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ARTICLE

Anthocyanins, Hydroxycinnamic Acid Derivatives, and Antioxidant Activity in Roots of Different Chinese Purple-Fleshed Sweetpotato Genotypes

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Anthocyanins and hydroxycinnamic acid derivatives in the crude extracts of peel, flesh, and whole roots of 10 Chinese purple-fleshed sweetpotato genotypes were simultaneously characterized by liquid chromatography−photodiode array detector−atmospheric pressure chemical ionization−mass spectrometry (LC−PDA−APCI−MS), as well as their antioxidant activities were systematically investigated and compared. Major anthocyanins were identified as peonidin or cyanidin 3-sophoroside-5-glucoside and their acylated derivatives, e.g., peonidin 3-sophoroside-5-glucoside, peonidin 3-(6′′-*p*-feruloylsophoroside)-5-glucoside, and cyanidin 3-(6′′-*p*-feruloylsophoroside)-5-glucoside, and main hydroxycinnamic acid derivatives were identified as mono- and dicaffeoylquinic acids (e.g., 5-*O*-caffeoylquinic acid and 3,5-di-*O*-caffeoylquinic acid) and caffeoyl-hexoside. These main phenolic compounds identified were important contributors to the total antioxidant capacity of the tested sweetpotato samples. Additionally, great variations in contents of both total and individual phenolic compounds as well as antioxidant activities between different genotypes and among various parts of the roots were observed. This study may provide value information for breeding new lines of Chinese purple-fleshed sweetpotato and also for quality control of bioactive components during production and processing.

KEYWORDS: Purple-fleshed sweetpotato; root; peel; flesh; phenolic compounds; anthocyanins; hydroxycinnamic acid derivatives; LC−PDA−APCI−MS; antioxidant activity

INTRODUCTION

Sweetpotato [*Ipomoea batatas* (L.) Lam.], a dicotyledonous plant in the family Convolvulaceae, is one of the most important food crops for many Asian, Latin American, and African countries in tropical and subtropical regions (*1*). Traditionally, it has been used as an important carbohydrate resource for energy for both human beings and livestocks because of the high content of starch in the storage roots (*2*). Purple-fleshed sweetpotatoes are rich in anthocyanins (*3*, *4*). Anthocyanins, a category of flavonoids, possess great potential in free-radical-scavenging activity, and moderate consumption of anthocyanin-rich foods and beverages is associated with a low risk of cardiovascular disease, neurological disorders, carcinogenesis, and improvement of visual functions (*5*,*6*). Extracts of purple sweetpotato or its related food products had good radical-scavenging activities *in vitro* (*7*,*8*). Purple sweetpotato rich in anthocyanins possessed a wide range of biological functions *in vivo*. Anthocyanins from a Japanese sweetpotato cultivar could suppress the development of atherosclerotic lesions against oxidative stress in apolipoprotein E-deficient mice (*9*). Purple colorants of sweetpotato could repair D-galactose-induced spatial learning and memory impairment by regulating the expression of synaptic proteins (*10*) and attenuate oxidative stress and inflammatory response induced by D-galactose in mouse liver (*11*). Additionally, many studies reported other phenolic compounds (mainly chlorogenic acid and its derivatives, also called hydroxycinnamic or hydroxycinnamoylquinic derivatives) in leaves and roots of common sweetpotato (mainly white-fleshed sweetpotato) (*12*−*15*). Sweetpotato genotypes/cultivars rich in phenolic acids contributed to the overall antioxidant capacities against free radicals, and the corresponding phenolics might protect the human body from oxidative stress (*12*, *14*). Thus, regularly consuming sweetpotato or its related food products, rich in anthocyanins and other phenolics, may be beneficial to human health. However, little is known about hydroxycinnamic acid derivatives in the roots of purple-fleshed sweetpotato.

China is the world's largest producer of sweetpotato and accounts for over 80% of the world production, with a harvested area of 4 761 003 acres in the year 2007 (World Sweetpotato Atlas, IPC). In some rural regions in China, sweetpotato plays an important role in local staple foods (*1*). Because of the great diversity in biogeography for cultivation of sweetpotato, China is rich in genetic resources of sweetpotato, including purple-fleshed sweetpotato. During the past few years, purple-fleshed sweetpotato has been under intensive agricultural development through

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breeding in China (*16*). A few purple-fleshed genotypes have been proven to be marketable for use in production.

However, there has been little systematic information on characteristics and chemical compositions of major phenolic compounds (anthocyanins and hydroxycinnamic acid derivatives) in purple-fleshed sweetpotato genotypes from different geographic regions in China. This seriously hinders further breeding of advanced new lines of purple-fleshed sweetpotato and also influences the development of purple-fleshed sweetpotato products as healthy functional foods in China. Furthermore, the peel (containing high levels of phenolics) of sweetpotato roots is usually treated as waste in the sweetpotato-processing industry in China. Thus, looking into the profiles of phenolics in the peel of sweetpotato roots may provide new insight for further use of these byproducts. Additionally, there have been few reports about simultaneous determination of both anthocyanins and hydroxycinnamic acid derivatives in the crude extracts of sweetpotato at the same chromatographic conditions using high-performance liquid chromatography (HPLC) or liquid chromatography−mass spectrometry (LC−MS).

Therefore, the aims of this study were to simultaneously characterize major phenolic compounds (anthocyanins and hydroxycinnamic acid derivatives) in the methanolic extracts of peel, flesh, and whole roots (WR) from 10 representative purple-fleshed sweetpotato genotypes collected from diverse geographic origins in China by liquid chromatography−photodiode array detector−atmospheric pressure chemical ionization−mass spectrometry (LC−PDA−APCI−MS); and to compare the contents of both total and individual phenolic compounds in the tested genotypes and their antioxidant activities against several model free radicals *in vitro*.

MATERIALS AND METHODS

Chemicals. 2,2′-Azino-bis(3-ethylbenzthiazoline-6-sulfonic acid (ABTS), 2,4,6-tripyridyl-*s*-triazine (TPTZ), 1,1-diphenyl-2-picrylhydrazyl (DPPH), potassium persulfate, ferric chloride, and authentic standard compounds of gallic acid and chlorogenic acid (5-*O*-caffeoylquinic acid) were from Sigma/Aldrich (St. Louis, MO). Cyanidin 3-*O*-glucoside was from Extrasynthese (Genay Cedex, France), and 6-hydroxy-2,5,7,8-tetramethylchromane 2-carboxylic acid (Trolox) was from Fluka Chemie (Buchs, Switzerland). Folin−Ciocalteu reagent, HPLC- or analytical-grade organic reagents, and formic acid were from BDH (Dorset, U.K.).

Sweetpotato Genotypes and Sample Preparation. A total of 10 purple-fleshed sweetpotato genotypes (including local landraces, advanced breeding lines, and cultivars) and 2 representative white-fleshed cultivars (as the control) were selected for use in this study, which were originated from different provinces in China, particularly from the Hubei province (**Table 1**). They were grown at the Experimental Farm of the Institute of Crop Science, Hubei Academy of Agricultural Sciences (Wuhan, China) in early May, 2008. The soil type of the experimental field was loam. The plot design was randomly in arrangement with three replications. Each plot was 12.15 m^2 (2.7 × 4.5 m) with five rows. The distance between each replication was 1 m. A guard row (2 m in width) was arranged around the test field. Vine cuttings of each genotype, about 30 cm long, were transplanted in the corresponding plot. The planting density was around 50 000 plants per hectare. Normal field managements were practiced. Harvesting was performed ∼160 days after transplanting, and the roots of five plants from each genotype per plot were randomly harvested from the three middle rows of the five-row plot. All harvested roots were packaged in nylon net bags and stored at a special sweetpotato storage room (12−15 °C and ∼85% relative humidity) for about 5 months prior to sampling for analysis.

Fresh sweetpotato roots were washed, cut into small thin pieces in three categories, i.e., peel, flesh, or whole root, and freeze-dried for around 48 h using a Heto FD3 freeze-dryer (Heto-Holten A/S, Allerod, Denmark), after frozen in liquid nitrogen. The dried sweetpotato samples were ground to fine powder by a Kenwood Multi-Mill (Kenwood, Watford, U.K.) and passed through a sieve (24 mesh). All powder samples were sealed in plastic bags and stored in a large plastic airtight container (Star Industrial Co. Ltd., Hong Kong) with silica gels in a cold room (in darkness at 4 °C) until use. During sample analysis, the air container with the powder samples were moved in a laboratory at room temperature (∼23 °C) or the powder samples were transferred in a desiccator with silica gels and stored at room temperature.

