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HYDROXYCINNAMIC ACID ESTERS OF PHENETHYLALCOHOL GLYCOSIDES FROM *REHMANNIA GLUTINOSA* VAR. *PURPUREA**

HIROSHI SASAKI, HIROAKI NISHIMURA, MASAO CHIN (CHEN ZHENGXIONG) and HIROSHI MITSUHASHI

Tsumura Laboratory, 3586 Yoshiwara, Ami-machi, Inashiki-gun, Ibaraki 300-11, Japan

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Key Word Index—*Rehmannia glutinosa* var. *purpurea*; Scrophulariaceae; phenethylalcohol glycosides; jionosides.

Abstract—Five new hydroxycinnamic acid esters of phenethylalcohol glycosides named jionosides C, D, E, A_2 and B_2, together with nine known compounds, have been isolated from roots of *Rehmannia glutinosa* var. *purpurea* and their structures elucidated on the basis of chemical and spectral evidences.

INTRODUCTION

In a previous paper, we reported the isolation of immunosuppressive phenolic glycosides from the steamed Chinese Rehmanniae radix [*Rehmannia glutinosa* Libosch. var. *hueichingensis* (Chao et Schih) Hsiao] [1]. In continuing studies on biological active components of Rehmanniae radix, 14 phenolic glycosides were isolated from the dried Japanese crude drug (*R. glutinosa* Libosch. var. *purpurea* Makino). This paper describes the structural elucidation of five new phenethyl alcohol glycosides isolated from the methanolic extract of this plant.

RESULTS AND DISCUSSION

The phenolic fraction of the methanolic extract was separated by using a combination of Sephadex LH-20, MCI gel CHP20P and μBondapak C_{18} column chromatography to afford 14 compounds, **1**–**14**. Among them, **1**, **2**, **8**, **10** and **12** were novel compounds named jionosides C, D, E, A_2 and B_2, respectively. Compounds **3**, **4**, **6**, **7**, **9**, **11**, **13** and **14** were identified as acteoside, 2'-acetylacteoside, martynoside, isoacteoside, jionoside A_1, jionoside B_1, purpureaside C and cistanoside F, respectively, by direct comparison with authentic samples [1–3]. Compound **5** was identical with leucosceptoside A by comparing the physico-chemical and spectral data with those described in the literature [4].

Jionoside C(**1**) was isolated as an off-white amorphous powder, $C_{29}H_{36}O_{13}\cdot 2H_2O$, FABMS m/z: 593[M + H]$^+$, $[\alpha]_D - 86.9°$ (MeOH), and gave a green coloration on spraying with ferric chloride reagent. Compound **1** was presumed to be a phenethylalcohol diglycoside (glucose and rhamnose) with a C_6–C_3 acid ester group from similarity of the ^{1}H and ^{13}C NMR spectra of **1** to those of acteoside (**3**). The majority of the phenethylalcohol glycosides obtained here usually bear four phenolic *O*-functional groups in both the aglycone and the acid moiety. The heptaacetate of **1**, however, revealed only two phenolic acetyl signals at δ2.30 and 2.31 (each 3H, *s*) in its ^{1}H NMR spectrum. The ^{1}H NMR spectrum of **1** exhibited a five-proton signal due to monosubstituted benzene protons at δ7.25 (*m*) and an ABX pattern [δ6.79 (*d*, $J = 8.3$ Hz), 6.95 (*dd*, $J = 8.3$, 1.7 Hz) and 7.07 (*d*, $J = 1.7$ Hz)], easily ascribable to protons of 1,3,4-trisubstituted benzene, indicating that both phenolic OH groups are present in either aglycone or acid moiety. The ^{13}C NMR spectrum of **1** showed that the signals attributable to glucose, rhamnose and acid moieties were superimposable with those of **3** except for the signals due to the aglycone moiety (Table 1). This indicates that the sugar linkage and the position of the acyl group of **1** are similar to those of **3**, and that two OH groups must be present in the acid moiety, namely the acid of **1** is caffeic acid. In fact, methanolysis of **1** with 2% sodium methoxide afforded caffeic acid methyl ester. Thus, jionoside C(**1**) was elucidated as 2-phenylethyl *O*-α-L-rhamnopyranosyl-(1 → 3)-4-*O*-caffeoyl-β-D-glucopyranoside.

