Vanicosides C−F, New Phenylpropanoid Glycosides from *Polygonum pensylvanicum*

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The isolation of the protein kinase C inhibitors, vanicoside A (**1**) and vanicoside B (**2**), from *Polygonum pensylvanicum* prompted continued interest in the active principles of this plant. A new, more efficient isolation procedure has been developed to facilitate separation of homologues of vanicosides A and B from the complex extract. Several new phenylpropanoid glycosides have since been isolated. The structures of these principles were determined to be 2′-*O*-acetylhydropiperoside (**4**), 6′-*O*-*p*-coumarylhydropiperoside (**5**), 4′-*O*-acetylvanicoside A (**6**), and 3′-*O*-acetylvanicoside B (**7**) using negative ion FABMS, ^{1}H NMR, and 2D NMR techniques.

The plant kingdom continues to be a major source of novel natural products with potential for use as drugs or pharmaceutical agents. A plant of current interest in our laboratory is *Polygonum pensylvanicum* (Polygonaceae). An ethanolic extract of the whole plant demonstrated significant inhibition of protein kinase C (PKC) activity with an IC_{50} of 38 μg/mL.[1] PKC is a Ca^{2+}- and phospholipid-dependent enzyme that appears to be the receptor protein for tumor-promoting phorbol esters.[2] PKC has been linked to tumor promotion,[3−6] the activation of HIV-1,[7−9] and the inhibition of apoptosis in leukemia cells.[10]

The major components responsible for the inhibition of PKC activity in *Polygonum pensylvanicum*, vanicosides A (**1**) and B (**2**), were previously reported.[1] Also isolated in this previous work was the known phenylpropanoid glycoside,[11] hydropiperoside (**3**). In more recent work, a new scheme was developed to isolate related phenylpropanoid glycosides from *Polygonum pensylvanicum*.[12] A continuous liquid−liquid partition of the ethanolic extract between ethyl acetate and water was used in the initial step of the improved scheme. The crude ethyl acetate fraction was then examined using a constant neutral loss mass spectrometry experiment to help identify at least 10 homologues of the vanicosides.[12] These homologues were targeted for isolation via HPLC−MS. The isolation and structure elucidation of four of these homologues (vanicosides C−F) are presented here.

Results and Discussion

Dried roots, stems, and leaves of *Polygonum pensylvanicum* were subjected to a Soxhlet extraction with 95% ethanol for 24 h. The ethanol extract was concentrated in vacuo to a dark gum, and the resulting dark gum was partitioned between water and ethyl acetate using a continuous liquid−liquid extractor for 72 h. The ethyl acetate extract was then concentrated to give a dark red-brown gum. Aliquots (1.5 g) of the dark gum were dissolved in 5 mL of ethyl acetate prior to isolation. Near baseline separation of the ethyl acetate extract was achieved via preparative HPLC using a Partisil 10 HPLC column and 4.5- to 5-mL sample injections. The mobile phase was 5% methanol in dichloromethane, and the flow rate was increased at planned intervals from 5 mL/min to 25 mL/min. Samples were collected at one-minute intervals and recombined to give fractions enriched in individual peaks. In cases where samples of significant weight were recovered, the fractions were rechromatographed using preparative HPLC to obtain pure samples of the major components. Other fractions with low weights were purified via preparative TLC.

Vanicoside C (**4**) was isolated as a white, amorphous solid. The IR spectrum for **4** showed a large hydroxyl absorbance at ca. 3380 cm^{-1} and a broad carbonyl absorbance at ca. 1708 cm^{-1}. The presence of aromatic rings was represented by the absorbances at ca. 1603 and 1514 cm^{-1}. The negative ion FABMS of **4** indicated a molecular weight of 822. The molecular weight along with the fragment ions at *m*/*z* 779 ($[M - 1-42]^-$) and *m*/*z* 761 ($[M - 1-60]^-$), assignable to the loss of an acetate, suggested that the structure of vanicoside C (**4**) differed from hydropiperoside (**3**) by an additional acetate group. The presence of the acetate group was confirmed by ^{1}H NMR data, which indicated an acetate singlet at ca. 2 ppm.