Table 1. Detailed Information of 10 Chinese Purple-Fleshed Sweetpotato Genotypes and 2 White-Fleshed Sweetpotato Cultivars

code of genotypes	category of genotypes	original provinces	flesh color	estimated yield (metric ton/ha)
Ea2	landrace	Hubei	deep purple	9.75
Ea3-1	landrace	Hubei	purple	9.20
Ea3-2	breeding line	Hubei	deep purple	8.80
Ea4	landrace	Hubei	light purple	8.50
E5306	breeding line	Hubei	light purple	10.0
E6107a	breeding line	Hubei	deep purple	11.0
E6107b	landrace	Hubei	light purple	11.5
EZX311[a]	cultivar	Hubei	purple	12
Xu13-4[b]	cultivar	Jiangsu	purple	26
Yuzi263[c]	cultivar	Chongqing	light purple	27
Eshu-6 (ck1)[a]	cultivar	Hubei	white	45
Xu-22 (ck2)[b]	cultivar	Jiangsu	white	40

[a] EZX311 (Ezi311) and Eshu-6 (Eshu number 6), bred by Institute of Crop Science, Hubei Academy of Agricultural Sciences, Wuhan, Hubei, China. [b] Xu13-4 (Xuzi13-4), bred by Xuzhou Sweetpotato Research Center, Chinese Academy of Agricultural Sciences, Xuzhou, Jiansu, China. [c] Xu-22 (Xushu 22), bred by Southwest University, Chongqing, China.

Preparation of Crude Methanolic Extracts. Different extraction methods were employed for different analytical purposes. For analysis of phenolic compounds, the dried powder of sweetpotato samples (0.5 g) was extracted in 4 mL of 85% methanol with 0.5% formic acid (FA) at room temperature (∼23 °C) for 2 h and the extract was centrifuged at 14 000 rpm for 5 min. The supernatant was transferred to a 20 mL cylinder glass vial and dried by a nitrogen gas flow. The dried extract residue was redissolved in 1 mL of 85% methanol with 0.5% FA. The crude methanolic solution was filtered using a Millipore filter (nylon membrane, 0.2 μm inner diameter) and then injected into LC−MS for qualitative and quantitative analysis of phenolic compounds. For assays of antioxidant activities, the dried powder of sweetpotato samples (1.0 g) was extracted with 25 mL of 80% methanol at room temperature for 12 h in a shaker. The crude extract was filtered through a Millipore filter with a 0.45 μm nylon membrane under vacuum at room temperature and immediately subjected to antioxidant activity assays within 3 h.

LC−PDA−APCI−MS Analysis. A LC−APCI−MS−2010EV system (Shimadzu, Kyoto, Japan) consisted of a LC-10ADvp binary pump, a SIL-10Avp autosampler, a PDA, a central controller, and a single quadrupole MS detector, with an APCI interface. The analytical reversed-phase column was a Zorbax SB-Aq column (4.6 × 250 mm, 5 μm) with a Zorbax SB-Aq guard column (4.6 × 12.5 mm, 5 μm) (Agilent Technologies, Santa Clara, CA). For all samples, the flow rate was 0.8 mL/min and injection volume was 6 μL. The UV/vis detection wavelengths were 325 nm for hydroxycinnamic acid derivatives and 520 nm for anthocyanins, respectively. LC conditions were as follows: solvent A (1.0% formic acid) and solvent B (MeOH with 0.1% formic acid). A gradient elution (60 min) was used: 0.00−2.00 min, 5% B; 2.00−10.00 min, 5−30% B; 10.00−15.00 min, 30% B; 15.00−30.00 min, 30−40% B; 30.00−35.00 min, 40% B; 35.00−50.00 min, 40−55% B; 50.00−53.00 min, 55−100% B; 53.00−56.00 min, 100% B; 56.0−56.01 min, 100−5% B; and 56.01−60.00 min, 5% B.

MS conditions were as follows: two scan ranges (i.e., m/z 130−450 and 260−1100) were used in both positive- and negative-ion modes for MS data acquisition of hydroxycinnamic acid derivatives and anthocyanins. The APCI temperature was 400 °C; the curved desolvation line (CDL) temperature was 250 °C; and the heat block temperature was 200 °C. The APCI probe voltage was 4.5 kV. A nebulizing gas of 2.5 L/min and a drying gas of 2.0 L/min were applied for ionization using nitrogen in both cases. The acquisition time for MS detection was from 0.01 to 55.00 min.

Quantitative Analysis of Individual and Total Phenolic Compounds. Individual phenolic compounds identified in the extracts of

Table 2. Typical LC−PDA−APCI−MS Data of Major Phenolic Compounds (Anthocyanins and Hydroxycinnamic Acid Derivatives) Identified in the Methanolic Crude Extracts of Purple-Fleshed Sweetpotato Genotypes Collected in China

peak number[a]	retention time (min)	tentative names of phenolic compounds	UV/vis spectra λ_{max} (nm)[b]	molecular mass	mass of observed adduct ions: negative $[M-H]^-$	mass of observed adduct ions: positive $[M+H]^+$	mass of observed fragmented ions: negative	mass of observed fragmented ions: positive
1	14.7	caffeoyl-hexoside	218, 293 sh, 327	342	341	343	323	325, 163
2	16.9	5-*O*-caffeoylquinic acid	215, 293 sh, 327	354	353	355	191, 161, 707[c]	337, 163
3	17.5	caffeic acid	227, 292 sh, 329	180	179		161	163
4	21.1	coumaroyl-hexoside?	212, 292 sh, 329	326	325			
5	24.3	feruloylquinic acid	210, 293 sh, 325	368	367	369	193	195
6	26.9	cyanidin 3-sophoroside-5-glucoside	281, 328, 526	772	771	773	609, 285	611, 287
7	27.9	cyanidin 3-(6″-*p*-caffeoylsophoroside)-5-glucoside	280, 328, 528	934	933	935	605, 447, 285	773, 449, 287
8	30.0	peonidin 3-sophoroside-5-glucoside	281, 329, 527	786	785	787	623, 461, 299	625, 463, 301
9	31.6	3,4-di-*O*-caffeoylquinic acid	212, 295 sh, 327	516	515	517	353, 497	355, 499, 163
10	33.2	cyanidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside	295, 329, 531	948	947	949	785, 447, 285	787, 449, 287
11	33.4	3,5-di-*O*-caffeoylquinic acid	212, 296 sh, 329	516	515	517	353, 497, 191	355, 499, 163
12	37.3	peonidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside	294, 329, 532	962	961	963	799, 661, 299	801, 663, 301

[a] The numbers of the peaks in this table coincide with the numbers of the peaks in **Figure 1** and the numbers of the phenolic compounds in **Table 3**. [b] sh = shoulder. [c] Dimeric adduct ion.

sweetpotato samples were quantified using the same LC−PDA system at the same chromatographic conditions described above and establishing external standard curves (compound concentration versus peak area) of the corresponding known phenolic compounds. Because of the limited commercial standards, we could not quantify the corresponding phenolic compounds of all peaks isolated in the sweetpotato samples. However, the chemical categories of the phenolic compounds could be identified from their chromatographic behavior and UV/vis spectroscopic characteristics. The hydroxycinnamic acid derivatives (i.e., peaks 1−5, 9, and 11) isolated in this study possessed a similar maximum absorption wavelength (λ_{max} = 325−329 nm), whereas anthocyanins (i.e., peaks 6−8, 10, and 12) had similar λ_{max} data (526−532 nm) (**Table 2**). Therefore, chlorogenic acid (5-*O*-caffeoylquinic acid) was used as an external standard to quantify individual hydroxycinnamic acid derivatives (compounds **1**−**5**, **9**, and **11**), and their contents were expressed as milligrams of chlorogenic acid per 100 g of dry weight (DW), whereas cyanidin 3-*O*-glucoside was used to quantify individual anthocyanins (compounds **6**−**8**, **10**, and **12**), and their contents were expressed as milligrams of cyanidin 3-glucoside per 100 g of DW (**Table 3**).

Total phenolic content (TPC) was estimated using the Folin−Ciocalteu colorimetric method according to Cai et al. (*17*) and Shan et al. (*18*), with minor modifications. Briefly, appropriately diluted sample extracts (0.2 mL) was reacted with 1.0 mL of Folin−Ciocalteu reagent (0.5 N) for 4 min at room temperature. The reaction was then neutralized with 1.0 mL of saturated sodium carbonate (75 g/L) and allowed to stand for 2 h in the dark at room temperature. The absorbance of the resulted blue color was measured at 760 nm with a spectrophotometer (U-1800, Hitachi, Japan). Quantification was performed on the basis of a standard curve with gallic acid. Results were expressed as milligram of gallic acid equivalents (GAE) per 100 g of DW.