Jionoside D(**2**) was obtained as an off-white amorphous powder, $C_{30}H_{38}O_{15}\cdot H_2O$, $[\alpha]_D - 95.7°$ (MeOH), FDMS m/z: 639[M + H]$^+$. In the ^{1}H and ^{13}C NMR spectra, **2** also revealed itself to be a phenethylalcohol diglycoside[rhamnose(1 → 3)glucose], having an OMe group [^{1}H: δ3.81 (*s*), ^{13}C: δ56.6 (*q*)] and three phenolic OH groups in both aglycone and acid moieties. Conveniently there are two similar compounds having OMe groups, leucosceptoside A(**5**) and martynoside (**6**). Both **5** and **6** have an OMe group in their acid moiety and the latter has another OMe group in its aglycone. When the chemical shifts of the aromatic carbons of **2** were compared with those of **5** and **6**, the ^{13}C shifts for the aglycone moiety of **2** were in good agreement with those for the aglycone moiety in **6**, i.e. 3-hydroxy-4-methoxyphenethylalcohol. Actually, on methanolysis with 5% acetylchloride in methanol, **2** gave 3-hydroxy-4-methoxyphenethylalcohol and caffeic acid methyl ester. The structure of jionoside D was thus formulated as **2**.

Jionoside E(**8**) was obtained as an amorphous powder, $[\alpha]_D - 68.6°$ (MeOH), FABMS m/z: 771 [M + H]$^+$, and was believed to have one more hexose than jionosides C(**1**) and D(**2**) because of the formation of the undecaacetate upon ordinary acetylation. The ^{1}H and ^{13}C NMR spectra of **8** showed that the signals due to the sugars and the aglycone moieties closely resembled those of purpureaside C(**13**) except for the signals attributable to an acid

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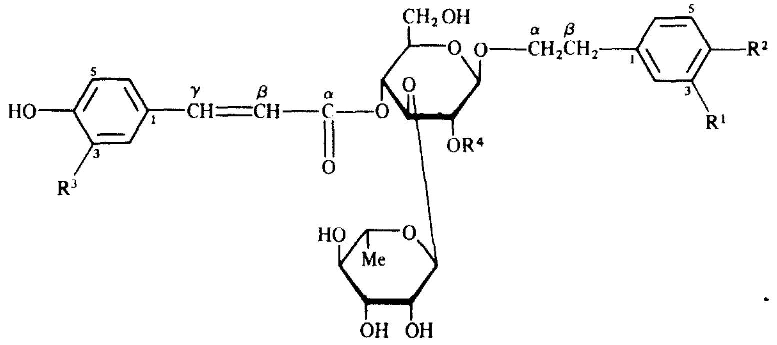
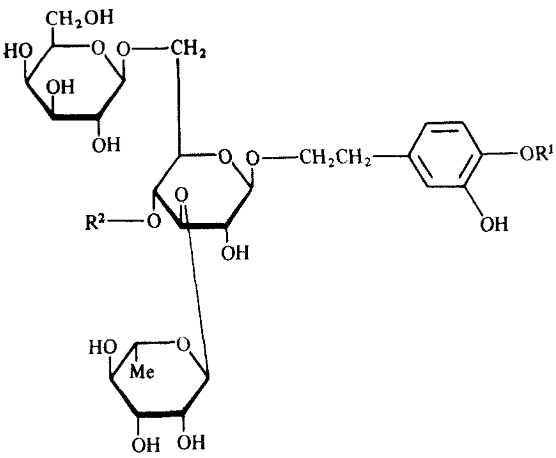
*Part 2 in the series 'Chemical and Biological Studies on Rehmanniae Radix' [1].



	R^1	R^2	R^3	R^4
1	H	H	OH	H
2	OH	OMe	OH	H
3	OH	OH	OH	H
4	OH	OH	OH	Ac
5	OH	OH	OMe	H
6	OH	OMe	OMe	H



	R^1	R^2
8	H	*p*-coumaroyl
9	H	*trans*-feruloyl
10	H	*cis*-feruloyl
11	Me	*trans*-feruloyl
12	Me	*cis*-feruloyl
13	H	caffeoyl

moiety, indicating that **8** was composed of 3,4-dihydroxyphenethylalcohol, glucose, rhamnose, galactose and a C_6–C_3 acid, and that the linkages among the sugars and the position of the acyl group were similar to those of **13**. With regard to the acid, it is easy to presume this acid to be *p*-coumaric acid from the observation of an A_2B_2 signal at δ6.81 and 7.47 (each 2H, *d*, $J = 8.7$ Hz) together with a pair of olefin proton signals at δ6.34 and 7.67 (each 1H, *d*, $J = 15.9$ Hz) in the ^{1}H NMR spectrum of **8** [5, 6]. In fact, on methanolysis of **8** with 5% acetylchloride in methanol, *p*-coumaric acid methyl ester and 3,4-dihydroxyphenethylalcohol were detected by TLC. Jionoside E(**8**) was ultimately established as 2-(3,4-dihydroxyphenyl)ethyl *O*-α-rhamnopyranosyl-(1 → 3)-[β-D-galactopyranosyl-(1→6)]-(4-*O*-*p*-coumaroyl)-β-D-glucopyranoside.

