder (0.8–1.0 g) was extracted with 5 mL of 80% ethanol using ultrasonication for 60 min at room temperature followed by centrifugation at 12000g for 10 min at 5 °C. This solution (20 μ L) was analyzed by HPLC.

Analysis of Phenolic Acids. **HPLC.** HPLC analysis was carried out on a Hitachi liquid chromatograph model 665-II equipped with a Shimadzu UV-vis detector (model SPD-10Avp, Kyoto, Japan) set at 280 and 340 nm. The column temperature was controlled with a Shimadzu CTO-10Asvp Thermometer. Chromatogram peak areas were integrated with a Hitachi D-2500 chromatointegrator. An Inertsil ODS-3v column [5 μ m, 4.0 mm \times 250 mm (GL Science Inc., Tokyo, Japan)] was used to analyze the phenolic acids. The mobile phase of the (A/B) gradient was (A) acetonitrile and (B) 0.5% formic acid. The content of acetonitrile in the solvent was increased as follows: 5 (0–5 min), 18 (30 min), 70 (90 min), and 5% (120 min). The flow rate was 1 mL/min at a column temperature of 20 °C. Three separate analyses were carried out with each sample.

LC-MS/MS. LC/MS analyses were performed with an ion trap mass spectrometer (LCQ, Thermo Fisher Scientific Inc., MA) equipped

with an HPLC system (Agilent, CA; model 1100) connected with a diode array detector (DAD, G1315A). The sample solution (1–5 μ L) was applied on an Inertsil ODS-3 column (2.1 mm \times 150 mm, 3 μ m, GL Sciences Inc., Tokyo, Japan) and was separated using gradient solvent system at the flow rate of 200 μ L/min. The content of acetonitrile in 0.5% formic acid was increased as follows: 5 (0–5 min), 18 (30 min), and 70% (90 min). The LC eluate was introduced into the mass spectrometer after 3 min of the sample injection. The MS/MS experiments were carried out in the negative ion modes. The parameters were optimized using a standard chlorogenic acid solution by mixing the mobile phase (50% acetonitrile) eluted from the LC system as follows: ESI spray voltages, 4.5 kV (negative mode); capillary temperature, 50 °C; capillary voltage, –42 V (negative mode); sheath gas, nitrogen; flow rate, 64 (arbitrary unit); auxiliary gas flow rate, 55 (arbitrary unit); tube lens offset voltage, –15 V; multipole 1 offset voltage, 1.0 V; multipole 2 offset voltage, –7.0 V; and intermultipole lens voltage, 14 V. Helium was used as the collision gas, and the relative collision energy was set at 40% for MS/MS and MS³ experiments over a selected mass window of 2 Da. Mass selection of the analyte by *m/z* was followed by fragmentation and analysis of the fragments.