ABTS Method. The antioxidant capacity against $ABTS^{\bullet+}$ radicals was assayed by the improved ABTS method (*17*). Briefly, The $ABTS^{\bullet+}$ solution was prepared by the reaction of ABTS (7 mM) and potassium persulphate (2.45 mM), after incubation at room temperature for around 16 h in the dark. The $ABTS^{\bullet+}$ solution was then diluted with 80% ethanol to obtain an absorbance of 0.700 ± 0.002 at 734 nm. The $ABTS^{\bullet+}$ solution (3.9 mL) was added to the properly diluted sample extracts (0.1 mL) and mixed thoroughly. The reaction mixture was for 6 min at room temperature, and the absorbance at 734 nm was recorded with a spectrophotometer. An external standard curve was obtained using Trolox standard solution at various concentrations (from 0 to 15 μM) in 80% ethanol. The absorbance of the reaction samples was compared to that of the Trolox standard, and the results were expressed as millimoles of Trolox equivalents per 100 g of DW of plant material.

DPPH Method. Antioxidant capacity against $DPPH^{\bullet}$ radicals was assayed according to a previous method (*19*), with some modifications. Briefly, $DPPH^{\bullet}$ solution (60 μM; absorbance = 0.670 ± 0.002) was prepared in 80% ethanol. The same extract samples diluted with 80% ethanol during the ABTS assay were also used in the DPPH assay. $DPPH^{\bullet}$ solution (3.9 mL) was added to the properly diluted extracts (0.1 mL) and vortex-shaken. The reaction was for 2 h at room temperature in the dark, and the absorbance was recorded at 515 nm. A Trolox external calibration curve was established. The results are expressed as millimoles of Trolox equivalents per 100 g of DW of plant material.

Ferric Reducing Ability of Plasma (FRAP) Method. FRAP was measured according to Benzie et al. (*20*), with small modifications. Briefly, the FRAP reagent was prepared by adding 10 volume of acetate buffer (300 mM, pH 3.6), including 3.1 g of sodium acetate and 16 mL of glacial acetic acid, 1 volume of 10 mM TPTZ prepared in 40 mM HCl, and 1 volume of 20 mM ferric chloride. The mixture was diluted to $^1/_3$ with pure methanol and prewarmed at 37 °C. Working FRAP reagent (3.0 mL) was mixed with properly diluted sample extracts (0.1 mL) similar to those for the ABTS methods. The mixture was vortex-shaken and incubated at 37 °C for 8 min, and the absorbance was read at 593 nm. A blank with 0.1 mL of 80% methanol for reaction was used for auto zero. An external standard curve was made with Trolox, and the results were expressed as millimoles of Trolox equivalents per 100 g of DW of plant material.

Statistical Analysis. All determinations were conducted in triplicate. Differences between means of data were compared by least significant difference (LSD) calculated using the statistical analysis system (SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

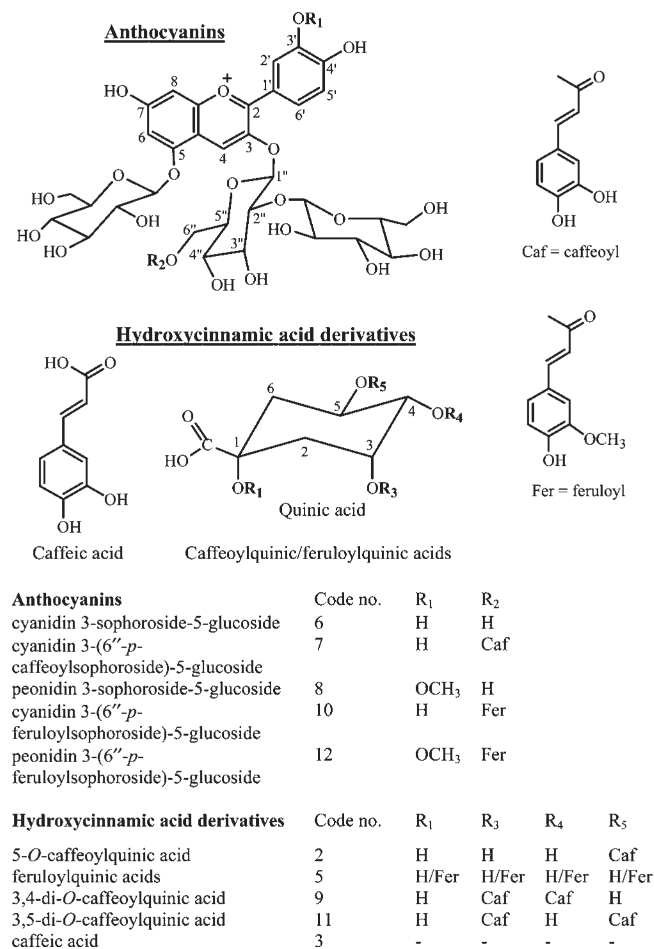
Identification of Major Phenolic Compounds from Chinese Purple-Fleshed Sweetpotato Genotypes. The results of LC−PDA−APCI−MS analysis showed that major phenolic compounds in the methanolic crude extracts of 10 Chinese purple-fleshed sweetpotato genotypes were identified as 5 anthocyanins (belonging to flavonoids) and 7 hydroxycinnamic acid derivatives (belonging to phenolic acid derivatives) (**Table 2**). Chemical structures of major phenolics identified are illustrated in **Figure 1**. Flesh, peel, and WR of all of the tested genotypes had similar peak profiles of anthocyanins and hydroxycinnamic acid derivatives (**Figure 2** shows typical chromatographs of one genotype Ea2). However, anthocyanins were nearly not detected in the roots of two white-fleshed sweetpotato cultivars (control) (except a trace amount of anthocyanins in the peel).

The peaks isolated in the tested genotypes were identified according to available authentic standards, by comparison of retention times and UV/vis spectral and MS data, and with

Table 3. Contents of Anthocyanins and Hydroxycinnamic Acid Derivatives from Purple-Fleshed Sweetpotato Genotypes Collected in China