Previously reported jionosides A_1 (**9**) and B_1 (**11**) are triglycosides (glucose, rhamnose and galactose) of phenethylalcohol derivatives carrying a feruloyl group at C-4 of the glucose moiety [1]. Both **9** and **11** were found to be accompanied with jionosides A_2 (**10**) and B_2 (**12**), respectively, and were distinguishable from the latter on HPLC. The volume ratio of **9** (or **11**) to **10** (or **12**) was *ca* 9:1. These two pairs of compounds seemed to be isomers from the observation that they readily interchanged in the daylight. Thereafter, separation was done carefully in the dark by using several forms of chromatography as described in Experimental to give **10** and **12**.

The ^{1}H and ^{13}C NMR spectra of jionoside A_2 (**10**) bore a close resemblance to that of **9** except for the signals due to an acid moiety. On the other hand, the ^{1}H NMR spectrum of **10** showed that the olefin proton signals at δ5.81 and 6.94 (each 1H, *d*) shifted upfield and that their coupling constant ($J = 12.9$ Hz) was smaller than that of **9**(δ6.38 and 7.67; each 1H, *d*, $J = 15.9$ Hz). This indicates that the configuration of the olefin in the feruloyl moiety of **10** is in the *cis*-form. Likewise, examination of the ^{1}H NMR data of jionoside B_2 (**12**) (δ5.81 and 6.93; each 1H, *d*, $J = 13.0$ Hz) led us to conclude that **12** is a *cis*-isomer of **11**. These *cis*-isomers, however, might be artifacts formed from their *trans*-isomers during extraction and isolation.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were measured at 199.5 and 50.10 MHz, respectively, with TMS as the int. standard. TLC was conducted on precoated SiO_2 plates and was visualized by spraying $FeCl_3$ and dil. H_2SO_4 reagents. Plant material was purchased from Raw Medical Trading Co., Ltd.

Extraction and isolation. The dried roots of *R. glutinosa* var. *purpurea* were extracted with MeOH (100 l × 2) at room temp. The MeOH extract, after concn, was subjected to CC on Diaion

Table 1. ^{13}C NMR data for **1**, **2**, **3**, **5**, **6**, **8**–**13** (50.10 MHz, CD_3OD)

