

## Notes

***p*-Coumaroyl Anthocyanins from the Tuber Epidermis of a Colored Potato  
*Solanum tuberosum* L. cv Jayoung**

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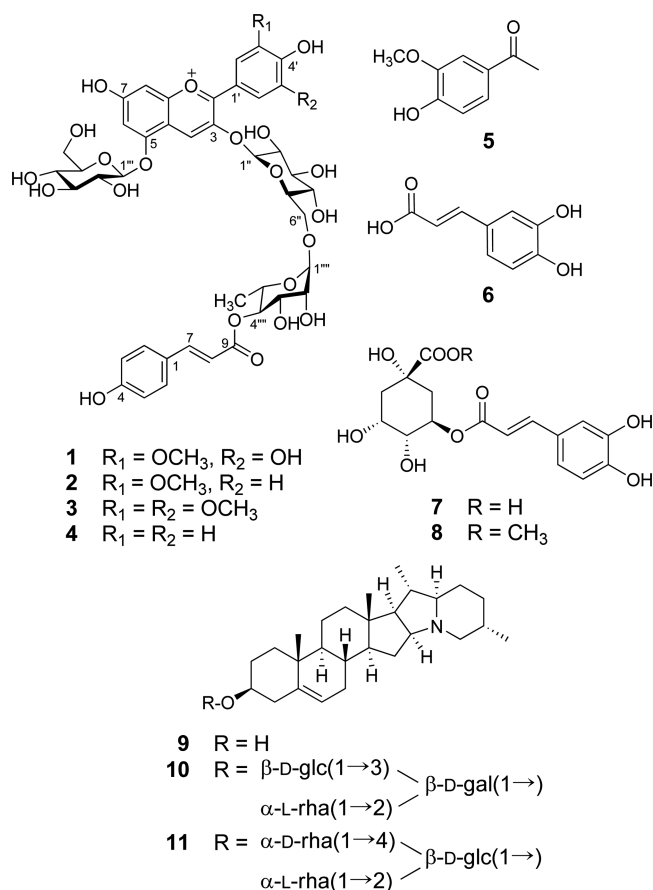
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Potatoes (*Solanum tuberosum* L.) rank as the world's fourth most important food crop, after maize, wheat, and rice<sup>1</sup> and colored potato cultivars are becoming popular, because of their color appeal, outstanding taste and mashability and their potential use in salads and novelty crisps.<sup>2-4</sup> The pigments in colored potatoes have been identified as the *p*-coumaroyl or feruloyl 5-glucoside-3-rhamnosylglucoside derivatives of pelargonidin, cyanidin, peonidin, delphinidin, petunidin and malvidin.<sup>5</sup> A new colored potato cultivar *Solanum tuberosum* L. cv Jayoung is widely cultivated in Korea, which was originally bred in the Republic of Korea during a joint program between the Highland Agriculture Research Center (HARC), the Korean National Institute of Crop Science, and the Rural Development Administration (RDA).<sup>6</sup> The colored potato 'Jayoung' has dark purple-flesh, and contains substantial amounts of polyphenols, such as, anthocyanin and phenolic acid.<sup>6,7</sup> Recent studies on 'Jayoung' showed that 70% EtOH extract and CHCl<sub>3</sub> fraction of the tuber epidermis have anti-inflammatory and anti-colitis effects.<sup>8,9</sup> However, no detailed phytochemical investigations have been reported on the colored potato 'Jayoung' to date. In the present study, repeated chromatography of the CH<sub>2</sub>Cl<sub>2</sub>- and BuOH-soluble fractions from the 70% EtOH extract of the tuber epidermis of *S. tuberosum* L. cv Jayoung led to the isolation and characterization of four *p*-coumaroyl anthocyanins (**1-4**), four phenolic compounds (**5-8**), and three steroidal alkaloids (**9-11**). The compounds **5-11** were identified to be acetovanillone (apocynin) (**5**),<sup>10</sup> caffeic acid (**6**),<sup>11</sup> chlorogenic acid (**7**),<sup>12</sup> methyl chlorogenate (**8**),<sup>13</sup> solanidine (**9**),<sup>14</sup>  $\alpha$ -solanine (**10**),<sup>15</sup> and  $\alpha$ -chaconine (**11**)<sup>16</sup> by physical (mp, [ $\alpha$ ]<sub>D</sub>) and spectroscopic data (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, 2D NMR, and MS) measurement and by comparison with published values (Figure 1). To our knowledge, this is the first report on the isolation of acetovanillone from *Solanum* spp. The structure elucidation of the anthocyanins