		compositions of individual phenolic compounds[a]													
		hydroxycinnamic acid derivatives (HAD)							anthocyanins (AC)						
genotypes[b]		1	2	3	4	5	9	11	6	7	8	10	12	total HAD (mg/100 g of DW)[c]	total AC (mg/100 g of DW)[d]
Ea2	WR	45.5 ± 0.1	127.9 ± 2.1	15.4 ± 1.2	55.2 ± 0.5	17.3 ± 1.4	23.9 ± 0.7	311.8 ± 0.8	20.7 ± 0.8	9.8 ± 0.3	87.4 ± 3.5	174.2 ± 3.0	111.0 ± 1.6	597.0 ± 6.4	403.2 ± 9.1
	P	64.2 ± 0.4	190.8 ± 0.3	18.3 ± 0.3	53.5 ± 0.6	21.5 ± 0.9	39.1 ± 0.3	543.7 ± 0.6	22.3 ± 1.1	7.8 ± 0.1	109.7 ± 2.7	258.7 ± 3.0	152.6 ± 2.5	931.1 ± 3.0	551.1 ± 9.3
	F	41.8 ± 2.2	127.2 ± 0.1	14.3 ± 0.1	56.8 ± 0.5	17.5 ± 2.7	19.6 ± 0.3	253.6 ± 1.0	18.3 ± 0.8	10.2 ± 0.3	75.0 ± 2.4	142.9 ± 1.6	102.7 ± 1.4	530.8 ± 6.8	349.1 ± 6.4
Ea3-1	WR	126.2 ± 0.2	245.8 ± 0.1	24.8 ± 0.0	72.4 ± 0.6	20.4 ± 0.8	47.0 ± 0.2	567.7 ± 16.4	36.0 ± 2.9	4.3 ± 0.1	117.5 ± 11.6	178.2 ± 10.8	109.4 ± 7.8	1093.3 ± 14.6	445.3 ± 52.1
	P	142.0 ± 0.2	245.3 ± 0.2	34.2 ± 0.1	60.0 ± 1.5	22.1 ± 0.7	49.9 ± 0.1	607.2 ± 10.7	50.6 ± 2.3	3.6 ± 0.0	120.0 ± 0.2	178.4 ± 1.6	111.8 ± 1.9	1160.7 ± 7.8	464.5 ± 11.3
	F	87.9 ± 0.1	255.5 ± 0.6	24.4 ± 1.3	73.4 ± 0.6	19.9 ± 0.7	36.2 ± 0.9	538.1 ± 0.7	33.6 ± 2.5	4.3 ± 0.0	110.7 ± 2.1	163.7 ± 0.2	104.3 ± 0.7	1046.4 ± 4.8	416.6 ± 11.6
Ea3-2	WR	92.9 ± 0.2	187.6 ± 0.9	21.8 ± 1.6	68.8 ± 0.3	25.8 ± 0.4	33.6 ± 0.1	435.4 ± 0.4	33.4 ± 0.6	10.2 ± 0.1	122.8 ± 1.1	213.5 ± 0.2	122.7 ± 0.2	865.9 ± 4.0	502.6 ± 2.3
	P	105.5 ± 0.1	286.9 ± 0.1	28.1 ± 0.0	70.3 ± 0.4	28.1 ± 0.7	42.6 ± 0.2	655.4 ± 34.1	41.5 ± 0.1	8.7 ± 0.0	158.6 ± 0.2	312.8 ± 1.9	174.2 ± 3.0	1216.8 ± 35.4	695.7 ± 5.2
	F	75.7 ± 0.1	172.3 ± 0.1	16.4 ± 0.0	62.9 ± 0.3	26.7 ± 0.6	31.2 ± 0.2	328.6 ± 10.8	23.5 ± 0.2	10.8 ± 0.1	96.5 ± 0.6	173.2 ± 4.1	105.0 ± 0.1	713.8 ± 9.7	409.0 ± 3.1
Ea4	WR	22.9 ± 0.2	225.2 ± 0.6	19.0 ± 0.6	10.0 ± 0.1	22.8 ± 0.4	81.6 ± 1.5	333.5 ± 2.1	10.6 ± 0.1	7.3 ± 0.6	37.0 ± 0.3	57.9 ± 0.7	13.4 ± 0.1	715.1 ± 5.4	117.8 ± 0.7
	P	33.7 ± 0.1	327.2 ± 2.4	24.1 ± 0.2	8.0 ± 0.0	18.4 ± 0.2	120.4 ± 1.8	666.6 ± 6.6	8.5 ± 1.0	7.3 ± 0.6	40.5 ± 2.6	52.2 ± 0.2	18.8 ± 0.3	1198.4 ± 11.4	133.0 ± 4.7
	F	17.9 ± 0.1	172.7 ± 0.2	tr	11.1 ± 0.5	24.4 ± 0.4	73.8 ± 1.4	272.0 ± 1.8	11.7 ± 0.2	6.9 ± 0.1	34.7 ± 0.5	62.2 ± 0.1	13.2 ± 0.2	571.9 ± 4.3	131.4 ± 1.1
E5306	WR	8.5 ± 0.1	179.3 ± 3.3	12.2 ± 0.3	24.3 ± 0.2	33.9 ± 0.2	40.4 ± 0.2	260.6 ± 0.4	12.4 ± 0.6	12.1 ± 0.3	40.3 ± 0.6	42.4 ± 1.5	39.6 ± 0.2	549.0 ± 1.7	157.0 ± 2.0
	P	8.8 ± 0.1	359.1 ± 5.2	26.5 ± 0.1	13.8 ± 0.4	30.0 ± 0.1	48.0 ± 0.1	335.1 ± 4.8	8.9 ± 0.9	11.7 ± 0.6	31.1 ± 3.7	72.8 ± 0.1	43.2 ± 0.2	825.2 ± 5.7	167.7 ± 5.4
	F	8.1 ± 0.3	168.7 ± 1.5	tr	25.9 ± 0.3	42.1 ± 0.2	32.6 ± 0.2	218.6 ± 0.4	16.3 ± 0.6	11.6 ± 0.2	44.0 ± 0.6	45.6 ± 0.2	35.8 ± 0.4	502.2 ± 1.3	142.8 ± 3.1
E6107a	WR	52.4 ± 0.1	175.4 ± 0.7	16.9 ± 0.0	55.4 ± 0.3	18.6 ± 2.1	26.6 ± 0.2	345.3 ± 10.8	24.7 ± 0.3	9.0 ± 0.1	99.7 ± 0.5	177.0 ± 0.2	116.6 ± 0.2	693.4 ± 8.2	424.1 ± 1.2
	P	60.4 ± 0.3	203.4 ± 0.1	19.0 ± 0.1	45.6 ± 0.3	21.4 ± 0.7	31.9 ± 0.1	521.1 ± 34.1	25.8 ± 0.2	7.8 ± 0.0	114.5 ± 0.6	247.2 ± 8.6	141.1 ± 1.9	902.8 ± 35.4	536.4 ± 11.4
	F	40.7 ± 0.1	138.4 ± 0.4	16.2 ± 0.0	58.0 ± 0.2	15.9 ± 2.1	17.9 ± 0.2	278.5 ± 0.4	24.2 ± 0.2	9.6 ± 0.0	92.3 ± 0.5	155.5 ± 4.1	113.6 ± 1.0	563.0 ± 3.0	398.1 ± 2.4
E6107b	WR	19.3 ± 0.2	185.3 ± 4.6	11.6 ± 0.1	tr	19.6 ± 0.1	62.9 ± 0.2	225.7 ± 17.8	8.1 ± 0.1	7.6 ± 0.0	29.1 ± 0.9	49.9 ± 1.5	13.4 ± 0.1	524.3 ± 22.9	108.1 ± 2.6
	P	50.3 ± 0.4	355.9 ± 0.5	33.7 ± 0.0	tr	19.5 ± 0.0	125.4 ± 0.8	628.3 ± 22.8	8.8 ± 0.0	8.2 ± 0.1	33.0 ± 1.0	52.8 ± 0.7	16.8 ± 0.1	1213.1 ± 23.7	119.5 ± 2.0
	F	13.9 ± 0.4	81.8 ± 0.1	tr	tr	15.8 ± 0.1	37.1 ± 0.7	116.1 ± 0.5	7.9 ± 0.1	6.5 ± 0.0	19.6 ± 0.2	35.2 ± 2.8	9.1 ± 0.0	264.6 ± 1.2	78.3 ± 3.1
EZX311	WR	10.8 ± 0.1	721.6 ± 7.1	tr	22.9 ± 0.3	33.7 ± 0.1	45.1 ± 0.1	626.9 ± 22.8	25.3 ± 0.7	15.3 ± 0.4	75.5 ± 1.1	121.5 ± 0.3	106.0 ± 0.4	1458.7 ± 23.4	343.6 ± 2.9
	P	12.3 ± 0.3	846.2 ± 4.5	tr	17.0 ± 0.4	22.9 ± 0.2	46.5 ± 0.5	657.1 ± 23.0	21.3 ± 0.8	15.6 ± 0.5	58.4 ± 2.1	149.7 ± 0.3	116.0 ± 0.6	1601.8 ± 29.3	360.9 ± 4.3
	F	12.1 ± 0.2	670.9 ± 2.1	tr	25.1 ± 0.2	44.7 ± 0.1	42.7 ± 0.1	609.2 ± 11.7	25.8 ± 0.8	14.1 ± 0.3	74.4 ± 0.8	104.9 ± 0.5	103.7 ± 0.3	1407.1 ± 12.2	322.9 ± 2.7
Xu13-4	WR	12.9 ± 0.5	180.6 ± 4.5	12.3 ± 0.1	30.4 ± 0.5	22.2 ± 0.4	76.5 ± 1.1	610.7 ± 23.0	16.1 ± 0.5	tr	70.8 ± 0.9	152.7 ± 0.2	88.7 ± 0.4	945.5 ± 29.9	328.3 ± 2.0
	P	15.7 ± 0.1	332.0 ± 3.4	15.3 ± 0.1	19.5 ± 0.3	31.6 ± 0.2	60.8 ± 0.2	618.2 ± 11.8	15.4 ± 0.4	tr	79.7 ± 3.0	191.8 ± 0.2	104.7 ± 0.5	1093.1 ± 13.0	391.6 ± 4.0
	F	11.1 ± 0.1	150.9 ± 2.3	11.3 ± 0.2	32.2 ± 0.3	17.9 ± 0.6	82.6 ± 0.5	597.8 ± 7.5	15.9 ± 0.6	tr	66.0 ± 0.7	138.3 ± 0.2	79.1 ± 0.3	903.8 ± 11.4	299.3 ± 1.9
Yuzi263	WR	20.4 ± 0.0	147.4 ± 0.1	10.9 ± 0.0	9.9 ± 0.1	17.0 ± 0.1	51.7 ± 0.1	195.1 ± 11.0	7.5 ± 0.1	6.8 ± 0.0	24.3 ± 0.1	56.5 ± 4.2	13.2 ± 0.0	452.4 ± 10.6	108.3 ± 4.4
	P	27.9 ± 0.4	256.0 ± 1.1	44.0 ± 0.1	9.6 ± 0.2	20.6 ± 0.1	65.9 ± 0.4	293.5 ± 11.4	7.5 ± 0.3	8.1 ± 0.1	32.0 ± 0.3	68.1 ± 1.5	20.1 ± 0.5	717.5 ± 12.3	135.8 ± 2.7
	F	19.0 ± 0.1	104.5 ± 0.3	tr	11.4 ± 0.3	16.8 ± 0.2	52.3 ± 0.4	169.1 ± 0.8	7.6 ± 0.1	7.0 ± 0.0	24.2 ± 0.1	57.5 ± 0.2	11.7 ± 0.1	373.0 ± 2.1	107.9 ± 0.3
Eshu-6[e] (control 1)	WR	9.1 ± 0.2	47.7 ± 1.2	8.7 ± 0.1	tr	tr	16.5 ± 3.1	45.4 ± 4.6						127.4 ± 9.2	
	P	12.3 ± 0.1	164.6 ± 0.1	26.3 ± 0.5	tr	tr	54.3 ± 0.2	256.3 ± 11.7				tr		513.7 ± 12.4	
	F	7.6 ± 0.2	40.5 ± 0.9	tr	tr	tr	12.4 ± 1.7	45.5 ± 0.1						106.1 ± 3.0	
Xu-22[e] (control 2)	WR	11.2 ± 0.0	118.3 ± 0.5	tr	tr	tr	20.5 ± 0.2	106.5 ± 4.6						256.5 ± 5.4	
	P	14.1 ± 0.1	239.7 ± 4.6	14.9 ± 0.0	tr	tr	60.2 ± 0.4	300.1 ± 11.6				tr		629.1 ± 16.6	
	F	8.5 ± 0.1	52.3 ± 0.7	tr	tr	tr	15.1 ± 0.3	47.8 ± 1.1						123.8 ± 0.5	
mean	purple	42.0	260.7	15.7	33.4	23.6	51.5	427.4	19.7	8.1	70.6	129.6	77.1	854.4	305.0
	white	10.3	110.5	8.3	tr	tr	29.8	133.6				tr		292.8	