C	**1**	**2**	**3**	**5**	**6**	**8**	**9**	**10**	**11**	**12**	**13**
Aglycone											
1	139.9	132.9	131.5	131.5	132.9	131.6	131.6	131.6	133.0	132.9	131.6
2	130.0	113.0	116.6	116.3	113.0	116.4	116.6	116.4	112.9	112.9	116.6
3	129.3	147.5	144.7	144.6	147.5	144.6	144.6	144.6	147.5	147.4	144.6
4	127.2	147.3	146.1	146.0	147.4	146.0	146.1	146.0	147.3	147.2	146.1
5	129.3	117.1	117.2	117.1	117.1	117.2	117.2	117.2	117.1	117.1	117.2
6	130.0	121.2	121.3	121.2	121.1	121.3	121.4	121.4	121.3	121.2	121.4
α	71.8	72.1	72.4	72.2	72.1	72.3	72.4	72.3	72.2	72.1	72.3
β	37.2	36.5	36.6	36.5	36.5	36.5	36.6	36.5	36.5	36.4	36.5
Acid moiety											
1	127.6	127.7	127.6	127.6	127.7	127.1	127.7	128.0	127.7	127.9	127.7
2	114.7	114.8	114.6	111.8	111.9	116.9	111.9	115.7	112.1	115.7	114.7
3	149.7	149.7	149.8	150.7	150.8	131.3	150.8	148.2	150.8	148.2	149.8
4	146.7	146.8	146.8	149.3	149.4	161.4	149.4	149.7	149.4	149.7	146.8
5	116.5	116.6	116.4	116.5	116.5	131.3	116.4	115.5	116.6	115.5	116.4
6	123.2	123.2	123.4	123.4	124.3	116.9	124.4	127.4	124.4	127.4	123.3
α	168.3	168.3	168.3	168.2	168.2	168.4	168.4	166.9	168.4	166.9	168.4
β	115.3	115.3	115.3	115.1	115.1	115.9	115.1	115.6	115.1	115.6	115.3
γ	148.0	148.0	148.0	147.8	147.8	147.8	148.1	147.8	148.1	147.8	148.2
Glucose											
1	104.2	104.2	104.2	104.1	104.2	104.1	104.1	104.0	104.1	104.0	104.1
2	76.1	76.0	76.0	75.9	76.0	76.1	76.2	76.0	76.1	75.9	76.1
3	81.6	81.6	81.7	81.4	81.5	81.6	81.6	81.9	81.6	81.9	81.7
4	70.4^{a}	70.4^{a}	70.4^{a}	70.3^{a}	70.4^{a}	70.4^{a}	70.5^{a}	70.4^{a}	70.5^{a}	70.3^{a}	70.4^{a}
5	76.0	76.2	76.2	76.1	76.2	74.9	75.0	74.7	75.0	74.7	74.9
6	62.4	62.4	62.4	62.3	62.4	69.1	69.2	69.1	69.2	69.1	69.1
Rhamnose											
1	103.0	103.0	103.0	102.9	102.9	103.0	103.0	103.1	103.0	103.1	103.0
2	72.1^{b}	72.1^{b}	72.1^{b}	72.0^{b}	72.1^{b}	72.1^{b}	72.1^{b}	72.2^{b}	72.2^{b}	72.1^{b}	72.1^{b}
3	72.3^{b}	72.3^{b}	72.3^{b}	72.3^{b}	72.4^{b}	72.3^{b}	72.4^{b}	72.3^{b}	72.3^{b}	72.1^{b}	72.3^{b}
4	73.8	73.8	73.8	73.8	73.8	73.8	73.8	73.8	73.8	73.7	73.8
5	70.6^{a}	70.6^{a}	70.6^{a}	70.6^{a}	70.7^{a}	70.5^{a}	70.3^{a}	70.4^{a}	70.3^{a}	70.3^{a}	70.3^{a}
6	18.5	18.5	18.5	18.4	18.4	18.4	18.5	18.2	18.5	18.2	18.5
Galactose											
1						105.2	105.3	105.2	105.3	105.2	105.2
2						72.6	72.6	72.6	72.6	72.5	72.6
3						74.8	74.8	75.0	74.8	75.0	74.7
4						70.2^{a}	70.4^{a}	70.2^{a}	70.4^{a}	70.1^{a}	70.4^{a}
5						76.6	76.6	76.5	76.6	76.4	76.6
6						62.5	62.5	62.4	62.5	62.3	62.5
OMe		56.6		56.5	56.5, 56.6		56.5	56.7	56.6 (2C)	56.6 (2C)	

^{a,b}May be interchanged in each column.

HP-20(14 kg), eluting with H_2O (100 l) and then MeOH (25 l). The MeOH eluates were rechromatographed on Sephadex LH-20 by developing with increasing amounts of MeOH in H_2O(0:1→1:0) and were divided into 4 fractions, A(44.0 g), B(40.2 g), C(30.6 g) and D(1.8 g). Subsequent separation of fr. B on MCI gel CHP20P column with mixtures of H_2O and MeOH(9:1→2:3) as an eluent afforded 4 further fractions, B-1 (10.9 g), B-2 (10.1 g), B-3 (15.9 g) and B-4 (4.0 g).

Fr. B-2 was applied to a μBondapak C_{18} column, eluting with increasing amounts of MeOH in H_2O (0:1→1:0) and then Sephadex LH-20, developing with EtOH, and afforded **13**(8.6 g) and **14**(55 mg). Fr. B-3 was repeatedly subjected to CC in the dark on μBondapak C_{18}, eluting with mixtures of H_2O–MeOH (1:0→3:2), MCI gel CHP20P, developing with mixtures of H_2O–MeOH (1:0→1:1), and then Sephadex LH-20, eluting with EtOH, and furnished **8**(60 mg), **9**(6.1 g) and **10**(355 mg). Similarly in the absence of light, fr. B-4 was rechromatographed on μBondapak C_{18}, developing with mixtures of H_2O–MeOH (1:0→3:2), and then Sephadex LH-20, eluting with EtOH, and gave **11**(1.5 g) and **12**(153 mg).

Fr. C was subjected to a combination of CC on MCI gel CHP20P, developing with mixtures of H_2O–MeOH (9:1→1:4), μBondapak C_{18}, eluting with mixtures of H_2O–MeOH (4:1→9:11), and Sephadex LH-20, eluting with a mixture of H_2O–MeOH (1:1), and afforded **1**(113 mg), **2**(57 mg), **3**(20.8 g), **4**(186 mg), **5**(1.3 g) and **6**(1.2 g). Fr. D was also chromatographed on MCI gel CHP20P, eluting with increasing amounts of MeOH in H_2O (3:7→9:11), μBondapak C_{18}, eluting with mixtures of H_2O–MeOH (7:3→31:19), and then Sephadex LH-20, eluting with EtOH, and afforded **7**(385 mg).