**Figure 1.** Chemical structures of **1-11** isolated from the tuber epidermis of *S. tuberosum* L. cv Jayoung.

**1-4** are described herein.

Compound **1** was obtained as violet powder. The UV-vis spectrum of **1** revealed  $\lambda_{\text{max}}$  at 532 nm, suggesting that **1** is an anthocyanin. The <sup>1</sup>H-NMR and COSY spectra of **1** (Table 1) revealed two sets of 2H AB-type signals [ $\delta_{\text{H}}$  8.00 (1H, d,

<sup>a</sup>These authors contributed equally to this work.

**Table 1.** The  $^1\text{H}$ -NMR spectral data for **1** and **2**<sup>a</sup>

Position	$\delta_{\text{H}}$ mult., (J/Hz)	
	1	2
<i>Aglycone</i>		
4	8.96 s	8.98 s
6	7.01 d (2.0)	7.02 br s
8	7.06 d (2.0)	7.07 br s
2'	8.00 d (2.4)	8.20 d (2.5)
5'		7.07 d (8.5)
6'	7.82 d (2.4)	8.27 dd (8.5, 2.5)
3'-OCH <sub>3</sub>	4.00 s	4.00 s
<i>3-O-β-Glucopyranoside</i>		
1''	5.50 d (8.0)	5.49 d (7.5)
2''	3.71	3.70
3''	3.58	3.59
4''	3.47	3.51
5''	3.60	3.60
6A''	4.03	4.03
6B''	3.72	3.73
<i>5-O-β-Glucopyranoside</i>		
1'''	5.19 d (7.6)	5.20 d (7.5)
2'''	3.69	3.70
3'''	3.82	3.81
4'''	3.55	3.54
5'''	3.60	3.59
6A'''	3.93	3.94
6B'''	3.79	3.77
<i>6''-O-α-Rhamnopyranosyl</i>		
1''''	4.71 d (1.2)	4.71 d (1.0)
2''''	3.79	3.80
3''''	3.83	3.83
4''''	4.90 t (9.6)	4.86 overlap
5''''	3.76	3.75
6''''	0.99 d (6.4)	0.99 d (6.5)
<i>4''''-E-p-Coumaroyl</i>		
2/6	7.43 d (8.8)	7.39 d (8.5)
3/5	6.80 d (8.4)	6.79 d (9.0)
7	7.57 d (16.0)	7.54 d (15.5)
8	6.25 d (15.6)	6.23 d (16.0)

<sup>a</sup>The assignments were based on COSY, HSQC and HMBC experiments.