[a] The numbers of the phenolic compounds in this table coincide with the numbers of the peaks in **Table 2** and **Figure 1**. The compounds **1**−**5**, **9**, and **11** were expressed as milligrams of chlorogenic acid (CA) per 100 g of DW, and the compounds **6**−**8**, **10**, and **12** were expressed as milligrams of cyanidin-3-glucosde per 100 g of DW. tr = trace amount. [b] Different parts of sweetpotato genotypes were tested: WR, whole root; P, peel; and F, flesh. [c] Total HAD, the sum of the contents of the compounds **1**−**5**, **9**, and **11** (HAD = hydroxycinnamic acid derivatives). [d] Total AC, the sum of the contents of the compounds **6**−**8**, **10**, and **12** (AC = anthocyanins). [e] Control = white-fleshed sweetpotato cultivars.



Anthocyanins	Code no.	R_1	R_2
cyanidin 3-sophoroside-5-glucoside	6	H	H
cyanidin 3-(6″-*p*-caffeoylsophoroside)-5-glucoside	7	H	Caf
peonidin 3-sophoroside-5-glucoside	8	OCH_3	H
cyanidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside	10	H	Fer
peonidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside	12	OCH_3	Fer

Hydroxycinnamic acid derivatives	Code no.	R_1	R_3	R_4	R_5
5-*O*-caffeoylquinic acid	2	H	H	H	Caf
feruloylquinic acids	5	H/Fer	H/Fer	H/Fer	H/Fer
3,4-di-*O*-caffeoylquinic acid	9	H	Caf	Caf	H
3,5-di-*O*-caffeoylquinic acid	11	H	Caf	H	Caf
caffeic acid	3	-	-	-	-

Figure 1. Chemical structures of major anthocyanins and hydroxycinnamic acid derivatives identified in the roots of purple-fleshed sweetpotato. Code numbers in this figure correspond to the numbers of the peaks in **Figure 2** and major phenolic compounds identified in **Table 2** and **3**.

reference to literature data (*4*, *12*, *13*, *15*, *21*). Seven peaks (peaks 1−5, 9, and 11) possessed typical UV/vis spectral characteristics of hydroxycinnamic acid derivatives with λ_{max} at 325−329 nm, whereas five peaks (peaks 6−8, 10, and 12) had typical UV/vis spectral characteristics of anthocyanins with λ_{max} = 526−532 (**Table 2**). Peaks 2 and 3 were readily identified as 5-*O*-caffeoylquinic acid and caffeic acid, respectively, by comparison to the corresponding authentic standards. Peaks 9 and 11 were tentatively identified as two dicaffeoylquinic acid isomers, i.e., 3,4-dicaffeoylquinic acid and 3,5-dicaffeoylquinic acid, respectively, according to their retention times and by comparison to reference data. However, the numbers of the peaks for dicaffeoylquinic acid isomers identified in the roots of purple-fleshed sweetpotato were less than those isolated in the leaves of sweetpotato genotypes/cultivars reported previously (*12*, *13*, *15*). Additionally, the numbers of the peaks for anthocyanins identified in this study were also less than those isolated in the roots of purple-fleshed sweetpotatoes from previous studies (*22*, *23*). It was likely due to the different analytical methods and various purple-fleshed sweetpotato genotypes or growing conditions between our and previous studies.

APCI−MS was successfully employed for identifying phenolic compounds in our recent study (*24*) and also in this study. Identification of most peaks could be further confirmed by APCI−MS data, such as the characteristic molecular ions ($[M + H]^+$ and $[M - H]^-$) and the observed fragmented ions resulting from the loss of small moieties (sugar or H_2O) from whole molecules (**Table 2**). For anthocyanins, the fragmented ions $[M + H]^+$ *m*/*z* 287 and $[M - H]^-$ *m*/*z* 285 (peaks 6, 7, and 10) were indicative of cyanidin (a common anthocyanidin aglycon), whereas the fragmented ions $[M + H]^+$ *m*/*z* 301 and $[M - H]^-$ *m*/*z* 299 (peaks 8 and 12) were indicative of peonidin (another common anthocyanidin aglycon). Other fragmented ions confirmed the sugar moieties in the molecules of the anthocyanins from purple-fleshed sweetpotato by a comparison to literature data (*3*, *4*, *21*). For hydroxycinnamic acid derivatives, typical protonated and fragmented ions were observed from peak 2 for 5-*O*-caffeoylquinic acid (e.g., $[M + H]^+$ at *m*/*z* 355, 337, and 163; $[M - H]^-$ at *m*/*z* 353, 191, and 161) and from peaks 9 and 11 for two dicaffeoylquinic acids (e.g., $[M + H]^+$ at *m*/*z* 517, 499, 355, and 163; $[M - H]^-$ at *m*/*z* 515 and 353). However, two hydroxycinnamic acid derivatives (peaks 1 and 4) were not reported previously in sweetpotato materials. The MS data of peak 4 was less abundant with only *m*/*z* 325 (negative), and it was tentatively identified as coumaroyl-hexoside according to its UV/vis spectral data and by comparison to reference data (*25*). Although peak 1 was readily identified as caffeoyl-hexoside, its detailed structural elucidation had not been undertaken. Thus, further identification by nuclear magnetic resonance (NMR) is required in the future.

Although many studies (*3*, *4*, *12*, *13*) reported identification of anthocyanins and other phenolics, including hydroxycinnamic acid derivatives, in sweetpotato, few researchers (*26*) used HPLC/LC−MS to simultaneously characterize such two different categories of phenolic compounds in the crude extracts of sweetpotato genotypes (especially purple-fleshed ones) at the same chromatographic conditions. Anthocyanins and hydroxycinnamic acid derivatives are normally required to use different chromatographic conditions for separating such two different categories of phenolic compounds because most of them have similar chemical polarities (*27*). In the present study, LC−PDA−APCI−MS was used for the first time to simultaneously and rapidly determine major anthocyanins and hydroxycinnamic acid derivatives in the crude extracts of purple-fleshed sweetpotatoes. The result showed that major anthocyanins and hydroxycinnamic acid derivatives of the methanolic extracts from sweetpotato roots were well-isolated under the same chromatographic conditions (**Figure 2**), indicating that the improved chromatographic conditions could be successfully used to simultaneously separate such two different kinds of phenolics and to easily acquire a high quality of MS data. The developed method may be employed to rapidly compare the differences in anthocyanins and hydroxycinnamic acid derivatives from hundreds of sweetpotato samples to screen the genotypes required for breeding.