Comparisons of the ^{1}H NMR data of vanicoside C (**4**) to those of **1**−**3** (Table 1) showed the typical resonances for the sucrose backbone as well as the characteristic resonances for *p*-coumaryl moieties, but no resonances that could be attributed to a feruloyl moiety. The region of the spectrum from δ 6.3 to 7.9 integrated for a total of 18 protons, indicating the presence of three *p*-coumaryl moieties, again suggesting that the structure of **4** was similar to the structure of **3**. The fragment ion at *m*/*z* 617 (assignable to the furanose ring fragment)[12] in the mass spectrum of **4** indicated that the three *p*-coumaryl esters were located on the furanose ring of the sucrose structure. From the chemical shifts (Table 1) of the protons on the furanose ring, the three esters must be located at C-1, C-3, and C-6 of the furanose ring, as in **3**.

Comparison of the ^{1}H NMR spectra of **3** and **4** revealed two principle differences. The resonance for the 1′-proton (δ 5.50) was upfield of the 3-proton (δ 5.54)

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Table 1: ^{1}H NMR (*J* in Hz) Chemical Shifts (δ in ppm) for **1**−**10** in Me_2CO-d_6

C	1	2	4	5	6	7	8[a]	9	10
1	4.25, 4.6 m	4.5, 4.7 m	4.30, 4.15 d (11.6)	5.15, 4.75 m					4.25 m
3	5.61 d (8.4)	5.69 d (8.5)	5.58 d (8.3)	5.65 d (8.3)	5.55 d (7.9)	5.65 d (8.6)	5.67 d (8.3)	5.6 d (8.3)	5.74 d(5.9)
4	4.65 m	4.8 m	4.52 m	4.8 m	4.6 m	4.75 m	5.54 m	5.45 m	5.57 m
5	4.3 m	4.25 m	4.22 m	4.4 m	4.25 m	4.25 m	4.35 m	5.0 dd	4.5 m
6	4.6 m	4.6 m	4.55 m	4.5 m		4.51 m		4.3 m	4.5 m
1′	5.66 d (3.6)	5.58 d (3.7)	5.6 d (3.6)	5.6 d (3.6)	5.69 d (3.6)	5.6 d (3.6)	5.78 d (3.6)	5.75 d (3.6)	5.83 d (3.3)
2′	4.69 m	3.51 dd (3.7,9.7)	4.6 m	3.55 m	4.75 dd (3.6,9.9)	3.45 m	4.95 dd	4.9 dd (3.6,9.9)	4.95 dd (3.4, 10.5)
3′	3.9 m	3.75 dd (9.7,9.4)	4.0 m	3.85 m	4.05 m	5.2 dd (9.7,10.1)	5.5 m	5.45 m	5.51 dd (10.5,9.7)
4′	3.51 dd (9.4,9.4)	3.40 dd (9.5,9.6)	3.45 dd (9.6,9.7)	3.45 m	4.91 dd (10.5, 10.4)	3.47 m	5.05 dd (9.6,9.7)	5.0 dd (9.6,9.9)	5.09 dd (9.7,9.7)
5′	4.3 m	4.35 m	4.02 m	4.35 m	4.42 m	4.4 m	4.4 m	4.4 m	4.5 m
6′	4.2, 4.35 m	4.2−4.4 m	3.75, 3.92 m	4.15, 4.3 m				4.2 m	4.54 m
2″	7.33 d (1.8)	7.37 d (1.8)			7.34 d (1.4)	7.35 d (1.9)			7.4 d (1.5)
5″	6.81	6.84 d (8.1)			6.8 d (8.1)	6.87 d (8.3)			7.05 d (8.1)
6″	7.11 dd (1.8,8.2)	7.13 dd (1.8,8.2)			7.1 dd (1.4,8.1)	7.1 dd (1.9,8.3)			7.21 dd (1.5,8.1)
7″,7‴	7.58, 7.62, 7.64, 7.72 ea d (16)	7.62, 7.65, 7.69, 7.75 ea d (16)	7.72, 7.65, 7.6 ea d (16)	7.7, 7.68, 7.65, 7.6 ea d (16)	7.75, 7.70, 7.65, 7.6 ea d (16)	7.7, 7.61, 7.55, 7.63 ea d (16)	7.72, 7.71, 7.77 ea d (16)	7.7, 7.65, 7.57, 7.5 ea d (16)	7.6−7.8 m
8″,8‴	6.33, 6.4, 6.45, 6.53 ea d (16)	6.38, 6.42, 6.43, 6.58 ea d (16)	6.47, 6.4, 6.41 ea d (16)	6.45,6.4, 6.39, 6.35 ea d (16)	6.6, 6.51, 6.45, 6.4 ea d (16)	6.6, 6.59, 6.55, 6.45 ea d (16)	6.44, 6.45, 6.47 ea d (16)	6.45, 6.4, 6.37, 6.35 ea d (16)	6.51, 6.55, 6.61, 6.64 ea d (16)
2‴,6‴	7.45−7.65 m	7.49−7.60 m	7.5−7.6 m	7.5−7.6 m	7.60−7.45 m	7.54−7.47 m	7.55−7.6 m	7.0−7.13 m	7.6−7.7 m
3‴,5‴	6.85−6.89 m	6.86−6.91 m	6.8−6.91 m	6.75−6.9	6.72−6.9 m	6.8−6.95 m	7.09−7.12 m	7.50−7.4	7.1−7.2 m
OCH_3	3.85 s (3H)	3.88 s (3H)			3.88 s (3H)	3.8 s (3H)		3.85 s	3.83 s
$COCH_3$	2.06 s (3H)		2.06 s (3H)		2.06 s (6H)	2.06 s (3H)	1.85, 1.97, 2.06 (2), 2.12, 2.31	1.81, 1.9, 1.95, 2.06(2), 2.3(3)	1.79, 1.9, 2.02, 2.04, 2.21, 2.22, 2.23 (2)