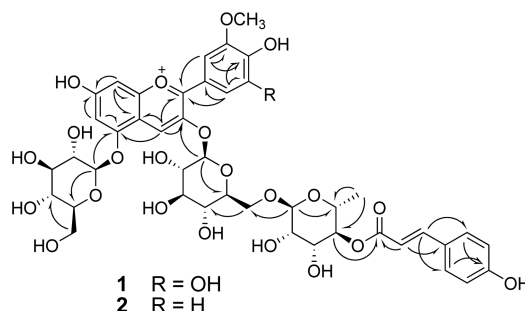
$J = 2.4$  Hz) and 7.82 (1H, d,  $J = 2.4$  Hz);  $\delta_{\text{H}}$  7.06 (1H, d,  $J = 2.0$  Hz) and 7.01 (1H, d,  $J = 2.0$  Hz)]. The  $^1\text{H}$ -NMR of **1** also showed two singlets at  $\delta_{\text{H}}$  8.96 (1H) and 4.00 (3H), indicating the aglycone of **1** as petunidin. The presence of a *trans*-*p*-coumaroyl moiety was suggested from the  $^1\text{H}$ -NMR resonances at  $\delta_{\text{H}}$  7.57 (1H, d,  $J = 16.0$  Hz), 7.43 (2H, d,  $J = 8.8$  Hz), 6.80 (2H, d,  $J = 8.4$  Hz), and 6.25 (1H, d,  $J = 15.6$  Hz). The sugar region of the  $^1\text{H}$ -NMR spectrum of **1** showed three anomeric proton signals at  $\delta_{\text{H}}$  5.50 (1H, d,  $J = 8.0$  Hz), 5.19 (1H, d,  $J = 7.6$  Hz), and 4.71 (1H, d,  $J = 1.2$  Hz), in accordance with two glucose and one rhamnose units.

Comparison of the above with data in the literature<sup>5,17</sup> suggested that **1** was a *p*-coumaroyl-5-glucoside-3-rhamnosylglucoside derivative of petunidin. The downfield shift of C-6'' ( $\delta_{\text{C}}$  65.9 ppm) in the HSQC spectrum of **1** showed the linkage between the 3-*O*-β-glucose and the rhamnose unit to be at the 6''-hydroxyl. The HMBC correlations (Figure 2) confirmed the assignments of all proton and carbon resonances and the location of the sugar units (C-3, C-5, C-6'') and *p*-coumaroyl group (C-4'''). Thus, **1** was identified as petanin {petunidin 3-*O*-[6-*O*-(4-*O*-*E*-*p*-coumaroyl-*O*-α-rhamnopyranosyl)-β-glucopyranoside]-5-*O*-β-glucopyranoside}.<sup>17</sup>

Compounds **2–4** were obtained as a mixture and as purple powder. The UV-vis spectrum of the mixture showed  $\lambda_{\text{max}}$  at 520 nm, suggesting a mixture of anthocyanins. We found that the mixture was composed with three anthocyanins (ratio 8:1:1) by analysis of peak integration of the  $^1\text{H}$ -NMR spectrum. API-ES-MS of the mixture also gave three molecular ion peaks at  $m/z$  947, 917, and 887. The proton and carbon signals in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **2**, the major compound in the mixture, exhibited strong similarities

**Table 2.** The  $^{13}\text{C}$ -NMR spectral data for aglycones of **1–4**<sup>a</sup>

Position	$\delta_{\text{C}}$ (ppm)			
	1	2	3	4
2	163.2	163.1	162.8	162.7
3	144.9	144.6	144.7	144.5
4	132.9	133.4	134.7	133.7
5	155.3	155.3	155.3	155.2
6	104.1	104.2	104.2	104.1
7	168.3	168.5	168.5	168.4
8	96.0	96.2	96.3	96.1
9	155.8	155.8	155.8	155.7
10	111.7	111.8	111.9	111.2
1'	118.4	119.4	118.1	119.5
2'	108.2	113.9	109.5	134.7
3'	148.5	148.2	148.4	116.7
4'	144.9	156.0	145.9	165.9
5'	146.4	116.5	148.4	116.7
6'	112.8	113.9	109.5	134.7
3'-OCH <sub>3</sub>	55.8	55.5	55.9	
5'-OCH <sub>3</sub>			55.9	

<sup>a</sup>The assignments were based on COSY, HSQC and HMBC experiments.**Figure 2.** Key HMBC (H→C) correlations of **1** and **2**.

with those of **1** except for an anthocyanidin B-ring (Tables 1 and 2). In detail, the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **2** revealed the 3H ABX system at  $\delta_{\text{H}}$  8.27 (1H, dd,  $J = 8.5, 2.5$  Hz, H-6'), 8.20 (1H, d,  $J = 2.5$  Hz, H-2'), and 7.07 (1H, d,  $J = 8.5$  Hz, H-5'), in accordance with peonidin. Thus, the structure of **2** was determined to be peonanin {peonidin 3-*O*-[6-*O*-(4-*O*-*E*-*p*-coumaroyl-*O*- $\alpha$ -rhamnopyranosyl)- $\beta$ -glucopyranoside]-5-*O*- $\beta$ -glucopyranoside}.<sup>18</sup>