Quantification of Major Phenolic Compounds in Peel, Flesh, and Whole Root of Chinese Purple-Fleshed Sweetpotato Genotypes. The quantified results of individual phenolic compounds in the tested genotypes (**Table 3**) showed that, for anthocyanins, cyanidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside (compound **10**) was the predominant anthocyanin (mean = 129.6 mg/100 g of DW) in all of the tested samples of purple-fleshed sweetpotato genotypes, followed by peonidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside (compound **12**) (77.1 mg/100 g of DW), whereas cyanidin 3-(6″-*p*-caffeoylsophoroside)-5-glucoside (compound **7**) was the least abundant anthocyanin (8.1 mg/100 g of DW). For hydroxycinnamic acid derivatives, 3,5-di-*O*-caffeoylquinic acid (compound **11**) was the main hydroxycinnamic acid (mean = 427.4 mg/100 g of DW) in all of the tested samples of purple-fleshed sweetpotato genotypes, followed by 5-*O*-caffeoylquinic acid (compound **2**) (260.7 mg/100 g of DW), while caffeic acid (compound **3**) was the least abundant hydroxycinnamic acid (15.7 mg/100 g of DW). Additionally, great genetic diversities in contents of individual phenolics (anthocyanins and hydroxycinnamic acid derivatives)

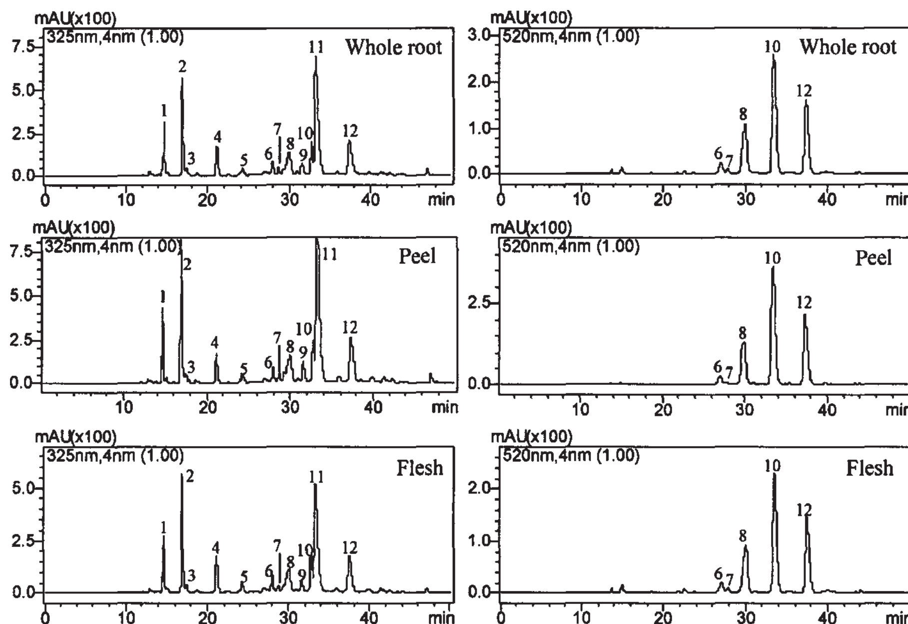


Figure 2. Representative chromatographs of major anthocyanins (520 nm) and hydroxycinnamic acid derivatives (325 nm) from WR, peel, and flesh of a selected purple-fleshed sweetpotato genotype (Ea2). Peak numbers in this figure correspond to the numbers of the phenolic compounds identified in **Table 2** and **3** and **Figure 1**.

between different Chinese purple-fleshed sweetpotato genotypes are clearly shown in **Table 3**. For example, the contents of cyanidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside (compound **10**) in WR ranged from 42.4 mg/100 g of DW in E5306 to 213.5 mg/100 g of DW in Ea3-2 and the contents of 3,5-di-*O*-caffeoylquinic acid (compound **11**) in WR ranged from 195.1 mg/100 g of DW in Yuzi263 to 626.9 mg/100 g of DW in EZX311. Islam et al. (*12*) and Truong et al. (*13*) reported that wide variations in contents of the phenolic acids, including caffeoylquinic acids, were also observed between different common sweetpotato cultivars/genotypes from the U.S.A. and Japan.

In comparison to white-fleshed sweetpotato cultivars, purple-fleshed sweetpotato genotypes contained much higher levels of phenolic compounds (**Table 3**). Total anthocyanin content (total AC) in WR of the purple-fleshed sweetpotato genotypes varied from 108.1 mg/100 g of DW in E6107b to 502.6 mg/100 g of DW in Ea3-2, whereas anthocyanins were nearly not detected in the white-fleshed sweetpotato roots, except a trace amount of cyanidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside in light-red-colored skin. Total hydroxycinnamic acid derivative content (total HAD) in WR of the purple-fleshed sweetpotato genotypes ranged from 452.4 mg/100 g of DW in Yuzi263 to 1458.7 mg/100 g of DW in EZX311. The mean value of total HAD for all purple-fleshed sweetpotato samples analyzed (including peel, flesh, and whole root) was 854.4 mg/100 g of DW, significantly higher than that of total HAD for white-fleshed sweetpotato cultivars (mean = 292.8 mg/100 g of DW). This was similar to the previous study of Padda et al. (*14*), who reported that the TPC of a purple-fleshed sweetpotato genotype was much higher than that of white- and orange-fleshed sweetpotato genotypes.

In addition, we measured and compared the contents of major phenolic compounds from three different part categories (peel, flesh, and whole root) of all of the tested purple-fleshed sweetpotato genotypes. Generally, peel (P) of most genotypes contained higher levels of both total and individual phenolic compounds (anthocyanins and hydroxycinnamic acid derivatives) than flesh (F) and whole root (WR) of most genotypes (**Table 3**). For example, total AC in P of Ea2 (551.0 mg/100 g of DW) was much higher than those in F and WR of Ea2 (349.1 and 403.2 mg/100 g of DW, respectively), whereas total HAD in P of Ea2 (931.1 mg/100 g of DW) was significantly higher than those in F and WR of Ea2 (530.8 and 596.0 mg/100 g of DW, respectively). It was also observed that there was a similar trend for contents of individual anthocyanins and hydroxycinnamic acid derivatives in P, F, and WR of most genotypes. This was basically consistent with previous studies on commercial sweetpotato cultivars from the U.S.A. (*13*, *28*). Our results indicated that the peel of Chinese purple-fleshed sweetpotato genotypes, normally discarded as waste after sweetpotato processing, might be used as raw resources for producing phenolics (particularly anthocyanin pigments).

Antioxidant Activities of Chinese Purple-Fleshed Sweetpotato Genotypes and Their Relationships with Total and Individual Phenolic Contents. Methanolic extracts of Chinese purple-fleshed sweetpotato genotypes exhibited a wide range of antioxidant activities (ABTS, FRAP, and DPPH assays) expressed as Trolox equivalent antioxidant capacity (TEAC) (**Table 4**). The TEAC values by the ABTS assay in the WR of the tested purple-fleshed sweetpotato genotypes ranged from 2.85 to 7.80 mmol/100 g of DW (i.e., Yuzi263 and Xu13-4, respectively); the TEAC values by the DPPH assay were from 3.54 to 6.36 mmol/100 g of DW (i.e., E6107b and Xu13-4, respectively); and the TEAC values by the FRAP assay were from 1.70 to 6.04 mmol/100 g of DW (i.e., Yuzi263 and EZX311, respectively). In comparison to the mean values of TEAC by three assay methods (**Table 4**), purple-fleshed sweetpotato genotypes had significantly stronger antioxidant activities than white-fleshed sweetpotato cultivars. This agreed with previous reports on sweetpotato cultivars/genotypes from the U.S.A. and Philippines (*29*,*30*). Moreover, all of the peel samples of sweetpotato roots generally showed higher TEAC values than the flesh samples, and the extent of the TEAC differences was in a genotype-dependent manner.

In addition, the determining results of TPC showed that the TPC values also had a great variation among all of the tested sweetpotato samples (**Table 4**). For example, the TPC values in the WR of purple-fleshed sweetpotato genotypes ranged from 503 to 1419 mg of GAE/100 g (i.e., Yuzi263 and EZX311, respectively). In comparison to the average TPC values,

Table 4. Antioxidant Capacities and Total Phenolics Contents in the Methanolic Extracts of Purple-Fleshed Sweetpotato Genotypes Collected in China[a]

