Pergamon

PII: S0031-9422(97)00409-3

Phytochemistry, Vol. 47, No. 2, pp. 259–263, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

n-ALKYL GLYCOSIDES AND *p*-HYDROXYBENZOYLOXY GLUCOSE FROM FRUITS OF *CRESCENTIA CUJETE*

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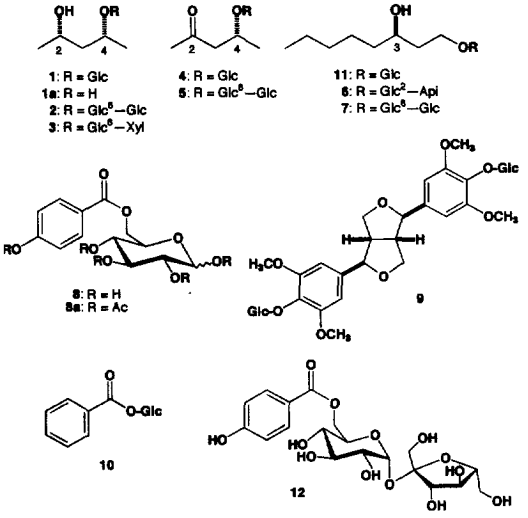
(*Received in revised form* 10 *March* 1997)

Key Word Index—*Crescentia cujete*; Bignoniaceae; fruits; (2*R*,4*S*)-2,4-pentanediol glycosides; (*R*)-4-hydroxy-2-pentanone glycosides; (*R*)-1,3-octanediol glycosides; 6-*O*-(*p*-hydroxybenzoyl)-D-glucose.

Abstract—The fruits of *Crescentia cujete* afforded eight new compounds, along with four known compounds, acanthoside D, β-D-glucopyransoyl benzoate, (*R*)-1-*O*-β-D-glucopyranosyl-1,3-octanediol, and β-D-fructofuranosyl 6-*O*-(*p*-hydroxybenzoyl)-α-D-glucopyranoside. The structures of the new glycosides were established as three glycosides of (2*R*,4*S*)-2,4-pentanediol, two glycosides of (*R*)-4-hydroxy-2-pentanone, two glycosides of (*R*)-1,3-octanediol and 6-*O*-(*p*-hydroybenzoyl)-D-glucose, by spectroscopic and chemical methods.

INTRODUCTION

Crescentia cujete L. is a small tree (3–5 m high) having spherical or oval fruits. It is distributed in South Asian countries. In Vietnam, the dried fruit is used in folk medicine, local name 'Dao Tien', as an expectorant, antitussive, laxative and a stomachia. Naphthoquinones [1] and iridoid glucosides [2] have been isolated from the leaves of this plant, although no chemical studies on the fruits have been performed. As part of our studies on the constituents of Bignoniaceous plants [3–6], we have undertaken the chemical investigation of the fruits of this plant. This has led to the isolation of eight new compounds (**1–8**) together with four known ones. This paper deals with the isolation, identification and structural elucidation of these compounds.



RESULTS AND DISCUSSION

The methanolic extract of *C. cujete* was worked up as described in the Experimental section to afford 12 compounds (**1–12**). Compounds **9–12** were identified as acanthoside D (**9**) [7–11], β-D-glucopyranosyl benzoate (**10**) [12], (*R*)-1-*O*-β-D-glucopyranosyl-1,3-octanediol (**11**) [13] and β-D-fructofuranosyl 6-*O*-(*p*-hydroxybenzoyl)-α-D-glucopyranoside (**12**) [14] by comparison of their physical and spectral data with those of the published data. Compound **12** has previously been obtained as a partially hydrolysed product on alkaline hydrolysis of tenuifoliside A [14], but has not been found in nature.

Compound **1** was assigned the molecular formula $C_{11}H_{22}O_7$ by NMR and high-resolution FAB-mass spectrometry. Inspection of the ^1H and ^{13}C NMR spectra allowed us to propose that compound **1** was a β-glucopyranoside of 2,4-pentanediol. On acid hydrolysis compound **1** gave D-glucose and compound

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1a as the aglycone. In the ^{1}H NMR spectrum of **1a**, a significant difference in the chemical shifts for H-3a (δ 1.60) and H-3b (δ 1.45) was observed which suggested a meso-isomer. Furthermore, the ^{1}H and ^{13}C NMR spectra of compound **1a** were in complete agreement with those of an authentic meso-isomer.

The location of the glucose moiety on aglycone **1a** was established by the glycosylation shifts rule [15]. The β-C [adjacent carbon to glycosylated carbon (α-C)] of an aglycone moiety is generally shielded on glycoside formation. In the case of glycosides of secondary alcohols, the magnitudes of the glycosylation shifts of signals due to two β-C's differ significantly from each other. The difference depends upon the stereochemical relationship between the chirality of the anomeric carbon of the sugar and the α-C of the aglycone in a free form. As shown in Table 1, comparison of the signals of compound **1** and its aglycone **1a** showed that on β-D-glucosylation one of the methyl carbons (C-1) was more shielded than the methylene carbon (C-3). This revealed that the glycosyl linkage of compound **1** was formed between the β-D-glucose and C-4, which has an *R*-configuration. Based on these findings the structure of compound **1** was determined as shown.