Jionoside C(**1**). An off-white amorphous powder, $[\alpha]_D^{25}$ −86.9° (MeOH; *c* 0.72). IR ν_{max}^{KBr} cm^{-1}: 3408 (OH), 1694 (C=O), 1632 (C=C), 1604 (arom). ^{1}H NMR (CD_3OD): δ1.10 (3H, *d*, *J* = 6.1 Hz, rham H-6), 2.94 (2H, *t*, *J* = 7.3 Hz, H-β), 3.3–4.2 (11H, *m*), 4.39 (1H, *d*, *J* = 7.8 Hz, glc H-1), 4.92 (1H, *t*, *J* = 9.8 Hz, glc H-4), 5.20 (1H, *br s*, rham H-1), 6.28 and 7.60 (each 1H, *d*, *J* = 16.0 Hz, caff H-β, γ), 6.79 (1H, *d*, *J* = 8.3 Hz, caff H-5), 6.95 (1H, *dd*, *J* = 8.3, 1.7 Hz, caff H-6), 7.07 (1H, *d*, *J* = 1.7 Hz, caff H-2), 7.25 (5H, *m*, H-2, 3, 4, 5, 6). ^{13}C NMR: see Table 1. FABMS *m/z*: 593$[M+H]^+$, 615 $[M+Na]^+$, 631 $[M+K]^+$. (Found: C, 55.67; H, 6.13. $C_{29}H_{36}O_{13}\cdot 2H_2O$ requires: C, 55.41; H, 6.41%).

Acetylation of **1**. A soln of **1** (10 mg) in pyridine (0.5 ml) was treated with Ac_2O (0.5 ml) for 3 hr at room temp. Usual work-up of the reaction mixture afforded jionoside C heptaacetate (10 mg), a white amorphous powder. ^{1}H NMR ($CDCl_3$): δ1.64 (3H, *d*, *J* = 6.3 Hz, rham H-6), 1.88, 1.94, 1.99, 2.08, 2.10 (each 3H, *s*, OAc), 2.30, 2.31 (each 3H, *s*, phenolic OAc), 2.89 (2H, *t*, *J* = 6.7 Hz, H-β), 3.5–4.2 (7H, *m*), 4.42 (1H, *d*, *J* = 8.1 Hz, glc H-1), 4.84 (1H, *d*, *J* = 2.0 Hz, rham H-1), 4.9–5.3 (5H, *m*), 6.35, 7.65 (each 1H, *d*, *J* = 16.0 Hz, caff H-β, γ), 7.2–7.5 (8H, *m*, arom H). FABMS *m/z*: 887$[M+H]^+$.

Alkaline hydrolysis of **1**. A soln of **1** (40 mg) in 5% NaOMe (5 ml) was refluxed for 30 min. The reaction mixture was neutralized with Amberlite 120B (H^+ form) and was chromatographed on SiO_2. Elution with EtOAc–MeOH (10:1) yielded caffeic acid methyl ester (5 mg), which was identified with authentic material on co-TLC and HPLC.

Jionoside D (**2**). An off-white amorphous powder, $[\alpha]_D^{28}$ $-95.7°$ (MeOH; *c* 0.22). IR ν_{max}^{KBr} cm^{-1}: 3424 (OH), 1698 (C=O), 1632 (C=C), 1604 (arom). ^{1}H NMR (CD_3OD): δ1.10 (3H, *d*, *J* = 6.1 Hz, rham H-6), 2.82 (2H, *t*, *J* = 7.3 Hz, H-β), 3.3–4.2 (11H, *m*), 3.81 (3H, *s*, OMe), 4.38 (1H, *d*, *J* = 7.8 Hz, glc H-1), 4.92 (1H, *t*, *J* = 9.3 Hz, glc H-4), 5.20 (1H, *d*, *J* = 1.5 Hz, rham H-1), 6.28, 7.60 (each 1H, *d*, *J* = 15.9 Hz, caff H-β, γ), 6.68 (1H, *dd*, *J* = 8.1, 2.0 Hz, H-6), 6.74 (1H, *d*, *J* = 2.0 Hz, H-2), 6.78 (1H, *d*, *J* = 8.1 Hz, caff H-5), 6.81 (1H, *d*, *J* = 8.1 Hz, H-5), 6.95 (1H, *dd*, *J* = 8.1, 2.0 Hz, caff H-6), 7.06 (1H, *d*, *J* = 2.0 Hz, caff H-2). ^{13}C NMR: see Table 1. FABMS *m/z*: 639$[M+H]^+$, 661$[M+Na]^+$. (Found: C, 54.71; H, 6.09. $C_{30}H_{38}O_{15}\cdot H_2O$ requires: C, 54.87; H, 6.14%).