The structure of **3**, one of the minor anthocyanins in the mixture, was determined to be malvanin {malvidin 3-*O*-[6-*O*-(4-*O*-*E*-*p*-coumaroyl-*O*- $\alpha$ -rhamnopyranosyl)- $\beta$ -glucopyranoside]-5-*O*- $\beta$ -glucopyranoside} by analysis of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data and by comparison with published values.<sup>19</sup> The presence of a molecular ion at  $m/z$  947 in the API-ES-MS spectrum of the mixture confirmed this identification.

The structure of **4**, another minor anthocyanin in the mixture, was also identified as pelanin {pelargonidin 3-*O*-[6-*O*-(4-*O*-*E*-*p*-coumaroyl-*O*- $\alpha$ -rhamnopyranosyl)- $\beta$ -glucopyranoside]-5-*O*- $\beta$ -glucopyranoside} by analysis of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data, by comparison with published values,<sup>20</sup> and by a molecular ion at  $m/z$  887 in the API-ES-MS spectrum.

To our knowledge, this is the first report on the characterization of **1**, **3**, and **4** in a Korean colored potato cultivar. Acylated anthocyanins like **1-4** have been found in the various colored potatoes such as Norwegian,<sup>5</sup> Japanese,<sup>17</sup> and Andean cultivars<sup>22</sup> as major pigments. Recently, it is reported that colored potatoes (Purple Majesty) are acute *in vivo* antioxidant source and hypotensive agent in human after supplementation to hypertensive subjects.<sup>23</sup> Although anthocyanins have many health-promoting benefits,<sup>24</sup> biological activity of **1-4** are little known to date. Meanwhile, there are some reports that the acylation of the saccharide moiety with *p*-coumarate or ferulate is considered the main reason for higher color stability of these anthocyanins than non-acylated anthocyanins at most pH values.<sup>3,5,21</sup> Thus these *p*-coumaroyl anthocyanins **1-4** are worthy of biological evaluation for their potential as new lead compounds.

## Experimental

**General Experimental Procedures.** 1D and 2D NMR experiments were performed on a Bruker 400 MHz or Varian 500 MHz FT-NMR instrument with tetramethylsilane (TMS) or solvent residues as internal standard. Mass spectra were obtained using an Agilent 1200 series coupled to a 6120 Quadrupole LC/MS system. Silica gel (70-230 mesh and 230-400 mesh, Merck, Germany) was used for column chromatography (CC). Thin-layer chromatographic (TLC) analysis was performed on Kieselgel 60 F 254 plates (silica gel, 0.25 mm layer thickness, Merck, Germany); compounds were visualized by UV light (254 and 365 nm) and 20% (v/v)  $\text{H}_2\text{SO}_4$  reagent (Aldrich). All solvents used for the chromatographic separations were distilled before use.

**Plant Material.** The purple colored potato cultivar, "Jayoung" (*Solanum tuberosum* L. cv Jayoung, Solanaceae) was supplied by Highland Agriculture Research Center (HARC), the Korean National Institute of Crop Science, and

the Rural Development Administration (RDA), Republic of Korea, in September 2012. A voucher specimen (KHP-2012-SOTU1) was deposited in the Lab. of Natural Product Medicine, College of Pharmacy, Kyung Hee University. The epidermis (< 5 mm thickness) from the fresh tubers of "Jayoung" were cut into small pieces and were freeze-dried.