[a] In $CDCl_3$.

in the spectrum of **3**, while the resonance for the 1′-proton (δ 5.6) was downfield of the 3-proton (δ 5.58) in the spectrum of **4**. The resonance for the 2′-proton was also shifted downfield to δ 4.6 in the spectrum of **4** from δ 3.44 in the spectrum of **3**. These differences were similar to differences found in the spectra of **1** and **2**. Therefore, **4** must bear the acetate moiety at C-2′ of the pyranose ring, and vanicoside C (**4**) must be 2′-*O*-acetylhydropiperoside.

Acetylation of **4** with acetic anhydride−pyridine gave the octaacetate **8**. ^{1}H NMR and COSY data for **8** showed significant shifts (Table 1) for the protons on C-3′, C-4′, C-6′, and C-4, which can be attributed to the introduction of acetate groups at these positions. TLC and ^{1}H NMR comparisons of **8** with the octaacetate derived from hydropiperoside (**3**) showed the two octaacetates to be identical, confirming the structure of **4**.

Vanicoside D (**5**) was isolated as a white, amorphous solid. The IR spectrum for **5** showed a large hydroxyl absorbance at ca. 3419 cm^{-1} and a broad carbonyl absorbance at ca. 1686 cm^{-1}. The presence of aromatic rings was represented by absorbances at ca. 1604 and 1515 cm^{-1}. A molecular weight of 926 amu for **5** was indicated by MS data. This weight implied that **5** differed from **3** by an additional *p*-coumaryl ester. The region between δ 6.4 and 7.6 in the ^{1}H NMR spectrum integrated for a total of 24 protons, confirming the presence of the fourth *p*-coumaryl ester. Comparison of the ^{1}H NMR spectra of **5** with those of **1**−**3** indicated that there was no feruloyl ester present in the structure of **5**.