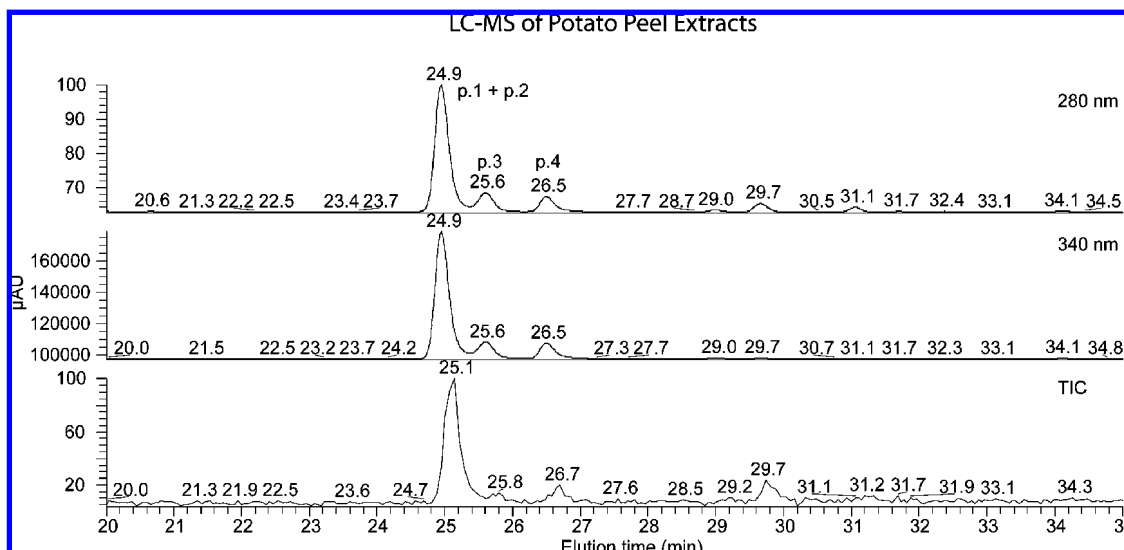


Figure 7. LC-MS chromatograms of an extract of Superior potato peel monitored at 280 nm, 340 nm, and TIC. Column, Inertsil ODS-3 (3 μ m, 4.0 mm \times 150 mm); flow rate, 0.2 mL/min; column temperature, 30 $^{\circ}$ C; and mobile phase, acetonitrile:0.5% formic acid (gradient mode).

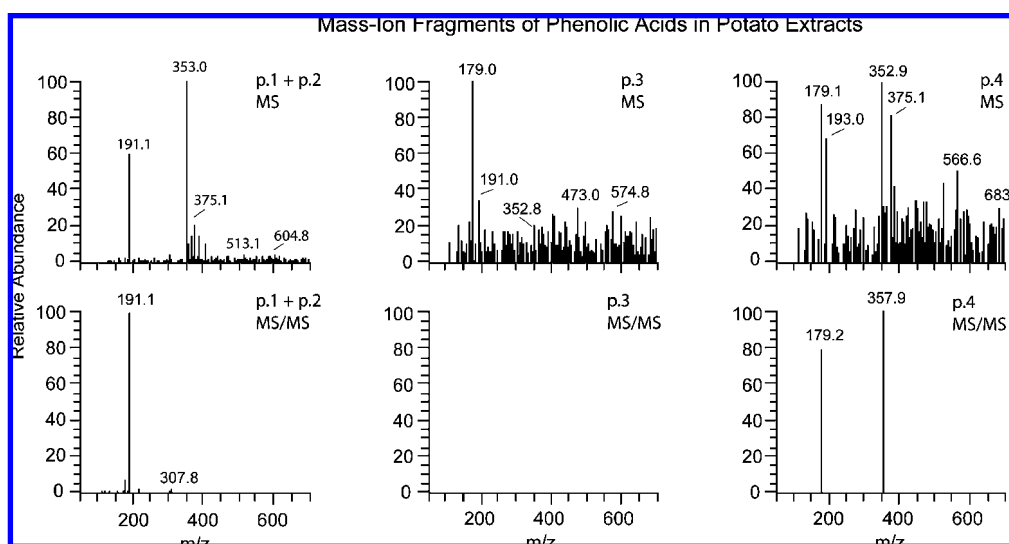


Figure 8. MS and MS/MS (negative ion mode) of peaks 1 + 2 (chlorogenic acid and its isomer), peak 3 (caffeic acid), and peak 4 (chlorogenic acid isomer) from isolated HPLC chromatograms of potato extracts.

Quantification. Integrated chromatographic peak areas from the test samples were compared to peak areas of known amounts of standard phenolic acids.

Recovery Test. Potato extracts were analyzed before and after addition of known amounts of phenolic compounds. Recovery (%) = (concentration of phenolic acid in spiked sample)/concentration of endogenous phenolic acid + spike \times 100. **Figure 2** illustrates the sampling of vertical and horizontal sections of a potato tuber used to determine the distribution of phenolic acids in the tuber.