**Extraction and Isolation.** The freeze-dried samples (7 kg) were extracted with 30 L of 70% EtOH three times by maceration. The extracts were combined and concentrated *in vacuo* to give a 70% EtOH extract (642 g). The 70% EtOH extract (641 g) was suspended in distilled water (2 L) and then successively extracted with *n*-hexane ( $3 \times 2$  L),  $\text{CH}_2\text{Cl}_2$  ( $3 \times 2$  L), EtOAc ( $3 \times 2$  L), and *n*-butanol ( $3 \times 2$  L) to give *n*-hexane- (66.2 g),  $\text{CH}_2\text{Cl}_2$ - (5.1 g), EtOAc- (2.3 g), *n*-butanol- (61.1 g), and water-soluble fractions (506.0 g). The  $\text{CH}_2\text{Cl}_2$ -soluble extract was chromatographed over silica gel (230-400 mesh,  $\phi$  4.2  $\times$  41.5 cm) as stationary phase with a  $\text{CH}_2\text{Cl}_2$ -MeOH gradient (from 95:5 to 85:15 v/v; final stage, MeOH 100%) as mobile phase to afford 14 pooled fractions (M1-M14). The fraction M4 (108 mg) was further fractionated using a Sephadex column ( $\phi$  2.5  $\times$  75 cm) with  $\text{CH}_2\text{Cl}_2$ -MeOH mixture (1:1 v/v), yielding compound **5** (5.0 mg). The fraction M9 (125.7 mg) was subjected to a Sephadex column ( $\phi$  3.6  $\times$  73.5 cm) with  $\text{CH}_2\text{Cl}_2$ -MeOH mixture (1:1 v/v) to give compound **9** (9.0 mg). Compound **10** (135.1 mg) was purified from the fraction M12 (408 mg) using a reversed phase column chromatography (CC) (YMC gel,  $\phi$  2.8  $\times$  28.5 cm) with a MeOH- $\text{H}_2\text{O}$  gradient (from 1:1 to 1:0 v/v) as mobile phase. A portion of the BuOH-soluble extract (20.2 g) was separated by Diaion HP20 CC ( $\phi$  5.0  $\times$  59.0 cm), using gradient mixtures of a MeOH- $\text{H}_2\text{O}$  (from 0:1 to 1:0 v/v) as mobile phases, affording 20 fractions (1B1-1B20). Compounds **6** (58.0 mg) and **7** (110.8 mg) were purified from the fraction 1B5 (570 mg) using a flash CC system with Redi Sep-C18 (48 g, MeOH- $\text{H}_2\text{O}$ -formic acid = 15:85/1  $\rightarrow$  30/70/1 v/v). Compound **8** (139.8 mg) was obtained from the fraction 1B9 (1.68 g) by using repeated silica gel CC. The fraction 1B12 (310 mg) was subjected to a Sephadex column ( $\phi$  3.2  $\times$  37.8 cm) with MeOH to obtain compound **11** (38.8 mg). For the isolation of anthocyanins, a portion of the BuOH-soluble extract (10.26 g) was separated by Diaion HP20 CC ( $\phi$  4.4  $\times$  48.8 cm), using gradient mixtures of a MeOH- $\text{H}_2\text{O}$ -TFA (from 0:100:0.1 to 100:0:0.1 v/v) as mobile phases, affording five fractions (2B1-2B5). The fraction 2B4 (2.29 g) was further fractionated using a Sephadex column ( $\phi$  3.5  $\times$  55.0 cm) with MeOH with 0.1% TFA, yielding seven fractions 2B4-1-2B4-7. An anthocyanin-rich fraction (2B4-4, 245.2 mg) was separated by using preparative HPLC with a gradient of MeCN- $\text{H}_2\text{O}$ -TFA (15:85:0.1 to 35:65:0.1), resulting in the isolation of compound **1** (11.0 mg, violet powder) and a mixture of compounds **2-4** (28.0 mg, purple powder).