Fragment ions at *m*/*z* 617 and *m*/*z* 453 in the MS for **5** indicated that three of the *p*-coumaryl esters were located on the furanose ring of the sucrose structure. The resonances in the COSY spectrum for **5** (Table 1) indicated that the three esters were in the C-1, C-3, and C-6 positions on the furanose ring, and the fourth ester was in the C-6′ position on the pyranose ring. Thus, the structure of vanicoside D (**5**) must be 6′-*O*-*p*-coumarylhydropiperoside.

Acetylation of **5** gave the peracetate **9**. The ^{1}H NMR and COSY data for **9** showed significant shifts (Table 1) for protons on C-4, C-2′, C-3′, and C-4′, which can be attributed to the replacement of hydroxyl groups with acetate groups. However, significant shifts were not observed for protons on C-3, C-6, C-1, and C-6′. This additional evidence confirmed that the four *p*-coumaryl esters must be in the C-1, C-3, C-6, and C-6′ positions, and the structure of **5** must be 6′-*O*-*p*-coumarylhydropiperoside.

Vanicoside E (**6**) was isolated as a white, amorphous solid. The IR spectrum for **6** showed a large hydroxyl absorbance at ca. 3399 cm^{-1} and a broad carbonyl absorbance at ca. 1694 cm^{-1}. The presence of aromatic rings was represented by absorbances at ca. 1604 and 1515 cm^{-1}. The molecular weight of **6** was determined to be 1040 amu from negative ion FABMS data. The molecular weight suggested that **6** differed from **1** by an additional acetate group. Typical resonances for the sucrose backbone, three *p*-coumaryl moieties, and the feruloyl protons were present in the ^{1}H NMR spectrum for vanicoside E (**6**) (Table 1). The downfield chemical shifts for the 1′ and 2′-protons, attributed to the pres-

ence of an ester in the C-2′ position of **1**, were observed in the ^{1}H NMR spectrum of **6** (Table 1). A downfield chemical shift for the 4′-proton (Table 1) was also observed in the spectrum of **6**. These data suggested that the structure of **6** differed from **1** by an ester in the C-4′ position.

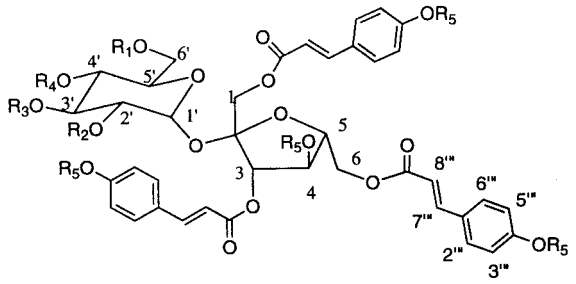
Acetylation of **6** with acetic anhydride−pyridine gave the octaacetate **10**. ^{1}H NMR and COSY data for **10** showed significant chemical shifts (Table 1) for the protons on C-3′ and C-4, which can be attributed to the introduction of acetate groups at these positions. TLC and ^{1}H NMR comparisons of **10** with the octaacetate derived from **1**[1] showed the two octaacetates to be identical. Thus, the structure of **6** must be 4′-*O*-acetylvanicoside A.

Vanicoside F (**7**) was isolated as a pale yellow oil in quantities too small to attempt crystallization. The IR spectrum for **7** showed a large hydroxyl absorbance at ca. 3408 cm^{-1} and a broad carbonyl absorbance at ca. 1699 cm^{-1}. The presence of aromatic rings was represented by absorbances at ca. 1604 and 1515 cm^{-1}. A molecular weight of 997 amu for **7** was indicated by MS data. The molecular weight, ^{1}H NMR, and COSY data suggested that **7** differed from **2** by an additional acetate group, implying at first that **7** was identical to vanicoside A (**1**). However, TLC and ^{1}H NMR comparisons indicated that **7** differed from **1**.