RESULTS AND DISCUSSION

Analytical Aspects. The HPLC and LC/MS methods that we previously used to determine glycoalkaloids and vitamin C in potatoes (3, 4), tea catechins (5–7), and pungent pepper compounds (8–10) were adapted and refined in the present study to the analysis of potato phenolic compounds.

The retention times of the five standards on the HPLC column ranged as follows: chlorogenic acid, 27.78 min; caffeic acid, 30.40 min; *p*-coumaric acid, 38.30 min; ferulic acid, 41.08 min;

and *trans*-cinnamic acid, 55.15 min (**Figure 3**). The corresponding limits of detection (LOD values in ng) from multiple determinations were 16.5, 4.7, 3.2, 8.0, and 2.0. Plots of concentration vs peak areas (calibration plots) were linear at the concentration range of 0–300 ng for ferulic acid, 0–400 ng for caffeic and *trans*-cinnamic acids, 0–600 ng for coumaric acid, and 0–800 ng for chlorogenic acid. Percent recoveries of spiked samples were as follows ($n = 3$): *trans*-cinnamic acid, 95.2 ± 1.1 ; chlorogenic acid, 97.2 ± 3.6 ; *p*-coumaric acid, 102.0 ± 1.5 ; ferulic acid, 102 ± 1 ; and caffeic acid, 107 ± 2 (**Figure 4**).

Structural identification of individual phenolic compounds in extracts was performed by associating the HPLC peak of each compound with the corresponding UV and mass spectrum. The HPLC chromatograms (**Figures 4** and **5**), the UV spectra (**Figure 6**), and the LC/MS mass chromatograms (**Figures 7–9**) demonstrate the presence of caffeic, chlorogenic acid, and a chlorogenic acid isomer with the same molecular weight as chlorogenic acid in the potato extracts. We saw no evidence in

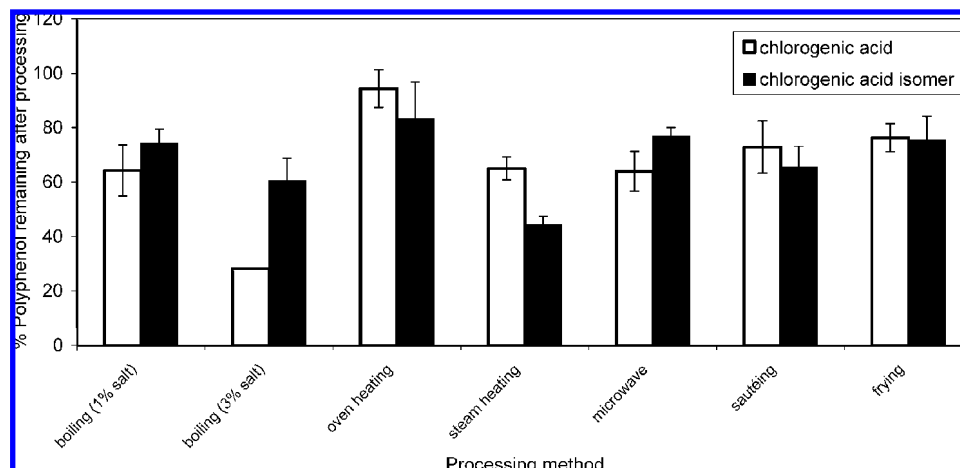


Figure 9. Effect of processing method on loss of phenolic compounds of Superior potato pulp. Values are averages from three separate determinations \pm SD vs matched controls. Caffeic acid values were too close to the LOD to allow quantifying % change.

Table 1. Distribution of Phenolic Compounds in Three Parts of Superior Potato Plants

| plant part | chlorogenic acid | chlorogenic acid isomer | caffeic acid | total |
|------------|--------------------------|-------------------------|-----------------|-------|
| flower | 424 \pm 0 ^a | 189 \pm 0 | 13.5 \pm 0.1 | 626 |
| leaf | 14.8 \pm 0.0 | 13.3 \pm 0.0 | 1.2 \pm 0.0 | 29.3 |
| stem | 4.19 \pm 0.04 | 6.13 \pm 0.05 | 0.39 \pm 0.04 | 10.7 |

^a Mean \pm SD ($n = 3$, mg/100 g fresh wt).