Acetylation of **2**. A soln of **2** (7 mg) in pyridine (0.5 ml) was treated with Ac_2O (0.5 ml) overnight at room temp. Usual work-up of the reaction mixture gave jionoside D octaacetate (7 mg), a white amorphous powder. ^{1}H NMR ($CDCl_3$): δ1.04 (3H, *d*, *J* = 6.4 Hz, rham H-6), 1.88, 1.94, 2.03, 2.08, 2.10 (each 3H, *s*, OAc), 2.30 (3H, *s*, phenolic OAc), 2.31 (6H, *s*, phenolic OAc), 2.82 (2H, *t*, *J* = 6.2 Hz, H-β), 3.6–4.2 (7H, *m*), 3.80 (3H, *s*, OMe), 4.40 (1H, *d*, *J* = 8.1 Hz, glc H-1), 4.84 (1H, *d*, *J* = 1.7 Hz, rham H-1), 4.9–5.3 (5H, *m*), 6.35, 7.65 (each 1H, *d*, *J* = 15.8 Hz, caff H-β, γ), 6.88 (1H, *d*, *J* = 2.2 Hz, H-2), 6.88 (1H, *d*, *J* = 8.3 Hz, H-5), 7.04 (1H, *dd*, *J* = 8.3, 2.2 Hz, H-6), 7.22 (1H, *d*, *J* = 8.3 Hz, caff H-5), 7.36 (1H, *d*, *J* = 2.2 Hz, caff H-2), 7.39 (1H, *dd*, *J* = 8.3, 2.2 Hz, caff H-6). FABMS *m/z*: 975$[M+H]^+$.

Methanolysis of **2**. A soln of **2** (1 mg) in 5% acetylchloride–MeOH (1 ml) was heated at 80° for 1 hr. The reaction mixture was evapd and subjected to TLC [$CHCl_3$–MeOH (19:1)]. 3-Hydroxy-4-methoxyphenethylalcohol and caffeic acid methyl ester were identified with authentic materials on co-TLC.

Leucosceptoside A (**5**). An off-white amorphous powder, $[\alpha]_D^{28}$ $-86.7°$ (MeOH; *c* 0.88). ^{1}H NMR (CD_3OD): δ1.11 (3H, *d*, *J* = 6.1 Hz, rham H-6), 2.79 (2H, *t*, *J* = 7.4 Hz, H-β), 3.2–4.1 (11H, *m*), 3.88 (3H, *s*, OMe), 4.37 (1H, *d*, *J* = 8.1 Hz, glc H-1), 4.93 (1H, *t*, *J* = 9.2 Hz, glc H-4),5.21 (1H, *d*, *J* = 1.6 Hz, rham H-1), 6.37, 7.66 (each 1H, *d*, *J* = 15.9 Hz, ferul H-β, γ), 6.56 (1H, *dd*, *J* = 8.1, 1.7 Hz, H-6), 6.69 (1H, *d*, *J* = 8.1 Hz, H-5), 6.71 (1H, *d*, *J* = 1.7 Hz, H-2), 6.82 (1H, *d*, *J* = 8.3 Hz, ferul H-5), 7.08 (1H, *dd*, *J* = 8.3, 1.7 Hz, ferul H-6), 7.18 (1H, *d*, *J* = 1.7 Hz, ferul H-2). ^{13}C NMR: see Table 1. FDMS *m/z*: 638 $[M]^+$. These data were identical with those described in the literature [4].

Jionoside E (**8**). An off-white amorphous powder, $[\alpha]_D^{28}$ $-64.6°$ (MeOH; *c* 0.11). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1704 (C=O), 1632 (C=C), 1606 (arom). ^{1}H NMR (CD_3OD): δ1.08 (3H, *d*, *J* = 6.1 Hz, rham H-6), 2.79 (2H, *t*, *J* = 7.5 Hz, H-β), 3.3–4.1 (17H, *m*), 4.26 (1H, *d*, *J* = 7.3 Hz, gal H-1), 4.38 (1H, *d*, *J* = 8.1 Hz, glc H-1), 5.01 (1H, *t*, *J* = 9.6 Hz, glc H-4), 5.19 (1H, *d*, *J* = 1.5 Hz, rham H-1), 6.34, 7.67 (each 1H, *d*, *J* = 15.9 Hz, *p*-coumar H-β, γ), 6.57 (1H, *dd*, *J* = 8.1, 1.7 Hz, H-6), 6.69 (1H, *d*, *J* = 8.1 Hz, H-5), 6.72 (1H, *d*, *J* = 1.7 Hz, H-2), 6.81 (2H, *d*, *J* = 8.7 Hz, *p*-coumar H-3, 5), 7.47 (2H, *d*, *J* = 8.7 Hz, *p*-coumar H-2, 6). ^{13}C NMR: see Table 1. FDMS *m/z*: 771 $[M+H]^+$, 793$[M+Na]^+$, 809$[M+K]^+$. (Found: C, 51.68; H, 6.14. $C_{35}H_{46}O_{19}\cdot 5/2H_2O$ requires: C, 51.53; H, 6.30%).