Characteristic resonances for the sucrose backbone, three *p*-coumaryl moieties, and the feruloyl protons were present in the ^{1}H NMR spectrum of **7**. Resonances for the 1′- and 2′-protons in the spectrum of **7** were shifted upfield similar to those observed in the spectrum of **2**. A downfield chemical shift for the 3′-proton (Table 1) was also observed in the spectrum of **7**. Fragment ions at *m*/*z* 617 and *m*/*z* 453 in the MS for **7** indicated that the three *p*-coumaryl esters were located on the furanose ring of the sucrose structure. The resonances in the COSY spectrum indicated that the three esters were in the C-1, C-3, and C-6 positions on the furanose ring. The feruloyl ester was assigned to the C-6′ position based upon comparisons made from the ^{1}H NMR and COSY spectra among **7**, **1**, and **2**. These data suggested that the structure of **7** differed from **2** by an ester in the C-3′ position.

Vanicoside F (**7**) was acetylated with acetic anhydride−pyridine, and the resulting peracetate was compared to the peracetate of vanicoside B by TLC. Because the R_f values were identical in several solvent systems, the vanicoside F peracetate was identical to the vanicoside B peracetate (**10**). Thus, the structure of **7** must be 3′-*O*-acetyllvanicoside B.

The new isolation scheme has proven to be an efficient procedure for the isolation of vanicoside derivatives. The use of the continuous liquid−liquid extractor helped to minimize the amount of solvent necessary to extract the components present in very small quantities. The constant neutral loss mass spectrometry experiment, along with UV absorption data, helped to identify the vanicoside derivatives such that the isolation of components that were not homologues of the vanicosides could be avoided. The four components that have been isolated using the improved scheme, vanicosides C−F, will be added to the growing library of vanicoside derivatives. Upon the isolation and synthesis of additional homologues, each compound will be assayed forPKC inhibition activity.



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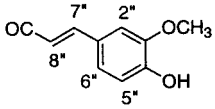
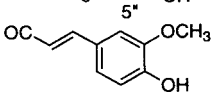
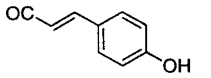
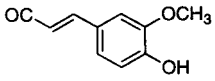
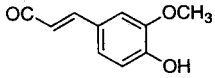
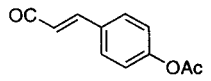
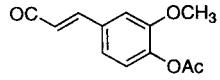
1		$COCH_3$	H	H	H
2		H	H	H	H
3	H	H	H	H	H
4	H	$COCH_3$	H	H	H
5		H	H	H	H
6		$COCH_3$	H	$COCH_3$	H
7		H	$COCH_3$	H	H
8	$COCH_3$	$COCH_3$	$COCH_3$	$COCH_3$	$COCH_3$
9		$COCH_3$	$COCH_3$	$COCH_3$	$COCH_3$
10		$COCH_3$	$COCH_3$	$COCH_3$	$COCH_3$

Experimental Section

General Experimental Procedures. Preparative HPLC analysis was achieved using a Waters Prep LC 3000, Waters 600E controller, Whatman Partisil 10 column, Waters model 440 absorbance detector with a prep cell at 254 nm, and a Waters fraction collector. Analytical HPLC analysis was achieved with a Hewlett−Packard HP 1090 mainframe, DR5 ternary pumping system, HP 1040 diode array detector, and Whatman Partisil 5 column. Negative ion LRMS were acquired using a JEOL SX-102/102 four-sector tandem mass spectrometer at Philip Morris USA Research Laboratories in Richmond, VA. Positive and negative ion HRMS were acquired using an IonSpec 4.7T Fourier transform ion cyclotron resonance mass spectrometer equipped with an electrospray injector at 0.2 μL/min. Samples were dissolved in 50:50 MeOH−H_2O. All ^{1}H and COSY NMR spectra were acquired with a General Electric QE−300 using either Me_2CO-d_6 or $CDCl_3$ as the solvent. IR data was obtained from a Perkin−Elmer 1600 series FTIR. Melting point values were obtained on an Electrothermal Digital melting point apparatus.