Table 2. Content of Phenolic Compounds in the Peel and Pulp of Five Korean Potato Varieties

| potato variety | potato section | chlorogenic | | | total | ratio: peel/pulp |
|----------------|----------------|-----------------------------|-----------------|-----------------|-------|------------------|
| | | chlorogenic acid | isomer | caffeic acid | | |
| Jasim | peel | 34.0 \pm 1.9 ^a | 6.8 \pm 0.6 | 1.2 \pm 0.1 | 42.1 | 2.6 |
| | pulp | 12.0 \pm 0.2 | 4.39 \pm 0.18 | 0.11 \pm 0.00 | 16.5 | |
| Atlantic | peel | 4.43 \pm 0.52 | 1.78 \pm 0.25 | 0.96 \pm 0.13 | 7.17 | 14.6 |
| | pulp | 0.35 \pm 0.02 | 0.13 \pm 0.01 | 0.01 \pm 0.00 | 0.49 | |
| Jowon | peel | 10.2 \pm 0.5 | 3.02 \pm 0.05 | 0.71 \pm 0.04 | 14.0 | 21.1 |
| | pulp | 0.45 \pm 0.01 | 0.17 \pm 0.01 | 0.04 \pm 0.00 | 0.66 | |
| Superior | peel | 8.72 \pm 0.08 | 0.99 \pm 0.04 | 1.18 \pm 0.03 | 10.9 | 20.2 |
| | pulp | 0.47 \pm 0.01 | 0.06 \pm 0.00 | 0.01 \pm 0.00 | 0.54 | |
| Jopung | peel | 4.85 \pm 0.21 | 1.25 \pm 0.09 | 0.39 \pm 0.02 | 6.49 | 7.64 |
| | pulp | 0.57 \pm 0.03 | 0.26 \pm 0.03 | 0.02 \pm 0.01 | 0.85 | |

^a Mean \pm SD ($n = 3$, mg/100 g fresh wt).

the HPLC and mass spectra for the presence of *p*-coumaric and ferulic acids in the extracts.

The content of chlorogenic acids in potatoes merits additional comment. At least three isomeric forms may be present in potatoes: 3-, 4-, and 5-caffeoylquinic acids (*I*, *II*). UV light induces the isomerization of naturally occurring *trans*-chlorogenic isomers to the *cis* form (*II*). The HPLC and LC/MS data of the present study indicate the presence of two isomeric forms, 5-caffeoylquinic acid, for which we had a standard, and another isomer with the same molecular weight, for which we do not have a standard. The LC/MS patterns illustrated in Figures 7 and 8 do not differentiate between the two isomers.

In analogy with the observation by Fernandes et al. (*II*) that the 5- and 4-caffeoylquinic isomers were present in quantifiable amounts in potatoes in a ratio of 8.5:1, it is likely that the smaller of the two isomer peaks is probably 4-caffeoylquinic acid.

Potato Plant Flowers, Leaves, and Stems. Table 1 shows the following levels of the three compounds in flowers (in mg/100 g fresh wt): chlorogenic acid, 424; chlorogenic acid isomer, 189; and caffeic acid, 13.5. The corresponding values in leaves are 14.8, 13.3, and 1.19, respectively, and in stems, 4.19, 6.13, and 0.36, respectively. The data also show that chlorogenic acid

and its isomer constituted \sim 96–98% of the total phenolic content and that the total in flowers was 2.74 times greater than in leaves and 58.5 times greater than in stems. Although we do not know the reason for the high levels in the flowers, a likely explanation is that the high amounts are needed to protect the flowers against attacks by phytopathogens.