genotypes		TEAC[b] (mmol/100 g of DW)			TPC[c] (mg of GAE/100 g of DW)
		ABTS	DPPH	FRAP	
Ea2	WR	6.34 ± 0.01	5.67 ± 0.01	4.01 ± 0.01	939 ± 3
	P	7.95 ± 0.03	5.63 ± 0.01	5.01 ± 0.01	1293 ± 10
	F	5.90 ± 0.01	5.16 ± 0.02	3.76 ± 0.01	888 ± 2
Ea3-1	WR	7.25 ± 0.01	5.50 ± 0.01	4.81 ± 0.01	1243 ± 2
	P	9.97 ± 0.03	6.88 ± 0.01	6.18 ± 0.01	1566 ± 1
	F	7.06 ± 0.02	5.31 ± 0.01	3.81 ± 0.01	1221 ± 3
Ea3-2	WR	6.78 ± 0.01	5.89 ± 0.01	4.16 ± 0.01	999 ± 1
	P	8.67 ± 0.01	6.47 ± 0.01	5.20 ± 0.02	1392 ± 4
	F	6.69 ± 0.00	5.15 ± 0.01	4.00 ± 0.01	899 ± 1
Ea4	WR	4.21 ± 0.01	3.84 ± 0.01	2.82 ± 0.01	722 ± 4
	P	7.28 ± 0.01	4.80 ± 0.01	5.03 ± 0.02	1272 ± 6
	F	4.04 ± 0.01	3.12 ± 0.01	2.86 ± 0.01	662 ± 5
E5306	WR	4.21 ± 0.01	3.65 ± 0.01	2.24 ± 0.01	668 ± 1
	P	4.89 ± 0.00	4.40 ± 0.01	2.30 ± 0.01	816 ± 1
	F	4.14 ± 0.01	2.97 ± 0.01	2.36 ± 0.01	652 ± 2
E6107a	WR	6.29 ± 0.01	5.87 ± 0.01	4.08 ± 0.01	941 ± 4
	P	6.25 ± 0.01	8.35 ± 0.01	4.20 ± 0.01	1046 ± 1
	F	6.18 ± 0.01	5.81 ± 0.01	3.68 ± 0.01	878 ± 1
E6107b	WR	3.23 ± 0.01	3.54 ± 0.01	2.16 ± 0.01	513 ± 1
	P	3.89 ± 0.01	3.87 ± 0.01	2.33 ± 0.01	774 ± 1
	F	2.06 ± 0.01	3.25 ± 0.00	1.23 ± 0.00	322 ± 3
EZX311	WR	7.32 ± 0.01	5.44 ± 0.01	6.04 ± 0.02	1419 ± 6
	P	8.97 ± 0.01	6.07 ± 0.01	6.81 ± 0.02	1775 ± 2
	F	7.06 ± 0.00	5.32 ± 0.01	5.32 ± 0.01	1385 ± 7
Xu13-4	WR	7.80 ± 0.02	6.36 ± 0.01	5.27 ± 0.01	1290 ± 1
	P	9.06 ± 0.01	6.69 ± 0.01	6.02 ± 0.01	1521 ± 5
	F	6.97 ± 0.01	5.31 ± 0.01	4.30 ± 0.01	1075 ± 4
Yuzi263	WR	2.85 ± 0.01	3.55 ± 0.01	1.70 ± 0.01	503 ± 1
	P	3.20 ± 0.01	3.56 ± 0.01	1.75 ± 0.01	590 ± 1
	F	2.43 ± 0.00	3.29 ± 0.01	1.54 ± 0.01	407 ± 1
Eshu-6[d] (control 1)	WR	0.69 ± 0.01	0.76 ± 0.00	0.24 ± 0.00	189 ± 4
	P	2.10 ± 0.01	1.82 ± 0.01	0.80 ± 0.01	418 ± 2
	F	0.56 ± 0.01	0.76 ± 0.01	0.18 ± 0.01	182 ± 3
Xu-22[d] (control 2)	WR	0.93 ± 0.01	1.00 ± 0.01	0.59 ± 0.01	231 ± 3
	P	2.32 ± 0.02	1.94 ± 0.01	1.03 ± 0.01	418 ± 5
	F	0.84 ± 0.01	0.76 ± 0.00	0.18 ± 0.00	183 ± 2
$LSD_{0.05}$[e]		0.21	0.21	0.16	0.36
mean	purple	5.96	5.02	3.83	989
	white	1.24	1.17	0.50	270

[a] Different parts of sweetpotato genotypes were tested: WR, whole root; P, peel; and F, flesh. [b] TEAC = Trolox equivalent antioxidant capacity. [c] TPC = total phenolics content. [d] Control = white-fleshed sweetpotato cultivars. [e] $LSD_{0.05}$ = least significant difference ($p < 0.05$), used for the difference comparison among means of various cultivars/genotypes.

Table 5. Pearson Correlation Coefficients (r) between Antioxidant Capacity Parameters and Contents of Individual Anthocyanins and Hydroxycinnamic Acid Derivatives from Purple-Fleshed Sweetpotato Genotypes Collected in China

TEAC	1	2	3	4	5	6	7	8	9	10	11	12	total HCQD[a]	total AC[b]
ABTS	0.456[c]	0.409[c]	0.181	0.590[d]	0.184	0.730[d]	−0.121	0.757[d]	−0.116	0.751[d]	0.810[d]	0.811[d]	0.738[d]	0.790[d]
FRAP	0.316	0.557[e]	0.008	0.448[c]	0.206	0.641[d]	−0.020	0.644[d]	−0.075	0.645[d]	0.811[d]	0.742[d]	0.790[d]	0.694[d]
DPPH	0.467[e]	0.218	0.235	0.623[d]	−0.011	0.688[d]	−0.160	0.803[d]	−0.279	0.853[d]	0.655[d]	0.865[d]	0.544[e]	0.858[d]
mean	0.413	0.395	0.141	0.554	0.126	0.686	−0.100	0.735	−0.157	0.750	0.759	0.806	0.691	0.781

[a] Total HAD, the sum of the contents of the compounds **1**−**5**, **9**, and **11** (HAD = hydroxycinnamic acid derivatives). [b] Total AC, the sum of the contents of the compounds **6**−**8**, **10**, and **12** (AC = anthocyanins). The numbers of the phenolic compounds in this table coincide with the numbers of the peaks in **Tables 2** and **3** and **Figure 1**. [c] $p < 0.05$. [d] $p < 0.001$. [e] $p < 0.01$.

purple-fleshed sweetpotato genotypes contained much higher levels of total phenolics (mean = 989 mg of GAE/100 g of DW) than white-fleshed sweetpotato cultivars (270 mg/100 g of DW).

Previous studies suggested that TPC of crude extracts from dietary plants and medicinal herbs could significantly contribute to their total antioxidant capacities (*17*, *18*, *24*). In the present study, Pearson correlation analysis showed that the TPC values positively correlated significantly ($p < 0.001$) with the TEAC values of all of the tested sweetpotato samples assayed by three methods (r = 0.9785 for FRAP; r = 0.9734 for ABTS; and r = 0.8640 for DPPH), indicating that the phenolic compounds in methanolic extracts of sweetpotato samples were significantly responsible for their antioxidant activities.

To understand which individual phenolic constituents specially contribute to the antioxidant capacity of purple-fleshed sweetpotato samples, Pearson correlation analysis was conducted between antioxidant capacity parameters and contents of individual anthocyanins and hydroxycinnamic acid derivatives (**Table 5**). The results showed that both total AC and total

HAD showed high and positive correlations with different TEAC values (ABTS, FRAP, and DPPH). For example, the correlative coefficient between total AC and ABTS was 0.790, and the correlative coefficient between total HCQD and ABTS was 0.738. This indicated that both anthocyanins and hydroxycinnamic acid derivatives considerably contributed to the overall antioxidant activity of purple-fleshed sweetpotato samples. Furthermore, some but not all individual phenolic compounds showed good correlation with antioxidant capacity parameters (ABTS, FRAP, and DPPH values) (**Table 5**). Taking the ABTS values for example, major phenolic compounds in purple-fleshed sweetpotato, e.g., compound **11** (3,5-di-*O*-caffeoylquinic acid) and compound **12** (peonidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside), showed higher positive correlations (r = 0.810 and 0.811, respectively) with the ABTS values, followed by compound **8** (peonidin 3-sophoroside-5-glucoside) (r = 0.757) and compound **10** (cyanidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside) (r = 0.751). However, minor phenolic compounds had no correlation or lower correlation with the ABTS values, e.g., compound **3** (caffeic acid), compound **7** (cyanidin 3-(6″-*p*-caffeoylsophoroside)-5-glucoside), and compound **9** (3,4-di-*O*-caffeoylquinic acid). This also indicated that major phenolic compounds in sweetpotato samples considerably contributed to their overall antioxidant capacity.

In conclusion, major phenolic constitutes and antioxidant capacities of purple-fleshed sweetpotato roots from a collection of representative genotypes/cultivars in China were systematically investigated in the present study for the first time. Chinese purple-fleshed sweetpotato genotypes contained a wide range of phenolic compounds, mainly including anthocyanins (cyanidin or peonidin 3-sophoroside-5-glucoside and their acylated derivatives) and hydroxycinnamic acid derivatives (3,5-di-*O*-caffeoylquinic acid, 5-*O*-caffeoylquinic acid, and caffeoyl-hexoside). Great genetic diversities in compositions and contents of phenolic compounds in the tested genotypes were revealed by LC−PDA−APCI−MS, with rapid simultaneous detections of both anthocyanins and hydroxycinnamic acid derivatives at the same chromatographic conditions. The developed method may be served for quality control of purple-fleshed sweetpotato or its related products during production and processing and also can be used to screen the suitable lines or varieties with desired quality for production.

Purple-fleshed sweetpotato genotypes contained much more abundant anthocyanins and hydroxycinnamic acid derivatives and showed stronger antioxidant capacity than white-fleshed sweetpotato genotypes, which may be used as a source of functional ingredients for healthy food processing. The peel of the purple-fleshed sweetpotato roots generally contained higher levels of both anthocyanins and hydroxycinnamic acid derivatives and also possessed stronger antioxidant activity than the flesh. This suggests that the peel of the purple-fleshed sweetpotato, traditionally discarded as waste during processing, may be used for production of concentrated phenolics. Pearson correlation analysis indicated that both anthocyanins and hydroxycinnamic acid derivatives in the tested genotypes significantly contributed to their overall antioxidant activity. Several major phenolics, such as 3,5-di-*O*-caffeoylquinic acid, peonidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside, peonidin 3-sophoroside-5-glucoside, and cyanidin 3-(6″-*p*-feruloylsophoroside)-5-glucoside, were the major contributors to total antioxidant activity. This study may provide useful information and scientific basis for breeding new lines of Chinese purple-fleshed sweetpotato with high levels of specific phenolic constitutes and strong antioxidant activity in a future program.