Plant Material. Stems, leaves, and roots of *P. pensylvanicum* (PR-17541) were collected in Florida in October 1968, and were supplied by the Medicinal Plant Resources Laboratory, USDA, Beltsville, Maryland, where voucher specimens are preserved.

Isolation of Vanicosides C−F. Dried roots, stems, and leaves (1.6 kg) of *Polygonum pensylvanicum* were subjected to a Soxhlet extraction with 95% EtOH for 24 h. The EtOH extract was concentrated in vacuo to a dark gum (131.7 g). The dark gum was partitioned between H_2O and EtOAc using a continuous liquid−liquid extractor for a total of 72 h. The H_2O solubles were saved for future inspection, and the EtOAc solubles were concentrated in vacuo to 35.4 g of a dark red residue. Samples of the dark gum (1.5 g each) were dissolved in 5 mL of EtOAc prior to isolation. Near baseline separation of the EtOAc extract was achieved via preparative HPLC using a Partisil 10 HPLC column and 4.5−5 mL sample injections. The mobile phase was 5% MeOH in CH_2Cl_2, and the flow rate was increased at planned intervals from 5 mL/min to 25 mL/min. Samples were collected at one-minute intervals and recombined to give fractions enriched in individual peaks. In cases where large weights were recovered, the fractions were rechromatographed using preparative HPLC to obtain pure samples of the major components. Other fractions of lesser weights were purified via preparative TLC.

Vanicoside C (4). Vanicoside C (**4**) was isolated from a preparative HPLC band, which eluted after 103 min on the HPLC chromatogram. The band was subjected to preparative TLC on Si gel using MeOH−H_2O−EtOAc (15:4:81). The least polar of the four components detected from TLC was extracted with 15% MeOH in CH_2Cl_2 to give 6.8 mg of **4** as an amorphous white solid: mp 65.3 °C; IR (KBr) ν_{max} 3380 (br), 1708 (br), 1603, 1514, 1167; ^{1}H NMR, Table 1; HRMS, *m/z* 845.2304 ($C_{41}H_{42}O_{18}$ + Na req. 845.2256); negative ion FABMS, *m/z* 821 (M − H)$^-$, 779 (M − H − 42)$^-$, 761 [M − H − 60]$^-$, 675 [M − H − 146 (*p*-coumaryl ketene)]$^-$, 617 [M − H − pyranose moiety]$^-$, 453 [M − H − pyranose moiety − 164 (*p*-coumaric acid)]$^-$,163 [*p*-coumaric acid − H]$^-$, 145 [*p*-coumaryl ketene − H]$^-$.

Vanicoside D (5). Vanicoside D (**5**) was isolated from a preparative HPLC band that eluted after 85 min on the HPLC chromatogram. The band was subjected to preparative TLC on Si gel using MeOH−H_2O−EtOAc (15:4:81) as the eluting solvent. The least polar of the four components detected from TLC was extracted with 30% MeOH in EtOAc to give 36 mg of **5** as an amorphous white solid: mp 147.6−154.2 °C; IR (KBr)ν_{max}: 3419 (br), 2345, 1686, 1630, 1604, 1515, 1438, 1262, 1169; ^{1}H NMR, Table 1; negative ion HRMS, *m/z* 925.2895 ($C_{48}H_{46}O_{19}$ − H req. 925.2541); negative ion FABMS, *m/z* 925 [M − H]$^-$, 779 [M − H − 146 (*p*-coumaryl ketene)]$^-$, 617 [M − H − pyranose moiety]$^-$, 453 [M − H − pyranose moiety − 164 (*p*-coumaric acid)]$^-$,163 [*p*-coumaric acid − H]$^-$, 145 [*p*-coumaryl ketene − H]$^-$.