Korean Potatoes. Table 2 shows the distribution of the three phenolics in the peel and pulp of five commercial potato varieties grown in Korea. Chlorogenic acid levels in the peel (in mg/100 g fresh wt) ranged from 4.43 for the Atlantic potatoes to 34.0 for the Jasim variety; for the chlorogenic acid isomer, from 1.25 for Jopung potatoes to 6.84 for the Jasim variety; and for caffeic acid, from 0.39 for Jopung potatoes to 1.23 for the Jasim variety. Chlorogenic acid levels of the pulp (flesh) ranged from 0.35 for Atlantic potatoes to 12.0 for Jasim potatoes. The corresponding range for the chlorogenic isomer was from 0.13 for Atlantic to 4.39 for Jasim potatoes and, for caffeic acid, from 0.01 for Atlantic potatoes to 0.11 for Jasim potatoes, respectively. Noteworthy is the large variation in the ratio of peel to pulp levels ranging from 2.55 for the Jasim to 21.1 for the Jowon potatoes.

Table 3 shows the distribution of the three phenolics in the peel and pulp of the Korean Superior potato variety available in four sizes: large, medium, small, and very small. The listed data indicate that the size of the potato does not seem to influence the total phenolic content, except that the ratio of peel to pulp for the very small potatoes (7.95) is about one-half the corresponding ratios of the other three potatoes.

These results indicate that the distribution of phenolic compounds between peel and pulp varies widely among different potato varieties. They also suggest that consumers and potato processors can select from available potato varieties and choose those with high, intermediate, or low amounts of phenolic compounds.

Vertical and Horizontal Sections of Superior Potatoes. Tables 4 and 5 list the distribution of the phenolic compounds in horizontal and vertical slices (sticks) of fresh Superior potatoes illustrated in Figure 2. The total phenolic content of the vertical slices ranged from 0.79 to 2.49 mg/100 g fresh wt, a 3.15-fold variation from highest to lowest. The corresponding range for the horizontal slices was from 0.84 to 6.58 mg/100 g fresh wt, a 7.83-fold variation from highest to lowest. These results suggest that it may be possible to select, depending on need, slices with high or low amounts of phenolic compounds

Table 3. Effect of Potato Size on the Phenolic Acid Content of the Peel and Pulp of Potatoes

| Superior potato size | potato part | chlorogenic acid | | | | total | peel/pulp ratio |
|----------------------|-------------|------------------------|-------------|--------------|------|-------|-----------------|
| | | chlorogenic acid | isomer | caffeic acid | | | |
| large | peel | 7.4 ± 0.1 ^a | 0.92 ± 0.06 | 1.05 ± 0.02 | 9.33 | 15.8 | |
| | pulp | 0.53 ± 0.04 | 0.04 ± 0.00 | 0.02 ± 0.00 | 0.59 | | |
| medium | peel | 8.72 ± 0.08 | 0.99 ± 0.04 | 1.18 ± 0.03 | 10.9 | 20.2 | |
| | pulp | 0.47 ± 0.01 | 0.06 ± 0.00 | 0.01 ± 0.00 | 0.54 | | |
| small | peel | 5.28 ± 0.08 | 0.61 ± 0.04 | 1.62 ± 0.04 | 7.51 | 16.7 | |
| | pulp | 0.39 ± 0.03 | 0.05 ± 0.01 | 0.01 ± 0.00 | 0.45 | | |
| very small | peel | 8.31 ± 0.07 | 1.03 ± 0.04 | 0.04 ± 0.03 | 9.38 | 7.95 | |
| | pulp | 1.03 ± 0.05 | 0.11 ± 0.00 | 0.04 ± 0.01 | 1.18 | | |