Acetylation of **8**. A soln of **8** (8 mg) in pyridine (0.5 ml) was treated with Ac_2O (0.5 ml) overnight at room temp. Usual work-up of the reaction mixture furnished jionoside E undecaacetate (9 mg), a white amorphous powder. ^{1}H NMR ($CDCl_3$): δ1.03 (3H, *d*, *J* = 6.1 Hz, rham H-6), 1.86, 1.90, 1.94, 1.97, 1.99, 2.01, 2.08, 2.09 (each 3H, *s*, OAc), 2.27, 2.29, 2.31 (each 3H, *s*, phenolic OAc), 2.87 (2H, *t*, *J* = 6.5 Hz, H-β), 3.5–4.2 (10H, *m*), 4.36 (1H, *d*, *J* = 8.1 Hz, glc H-1), 4.52 (1H, *d*, *J* = 7.8 Hz, gal H-1), 4.85 (1H, *d*, *J* = 1.7 Hz, rham H-1), 4.9–5.4 (8H, *m*), 6.35, 7.69 (each 1H, *d*, *J* = 16.0 Hz, *p*-coumar H-β, γ), 7.0–7.2 (3H, *m*, H-2, 5, 6), 7.14 (2H, *d*, *J* = 8.7 Hz, *p*-coumar H-3, 5), 7.54 (2H, *d*, *J* = 8.7 Hz, *p*-coumar H-2, 6). FABMS *m/z*: 1233$[M+H]^+$, 1255$[M+Na]^+$, 1271$[M+K]^+$.

Methanolysis of **8**. A soln of **8** (1 mg) in 5% acetylchloride–MeOH (0.5 ml) was heated at 80° for 3 hr. The reaction mixture was evapd and was subjected to TLC [$CHCl_3$–MeOH (19:1)]. 3,4-Dihydroxyphenethylalcohol and *p*-coumaric acid methyl ester were identified with authentic materials on co-TLC.

Jionoside A_1 (**9**). An off-white amorphous powder, $[\alpha]_D^{24}$ $-59.8°$ (MeOH; *c* 0.38). ^{1}H NMR (CD_3OD): δ1.09 (3H, *d*, *J* = 6.4 Hz, rham H-6), 2.79 (2H, *t*, *J* = 7.3 Hz, H-β), 3.2–4.1 (17H, *m*), 3.89 (3H, *s*, OMe), 4.26 (1H, *d*, *J* = 7.4 Hz, gal H-1), 4.38 (1H, *d*, *J* = 7.8 Hz, glc H-1), 5.00 (1H, *t*, *J* = 9.3 Hz, glc H-4), 5.19 (1H, *d*, *J* = 1.4 Hz, rham H-1), 6.38, 7.67 (each 1H, *d*, *J* = 15.9 Hz, *trans*-ferul H-β, γ), 6.57 (1H, *dd*, *J* = 8.1, 2.0 Hz, H-6), 6.69 (1H, *d*, *J* = 8.1 Hz, H-5), 6.72 (1H, *d*, *J* = 2.0 Hz, H-6), 6.81 (1H, *d*, *J* = 8.1 Hz, *trans*-ferul H-5), 7.09 (1H, *dd*, *J* = 8.1, 2.0 Hz, *trans*-ferul H-6), 7.19 (1H, *d*, *J* = 2.0 Hz, *trans*-ferul H-2). ^{13}C NMR: see Table 1. FDMS *m/z*: 800$[M]^+$ [1].