**Petanin (1):** Amorphous violet powder; UV (On-line HPLC-DAD)  $\lambda_{\text{max}}$  nm: 532;  $^1\text{H}$ -NMR (0.1%  $\text{CF}_3\text{COOD}$  in  $\text{CD}_3\text{OD}$ , 400 MHz), see Table 1;  $^{13}\text{C}$ -NMR (0.1%  $\text{CF}_3\text{COOD}$  in  $\text{CD}_3\text{OD}$ , 100 MHz), aglycone: see Table 2, 3-*O*- $\beta$ -*Glu*:  $\delta$  101.3 (C-1"), 73.3 (C-2"), 76.8 (C-3"), 69.9 (C-4"), 76.5 (C-

5"), 65.9 (C-6"), 5-*O*- $\beta$ -*Glu*:  $\delta$  101.4 (C-1"), 73.4 (C-2"), 76.2 (C-3"), 69.6 (C-4"), 77.3 (C-5"), 60.8 (C-6"), 6"-*O*- $\alpha$ -*Rha*:  $\delta$  100.7 (C-1"), 70.7 (C-2"), 68.9 (C-3"), 73.9 (C-4"), 66.4 (C-5"), 16.5 (C-6"), 4"-*E*-*p*-*Cou*:  $\delta$  125.7 (C-1), 129.9 (C-2/C-6), 115.5 (C-3/C-5), 159.9 (C-4), 145.6 (C-7), 113.6 (C-8), 167.6 (C-9); APT-ES-MS (positive mode)  $m/z$  = 933 [M]<sup>+</sup>.

**Peonanin (2):** Amorphous purple powder; UV (On-line HPLC-DAD)  $\lambda_{\max}$  nm: 520; <sup>1</sup>H-NMR (0.1% CF<sub>3</sub>COOD in CD<sub>3</sub>OD, 500 MHz), see Table 1; <sup>13</sup>C-NMR (0.1% CF<sub>3</sub>COOD in CD<sub>3</sub>OD, 125 MHz), aglycone: see Table 2, 3-*O*- $\beta$ -*Glu*:  $\delta$  101.4 (C-1"), 73.3 (C-2"), 76.8 (C-3"), 69.8 (C-4"), 76.5 (C-5"), 65.9 (C-6"), 5-*O*- $\beta$ -*Glu*:  $\delta$  101.3 (C-1"), 73.4 (C-2"), 76.2 (C-3"), 69.6 (C-4"), 77.3 (C-5"), 60.7 (C-6"), 6"-*O*- $\alpha$ -*Rha*:  $\delta$  100.7 (C-1"), 70.7 (C-2"), 68.9 (C-3"), 73.9 (C-4"), 66.4 (C-5"), 16.5 (C-6"), 4"-*E*-*p*-*Cou*:  $\delta$  125.7 (C-1), 129.8 (C-2/C-6), 115.4 (C-3/C-5), 159.9 (C-4), 145.6 (C-7), 113.6 (C-8), 167.5 (C-9); APT-ES-MS (positive mode)  $m/z$  = 917 [M]<sup>+</sup>.

**Malvanin (3):** <sup>1</sup>H-NMR (0.1% CF<sub>3</sub>COOD in CD<sub>3</sub>OD, 500 MHz):  $\delta$  9.00 (1H, s, H-4), 7.98 (2H, s, H-2'/H-6'); <sup>13</sup>C-NMR (0.1% CF<sub>3</sub>COOD in CD<sub>3</sub>OD, 125 MHz), aglycone: see Table 2; APT-ES-MS (positive mode)  $m/z$  = 947 [M]<sup>+</sup>.

**Pelanin (4):** <sup>1</sup>H-NMR (0.1% CF<sub>3</sub>COOD in CD<sub>3</sub>OD, 500 MHz):  $\delta$  9.00 (1H, s, H-4), 8.59 (2H, d,  $J$  = 9.0 Hz, H-2'/H-6'), 7.06 (2H, d,  $J$  = 9.0 Hz, H-3'/H-5'); <sup>13</sup>C-NMR (0.1% CF<sub>3</sub>COOD in CD<sub>3</sub>OD, 125 MHz), aglycone: see Table 2; APT-ES-MS (positive mode)  $m/z$  = 887 [M]<sup>+</sup>.

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**Supporting Information.** The NMR spectra of 1-4 are available on request from the correspondence author.

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