^a Mean ± SD (*n* = 3, mg/100 g fresh wt).**Table 4.** Content of Phenolic Compounds of Five Equal Vertical Sections of Superior Potatoes Shown in Figure 2

| vertical section | chlorogenic acid | chlorogenic acid isomer | caffeic acid | total |
|------------------|--------------------------|-------------------------|--------------|-------|
| A | 1.65 ± 0.03 ^a | 0.34 ± 0.03 | 0.04 ± 0.00 | 2.03 |
| B | 0.82 ± 0.07 | 0.28 ± 0.03 | 0.01 ± 0.00 | 1.11 |
| C | 0.62 ± 0.02 | 0.16 ± 0.02 | 0.01 ± 0.00 | 0.79 |
| D | 0.75 ± 0.03 | 0.19 ± 0.03 | 0.02 ± 0.00 | 0.96 |
| E | 2.08 ± 0.06 | 0.37 ± 0.05 | 0.04 ± 0.00 | 2.49 |

^a Mean ± SD (*n* = 3, mg/100 g fresh wt).**Table 5.** Content of Phenolic Compounds of Six Equal Cross-Sections of Superior Potatoes Shown in Figure 2

| cross-section | chlorogenic acid | chlorogenic acid isomer | caffeic acid | total |
|---------------|--------------------------|-------------------------|--------------|-------|
| 1 | 2.11 ± 0.02 ^a | 0.29 ± 0.02 | 0.08 ± 0.01 | 2.48 |
| 2 | 0.72 ± 0.01 | 0.25 ± 0.03 | 0.05 ± 0.01 | 1.02 |
| 3 | 0.45 ± 0.05 | 0.17 ± 0.01 | 0.00 ± 0.00 | 0.62 |
| 4 | 0.62 ± 0.04 | 0.20 ± 0.02 | 0.02 ± 0.00 | 0.84 |
| 5 | 1.46 ± 0.07 | 1.38 ± 0.05 | 0.14 ± 0.02 | 2.98 |
| 6 | 3.23 ± 0.15 | 2.76 ± 0.04 | 0.59 ± 0.02 | 6.58 |

^a Mean ± SD (*n* = 3, mg/100 g fresh wt).

for the preparation of potato-based foods. Such selection should take into account possible variability of phenolic content in different tubers of the same cultivar.

American Potatoes. Table 6 lists the phenolic acid content of 25 potato powders prepared by lyophilization of commercial potatoes with unknown history. For the dry lyophilized powders, the data show that chlorogenic acid levels (in mg/100 g wt) ranged from 3.28 for Kenebec potatoes to 637 for Purple Peruvian potatoes, a 194-fold variation from lowest to highest value. The corresponding range for the chlorogenic acid isomer was from 0.34 to 90.5, a 266-fold variation, and for caffeic acid, from 0.47 to 29.3, a 62.3-fold variation. Total amounts of phenolic compounds for the dry powders ranged from 4.09 to 757, a 185-fold variation, and for fresh tubers, from 1.03 to 172, a 167-fold variation.

The cited observations demonstrate wide variation in both individual and total phenolic acid content of commercial potatoes. The red- and purple-colored potatoes contained the highest amounts of phenolic compounds. Our data show that evaluated commercial potatoes differ widely in their content of phenolic acids. The data also suggest the need to determine possible relationships between phenolic content and health-promoting potentials of different commercial potato varieties (13–19).

Home-Processed Potatoes. Figure 9 shows the effect of several home-processing methods on polyphenol content in

Table 6. Content of Phenolic Compounds of Freeze-Dried Powders Prepared from Fresh Potatoes Sold in the United States