Jionoside A_2 (**10**). An off-white amorphous powder, $[\alpha]_D^{24}$ $-40.3°$ (MeOH; *c* 0.36). IR ν_{max}^{KBr} cm^{-1}: 3416 (OH), 1712 (C=O), 1628 (C=C), 1602 (arom). ^{1}H NMR (CD_3OD): δ1.15 (3H, *d*, *J* = 6.1 Hz, rham H-1), 2.78 (2H, *t*, *J* = 7.3 Hz, H-β), 3.2–4.1 (17H, *m*), 3.90 (3H, *s*, OMe), 4.24 (1H, *d*, *J* = 7.3 Hz, gal H-1), 4.36 (1H, *d*, *J* = 7.8 Hz, glc H-1), 4.92 (1H, *t*, *J* = 9.3 Hz, glc H-4), 5.16 (1H, *br s*, rham H-1), 5.81, 6.94 (each 1H, *d*, *J* = 12.9 Hz, *cis*-ferul H-β, γ), 6.57 (1H, *dd*, *J* = 8.1, 1.7 Hz, H-6), 6.69 (1H, *d*, *J* = 8.1 Hz, H-5), 6.72 (1H, *d*, *J* = 1.7 Hz, H-2), 6.78 (1H, *d*, *J* = 8.3 Hz, *cis*-ferul H-5), 7.17 (1H, *dd*, *J* = 8.3, 1.9 Hz, *cis*-ferul H-6), 7.87 (1H, *d*, *J* = 1.9 Hz, *cis*-ferul H-2). ^{13}C NMR: see Table 1. FDMS *m/z*: 823$[M+Na]^+$.

Jionoside B_1 (**11**). An off-white amorphous powder, $[\alpha]_D^{24}$ $-62.8°$ (MeOH; *c* 0.31). ^{1}H NMR (CD_3OD): δ1.10 (3H, *d*, *J* = 6.1 Hz, rham H-1), 2.82 (2H, *t*, *J* = 7.1 Hz, H-β), 3.2–4.1 (17H, *m*), 3.81, 3.88 (each 3H, *s*, OMe), 4.27 (1H, *d*, *J* = 8.1 Hz, gal H-1), 4.38 (1H, *d*, *J* = 7.6 Hz, glc H-1), 4.96 (1H, *t*, *J* = 9.8 Hz, glc H-4), 5.20 (1H, *d*, *J* = 1.4 Hz, rham H-1), 6.38, 7.67 (each 1H, *d*, *J* = 16.0 Hz, *trans*-ferul H-β, γ), 6.69 (1H, *dd*, *J* = 8.0, 2.0 Hz, H-6), 6.76 (1H, *d*, *J* = 2.0 Hz, H-2), 6.78 (1H, *d*, *J* = 8.0 Hz, H-5), 6.82 (1H, *d*, *J* = 8.0 Hz, *trans*-ferul H-5), 7.08 (1H, *dd*, *J* = 8.0, 1.8 Hz, *trans*-ferul H-6), 7.67 (1H, *d*, *J* = 1.8 Hz, *trans*-ferul H-2). ^{13}C NMR: see Table 1. FDMS *m/z*: 814$[M]^+$ [1].

Jionoside B_2 (**12**). An off-white amorphous powder, $[\alpha]_D^{24}$ $-42.5°$ (MeOH; *c* 0.34). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1714 (C=O), 1626 (C=C), 1594 (arom). ^{1}H NMR (CD_3OD): δ1.16 (3H, *d*, *J*

$=6.1$ Hz, rham H-1), 2.81 (2H, *t*, $J=7.3$ Hz, H-β), 3.3–4.1 (17H, *m*), 3.79, 3.89 (each 3H, *s*, OMe), 4.25 (1H, *d*, $J=7.6$ Hz, gal H-1), 4.36 (1H, *d*, $J=7.8$ Hz, glc H-1), 4.93 (1H, *t*, $J=9.4$ Hz, glc H-4), 5.17 (1H, *d*, $J=1.2$ Hz, rham H-1), 5.81, 6.93 (each 1H, *d*, $J=13.0$ Hz, *cis*-ferul H-β, γ), 6.69 (1H, *dd*, $J=8.1$, 2.0 Hz, H-6), 6.77 (1H, *d*, $J=2.0$ Hz, H-2), 6.79 (1H, *d*, $J=8.1$ Hz, H-5), 6.81 (1H, *d*, $J=8.3$ Hz, *cis*-ferul H-5), 7.18 (1H, *dd*, $J=8.3$, 1.7 Hz, *cis*-ferul H-6), 7.86 (1H, *d*, $J=1.7$ Hz, *cis*-ferul H-2). ^{13}C NMR: see Table 1. FDMS *m/z*: 814[M]$^+$.

HPLC of **9**–**12**. Column: TSK gel LS-410K ODS SIL 30 cm × 4 mm i.d. Column temp.: room temp. Mobile phase: 18% CH_3CN in 50 mM NaH_2PO_4. Flow rate: 0.7 ml/min. Detection: UV 280 nm. R_t (compds, min): **9**, 12.8; **10**, 14.3; **11**, 17.2; **12**, 18.8.

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