Vanicoside E (6). Vanicoside E (**6**) was isolated from a preparative HPLC band that eluted after 25 min on the HPLC chromatogram. This band was subjected to preparative TLC on Si gel using MeOH−CH_2Cl_2−EtOAc (15:42.5:42.5) as the eluting solvent. The least polar of the four components detected from TLC was extracted with 20% MeOH in EtOAc to give 8 mg of **6** as an amorphous white solid: mp 143.1−147.4 °C; IR (KBr)ν_{max}: 3399 (br), 2921, 1694, 1633, 1603, 1514, 1445, 1371, 1250, 1159, 1034; ^{1}H NMR, Table 1; HRMS, *m/z* 1063.3037 ($C_{53}H_{52}O_{22}$ + Na req. 1063.2832); negative ion FABMS, *m/z* 1039 [M − H]$^-$, 997 [M − H − 42]$^-$, 893 [M − H − 146 (*p*-coumaryl ketene)]$^-$, 863 [M − H − 176 (feruloyl ketene)]$^-$, 453 [M − H − pyranose moiety − 164 (*p*-coumaric acid)]$^-$, 193 [ferulic acid − H]$^-$, 175 [feruloyl ketene − H]$^-$,163 [*p*-coumaric acid − H]$^-$, 145 [*p*-coumaryl ketene − H]$^-$.

Vanicoside F (7). Vanicoside F (**7**) was isolated from a preparative HPLC band that eluted after 31 min on the HPLC chromatogram. The band was subjected to preparative TLC on Si gel using MeOH−CH_2Cl_2−EtOAc (15:42.5:42.5) as the eluting solvent. The least polar of the two bands appeared to contain two components. The band was purified further via preparative TLC on Silica gel using MeOH−CH_2Cl_2−EtOAc (5:47.5:47.5) as the eluting solvent. The more polar of the two components was then extracted with 20% MeOH in EtOAc to give 3.1 mg of **7** as a pale yellow oil: IR (KBr)ν_{max}: 3408 (br), 1699, 1633, 1604, 1515, 1445, 1259, 1162; ^{1}H NMR, Table 1; negative ion HRMS, *m/z* 997.2753 ($C_{51}H_{50}O_{21}$ − H req. 997.2751); negative ion FABMS, *m/z* 997 [M − H]$^-$, 937 [M − H − 60]$^-$, 955 [M − H − 42)]$^-$, 851 [M − H − 146 (*p*-coumaryl ketene)]$^-$, 803 [M − H − 194 (ferulic acid)]$^-$, 617 [M − H − pyranose moiety]$^-$, 453 [M − H − pyranose moiety − 164 (*p*-coumaric acid)]$^-$, 193 [ferulic acid − H]$^-$, 175 [feruloyl ketene − H]$^-$, 163 [*p*-coumaric acid − H]$^-$, 145 [*p*-coumaryl ketene − H]$^-$.

Acetylation of Vanicosides. The appropriate vanicoside was suspended in 1 mL of pyridine−Ac_2O(1:1) and stirred at room temperature for 24 h. The solution was poured into iced H_2O (5 mL) and extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were washed with 1N HCL (3 × 10 mL), saturated NaCl (10 mL), dried over anhydrous Na_2SO_4, and evaporated in vacuo to a white foam.

Vanicoside C: 2 mg of **4** was acetylated yielding 2.3 mg of **8**, ^{1}H NMR, Table 1.

Vanicoside D: 9 mg of **5** was acetylated yielding 5.4 mg of **9**, ^{1}H NMR, Table 1; HRMS, *m/z* 1285.4052 ($C_{64}H_{62}O_{27}$ + Na req. 1285.3357).

Vanicoside E: 3 mg of **6** was acetylated yielding 2.5 mg of **10**; ^{1}H NMR, Table 1.

Vanicoside F: 0.8 mg of **7** was acetylated yielding 0.2 mg of **10**.

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