| potato variety | chlorogenic acid | chlorogenic acid isomer | caffeic acid | H ₂ O in fresh tubers (%) | total phenolics (mg/100 g) | |
|--|--------------------------|-------------------------|--------------|--------------------------------------|----------------------------|--------------|
| | | | | | dry tubers | fresh tubers |
| Kenebec | 3.28 ± 0.10 ^a | 0.34 ± 0.02 | 0.47 ± 0.04 | 75.0 | 4.09 | 1.03 |
| Russet, baking, batch 1 | 18.2 ± 0.0 | 1.02 ± 0.00 | 1.82 ± 0.00 | 79.5 | 21.0 | 4.31 |
| White, large, batch 2 | 14.5 ± 0.9 | 4.86 ± 0.28 | 2.01 ± 0.07 | 83.4 | 21.4 | 3.55 |
| Yukon Gold, grade "A", large | 14.3 ± 0.5 | 4.69 ± 0.23 | 4.55 ± 0.17 | 76.9 | 23.6 | 5.45 |
| Yukon Gold, grade "B", medium, batch 1 | 19.0 ± 0.6 | 6.01 ± 0.12 | 5.04 ± 0.23 | 75.5 | 30.0 | 7.36 |
| White, large, batch 1 | 21.6 ± 0.27 | 6.71 ± 0.52 | 2.83 ± 0.10 | 79.9 | 31.1 | 6.27 |
| Russet, baking, batch 2 | 25.9 ± 0.6 | 10.9 ± 0.2 | 2.53 ± 0.06 | 79.6 | 39.1 | 7.98 |
| Yukon Gold, grade "C", small, batch 1 | 26.7 ± 3.1 | 7.47 ± 0.86 | 7.86 ± 1.08 | 82.3 | 42.1 | 7.45 |
| Yukon Gold, grade "C", small, batch 2 | 26.0 ± 0.6 | 12.3 ± 0.4 | 5.31 ± 0.07 | 82.7 | 43.6 | 7.54 |
| Red, medium, organic | 35.1 ± 1.1 | 7.98 ± 0.13 | 4.01 ± 0.24 | 82.3 | 47.0 | 8.33 |
| White, medium | 34.1 ± 1.9 | 12.8 ± 0.6 | 6.05 ± 0.52 | 79.4 | 53.0 | 10.9 |
| Yukon Gold, grade "B", medium, batch 2 | 35.6 ± 3.9 | 8.91 ± 0.98 | 9.33 ± 0.32 | 82.4 | 53.8 | 9.47 |
| Butterball Creamer, organic, German | 36.0 ± 2.4 | 13.4 ± 0.2 | 7.14 ± 0.19 | 80.5 | 56.5 | 11.0 |
| White Creamer, small | 41.9 ± 0.2 | 10.4 ± 0.7 | 9.83 ± 0.56 | 83.4 | 62.1 | 10.3 |
| Ruby Red Crescent | 49.5 ± 0.9 | 16.4 ± 0.6 | 6.47 ± 0.32 | 78.9 | 72.3 | 15.3 |
| Red, grade "A", large, batch 1 | 56.4 ± 1.6 | 17.0 ± 0.6 | 7.90 ± 0.08 | 80.9 | 81.3 | 15.5 |
| Red, grade "A", large, batch 2 | 64.5 ± 1.4 | 16.7 ± 0.9 | 10.5 ± 0.4 | 83.1 | 91.7 | 15.5 |
| Red Creamer Marble | 65.6 ± 0.6 | 37.2 ± 0.6 | 1.07 ± 0.27 | 84.2 | 103 | 16.4 |
| Red, grade "C", small | 73.1 ± 0.5 | 22.3 ± 1.6 | 15.2 ± 0.5 | 81.3 | 110 | 20.7 |
| Fingerling, Ozette, batch 3 | 92 ± 1 | 44.9 ± 0.2 | 10.4 ± 0.4 | 79.5 | 148 | 30.3 |
| Purple, large | 109 ± 1 | 37.9 ± 3.3 | 5.27 ± 0.82 | 75.3 | 152 | 37.5 |
| Fingerling, Ozette, batch 1 | 105 ± 4 | 49.7 ± 1.6 | 13.8 ± 0.2 | 80.0 | 168 | 33.6 |
| Fingerling, Ozette, batch 2 | 113 ± 2 | 41.9 ± 0.1 | 12.7 ± 0.3 | 78.5 | 168 | 36.1 |
| Fingerling French | 203 ± 1 | 69.7 ± 1.8 | 7.83 ± 0.30 | 79.3 | 281 | 58.1 |
| Purple Peruvian | 637 ± 6 | 90.5 ± 1.2 | 29.3 ± 1.3 | 77.3 | 757 | 171 |

^a Mean ± SD (*n* = 3).

potatoes. Chlorogenic acid loss is greatest with boiling in 3% salt, suggesting that the compound is leaching into the water. Oven heating provides the best retention of both compounds.