LITERATURE CITED

(1) Zhang, Z. T. Nutritional quality and starch physicochemical properties in sweetpotato. Ph.D. Thesis, The University of Hong Kong, Hong Kong, China, 2001.

(2) Tian, S. J.; Rickard, J. E.; Blanshard, J. M. V. Physicochemical properties of sweet potato starch. *J. Sci. Food Agric.* **1991**, *57*, 459–491.

(3) Odake, K.; Terahara, N.; Saito, N.; Toki, K.; Honda, T. Chemical structures of two anthocyanins form purple sweet potato, *Ipomoea batatas*. *Phytochemistry* **1992**, *31*, 2127–2130.

(4) Terahara, N.; Shimizu, T.; Kato, Y.; Nakamura, M.; Maitani, T.; Yamaguchi, M.; Goda, Y. Six diacylated anthocyanins from the storage roots of purple sweet potato, *Ipomoea batatas*. *Biosci., Biotechnol., Biochem.* **1999**, *63*, 1420–1424.

(5) Hou, D. X. Potential mechanisms of cancer chemoprevention by anthocyanins. *Curr. Mol. Med.* **2003**, *3*, 149–159.

(6) Philpott, M.; Lim, C. C.; Ferguson, L. R. Dietary protection against free radicals: A case for multiple testing to establish structure−activity relationships for antioxidant potential of anthocyanic plant species. *Int. J. Mol. Sci.* **2009**, *10*, 1081–1103.

(7) Kano, N.; Takayanagi, T.; Harada, K.; Makino, K.; Ishikawa, F. Antioxidative activity of anthocyanins from purple sweet potato, *Ipomoera batatas* cultivar Ayamurasaki. *Biosci., Biotechnol., Biochem.* **2005**, *69*, 979–988.

(8) Saigusa, N.; Terahara, N.; Ohba, R. Evaluation of DPPH-radical-scavenging activity and antimutagenicity and analysis of anthocyanins in an alcoholic fermented beverage produced from cooked or raw purple-fleshed sweet potato (*Ipomoea batatas* cv. Ayamurasaki) roots. *Food Sci. Technol. Res.* **2005**, *11*, 390–394.

(9) Miyazaki, K.; Makino, K.; Iwadate, E.; Deguchi, Y.; Ishikawa, F. Anthocyanins from purple sweet potato *Ipomoea batatas* cultivar Ayamurasaki suppress the development of atherosclerotic lesions and both enhancements of oxidative stress and soluble vascular cell adhesion molecule-1 in apolipoprotein E-deficient mice. *J. Agric. Food Chem.* **2008**, *56*, 11485–11492.

(10) Wu, D. M.; Lu, J.; Zheng, Y. L.; Zhou, Z.; Shan, Q.; Ma, D. F. Purple sweet potato color repairs D-galactose-induced spatial learning and memory impairment by regulating the expression of synaptic proteins. *Neurobiol. Learn. Mem.* **2008**, *90*, 19–27.

(11) Zhang, Z. F.; Fan, S. H.; Zheng, Y. L.; Lu, J.; Wu, D. M.; Shan, Q.; Hu, B. Purple sweet potato color attenuates oxidative stress and inflammatory response induced by D-galactose in mouse liver. *Food Chem. Toxicol.* **2009**, *47*, 496–501.

(12) Islam, M. S.; Yoshimoto, M.; Yamakawa, O. Distribution and physiological functions of caffeoylquinic acid derivatives in leaves of sweetpotato genotypes. *J. Food Sci.* **2003**, *68*, 111–116.

(13) Truong, V. D.; McFeeters, R. F.; Thompson, R. T.; Dean, L. L.; Shofran, B. Phenolic acid content and composition in leaves and roots of common commercial sweetpotato (*Ipomea batatas* L.) cultivars in the United States. *J. Food Sci.* **2007**, *72*, 343–349.

(14) Padda, M. S.; Picha, D. H. Quantification of phenolic acids and antioxidant activity in sweetpotato genotypes. *Sci. Hortic.* **2008**, *119*, 17–20.

(15) Zheng, W.; Clifford, M. N. Profiling the chlorogenic acids of sweet potato (*Ipomoea batatas*) from China. *Food Chem.* **2008**, *106*, 147–152.

(16) Fu, Y. F. Studies on the major characters and their influence factors of the rare purple-fleshed sweetpotato [*Ipomoea batatas* (L.) Lam.]. Ph.D. Thesis, Southwest University, Xi'an, China, 2008 (in Chinese with an English abstract).

(17) Cai, Y. Z.; Luo, Q.; Sun, M.; Corke, H. Antioxidant activity and phenolic compounds of 112 traditional Chinese medicinal plants associated with anticancer. *Life Sci.* **2004**, *74*, 2157–2184.

(18) Shan, B.; Cai, Y. Z.; Sun, M.; Corke, H. Antioxidant capacity of 26 spice extracts and characterization of their phenolic constituents. *J. Agric. Food Chem.* **2005**, *53*, 7749–7759.

(19) Brand-Williams, W.; Cuvelier, M. E.; Berset, C. Use of a free radical method to evaluate antioxidant activity. *Lebensm.-Wiss. Technol.* **1995**, *28*, 25–30.

(20) Benzie, I. F. F.; Strain, J. J. The ferric reducing ability of plasma (FRAP) as a measure of "antioxidant power": The FRAP assay. *Anal. Biochem.* **1996**, *239*, 70–76.

(21) Tian, Q. G.; Konczak, I.; Schwartz, S. J. Probing anthocyanin profiles in purple sweet potato cell line (*Ipomoea batatas* L. cv. Ayamurasaki) by high-performance liquid chromatography and electrospray ionization tandem mass spectrometry. *J. Agric. Food Chem.* **2005**, *53*, 6503–6509.

(22) Truong, V. D.; Deighton, N.; Thompson, R. L.; McFeeters, R. F.; Dean, L. O.; Pecota, K. V.; Yencho, G. C. Characterization of anthocyanins and anthocyanidins in purple-fleshed sweetpotatoes by HPLC−DAD/ESI−MS/MS. *J. Agric. Food Chem.* **2010**, *58*, 404–410.

(23) Oki, T.; Masuda, M.; Nishiba, Y.; Terahara, N.; Suda, I. Involvement of anthocyanins and other phenolic compounds in radical-scavenging activity of purple-fleshed sweet potato cultivars. *J. Food Sci.* **2002**, *67*, 1752–1756.

(24) Zhu, F.; Cai, Y. Z.; Sun, M.; Ke, J. X.; Lu, D. Y.; Corke, H. Comparison of major phenolic constituents and in vitro antioxidant activity of diverse kudingcha genotypes from *Ilex kudingcha*, *Ilex cornuta*, and *Ligustrum robustum*. *J. Agric. Food Chem.* **2009**, *57*, 6082–6089.

(25) Ferreres, F.; Ribeiro, V.; Gil-Izquierdo, A.; Rodrigues, M. A.; Seabra, R. M.; Andrade, P. B.; Valentao, P. *Rumex induratus* leaves: Interesting dietary source of potential bioactive compounds. *J. Agric. Food Chem.* **2006**, *54*, 5782–5789.

(26) Oki, T.; Osame, M.; Masuda, M.; Kobayashi, M.; Furuta, S.; Nishiba, Y.; Kumagai, T.; Sato, T.; Suda, I. Simple and rapid spectrophotometric method for selecting purple-fleshed sweetpotato cultivars with high radical-scavenging activity. *Breed. Sci.* **2003**, *53*, 101–107.

(27) Santos-Buelga, C.; Williamson, G. *Methods in Polyphenol Analysis*; Royal Society of Chemistry: Cambridge, U.K., 2003.

(28) Steed, L. E.; Truong, V. D. Anthocyanin content, antioxidant activity, and selected physical properties of flowable purple-fleshed sweetpotato purees. *J. Food Sci.* **2008**, *73*, S215–S221.

(29) Teow, C. C.; Truong, V. D.; McFeeters, R. F.; Thompson, R. L.; Pecota, K. V.; Yencho, G. C. Antioxidant activities, phenolic and β-carotene contents of sweet potato genotypes with varying flesh colours. *Food Chem.* **2007**, *103*, 829–838.

(30) Rumbaoa, R. G. O.; Cornago, D. F.; Geronimo, I. M. Phenolic content and antioxidant capacity of Philippine sweet potato (*Ipomoea batatas*) varieties. *Food Chem.* **2009**, *113*, 1133–1138.

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