Related Studies. Reported analytical methods for potato phenolics include HPLC (2, 20–24), capillary electrophoresis (11), colorimetry/spectrophotometry (13, 20, 25–29), and GC/MS (30). To place our findings in proper perspective, we will briefly summarize several reported studies on the chlorogenic and caffeic acid contents of potatoes.

The chlorogenic acid content of seven potato varieties that we determined by UV spectroscopy ranged from 9.6 to 18.7 mg/100 g fresh wt and of leaves harvested at different times from 132 to 242 mg/100 g fresh wt (1, 26, 27). The chlorogenic acid content of 145 mg/100 g freeze-dried potatoes determined by electrophoresis was similar to that determined by HPLC (154 mg/100 g) (11). No other phenolic compounds were detected in quantifiable amounts. These authors also reported that exposure of the tubers to light resulted in significant increases in chlorogenic acid content, confirming related observations by other investigators (20, 27). The total phenolic acid content of potatoes (in mg/100 g fresh wt) grown in India increased from 50.6 to 83.7 during storage for 120 days (31). Genetic modification induced significant increases in the phenolic acid content in some potato varieties (32, 33) but not in Spunta potatoes (15, 34).

The average chlorogenic and caffeic acid contents of five potato varieties (in mg/100 g fresh wt) grown in the Canary Islands ranged from 21.0 to 28.3 and from 0.73 to 1.12, respectively (22). The total phenolic acid content of 74 potato cultivars grown in the Andes of South America ranged from 1.12 to 12.37 mg of gallic acid equiv/g dry wt, an 11-fold variation from lowest to highest value (35). The total phenolic acid content of specialty potato selections grown in Texas ranged from 221 to 1252 μ g chlorogenic acid equiv, a 5.7-fold variation from lowest to highest value (24). Purple flesh selections had the highest amounts, followed by red flesh and yellow selections. Other studies found that the caffeic acid content of different potato cultivars varied widely, ranging from 0.3 to 3.6 mg/100 g in tubers and from 18.8 to 28 mg/100 g in peels (2, 26, 27, 36).

The contents of soluble phenolic acids in raw potato peels determined by HPLC varied from 23 to 45 mg/100 g fresh wt. Boiled peels contained lower amounts (2). Cooking of potatoes and other vegetables in small amounts of water retained most of the phenolic compounds (37). Steamed potato strips retained 42% of the initial chlorogenic acid content, and frying retained 24% (21). Similar decreases were observed in the content of caffeic acids following exposure of the strips to home-processing conditions. The cited observations and the results of the present study suggest that it is possible to identify potato cultivars with low or high phenolic acid contents for human use and to select processing conditions that minimize losses of phenolic compounds.

In summary, the methods that we developed and used in the present study to obtain the cited data on the content and distribution of phenolic compounds in potato plant flowers, leaves, and tubers, in the peel and pulp parts of potato tubers, and in freeze-dried and processed commercial potatoes merit application in numerous studies designed to assess the role of potato phenolic compounds in host–plant resistance, plant breeding, plant molecular biology, food chemistry, food microbiology, nutrition, and medicine. In addition, the findings of the present study on the observed wide distribution of phenolic compounds in different commercial potato varieties and on changes in phenolic compound content during home

processing of potatoes may also help consumers to select, depending on need, potatoes with low or high levels of health-promoting phenolic compounds, to use processing conditions that minimize their degradation, and to control enzymatic browning reactions (38, 39) that are reported to cause undesirable discolorations and to damage nutritional quality. Potatoes can also be selected for low content of acrylamide precursors (40).

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