Compounds **2**, $C_{17}H_{32}O_{12}$, and **3**, $C_{16}H_{30}O_{11}$, were obtained as oils. D-Glucose was detected in the acid hydrolysate of compound **2**, and D-glucose and D-xylose in that of compound **3**. The ^{1}H and ^{13}C NMR spectra of both compounds were essentially the same to those of **1** except for the signals due to an additional β-glucopyranosyl unit for **2**, and a β-xylopyranosyl unit for **3**. It was observed that glycosylation at the C-6 of the glucose moiety of both compounds resulted in a downfield shift of the C-6 and upfield shift of the C-5 (Table 1). These evidences led to the formulation of the structures of compounds **2** and **3** as shown.

Compound **4**, $C_{11}H_{20}O_7$, was obtained as a powder. This compound was similar to **1**, but lacked a signal due to one of the CHOH of **1** and instead had an additional carbonyl signal in the ^{13}C NMR spectrum. This demonstrated that compound **4** was a β-glucopyranoside of 4-hydroxy-2-pentanone. Acid hydrolysis of compound **4** afforded D-glucose, but the aglycone could not be obtained because of the limited amount of sample. The chirality of C-4 was determined as *R* by comparison of the ^{13}C NMR spectra of compound **4** and synthetic 4-hydroxy-2-pentanone (a mixture of the enantiomers), taking the glucosylation shift rule into consideration. Therefore, compound **4** as shown, is the 2-keto homologue of **1**.

Compound **5**, $C_{17}H_{30}O_{12}$, was obtained as a powder. By analogous methods to those applied in the cases of compounds **2** and **3**, the structure of compound **5** was formulated as shown.

Compounds **6**, $C_{17}H_{32}O_{12}$, and **7**, $C_{20}H_{38}O_{12}$, were obtained as oils. Both compounds were characterized as (*R*)-1,3-octanediol glycosides by comparison of their ^{1}H and ^{13}C NMR spectra with those of the reference data of compound **11** [13]. Following acid hydrolysis of compounds **6** and **7**, the component sugars were identified as D-glucose and D-apiose for **6**, and two D-glucose for **7**. The ^{1}H and ^{13}C NMR signals attributable to the sugar moieties of compound **6** closely corresponded to the reported data for syringaresinol-4,4′-bis-*O*-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranoside [11]. On the other hand, the signals due to the sugar moiety of compound **7** could be assigned to those of β-gentiobiosyl which is the same sugar unit as that of compound **2**. Accordingly, the structures of compounds **6** and **7** were characterized as shown.

Compound **8**, $C_{13}H_{16}O_8$, was obtained as a powder. The ^{1}H and ^{13}C NMR spectra established the presence of *p*-hydroxybenzoic acid moiety as an acyl residue. Furthermore, the doubling of the signals for the carbons of the glucosyl moiety (C-1–C-5) was consistent with the presence of a mixture of α- and β-glucose. Acetylation of compound **8** with acetic anhydride–pyridine gave only the β-anomeric product (**8a**). In the HMBC spectrum of the penta-acetate (**8a**), the ester carbonyl carbon was correlated to the H-6 of the glucose, indicating the formation of an ester linkage between the carboxyl of the acyl and the C-6 hydroxyl of the glucose. Based on these observations, the structure of compound **8** was established as shown.

EXPERIMENTAL

General. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz): TMS or dioxane as int. standard; CC: silica gel (Kieselgel 60, 70–230 mesh, Merck), Styrene–divinylbenzene copolymer resin (Diaion HP-20, Mitsubishi Chem. Ind., Japan); MPLC: ODA-AQ 120-S50 (23 mm × 42 cm, YMC, Japan); HPLC: R-ODS-10 S-10 120A (25 mm × 25 cm, YMC, Japan) or AQ-312 S-5 120A ODS (6 mm × 15 cm, YMC, Japan). All solvent systems for chromatography were homogeneous unless otherwise stated. (2*R*,4*R*)-2,4-Pentanediol and meso-2,4-pentanediol were purchased from Aldrich Chem. Co. and Janssen Chimica, respectively. Acid hydrolysis of glycosides and identification of resulting monosaccharides: see ref. [16].

Plant material. Fruits of *Crescentia cujete* L. were collected in Long Thanh, Ba Ria-Vung Tau province, Vietnam in 1994. A voucher specimen has been deposited in the Herbarium of Ho Chi Minh City University of Medicine and Pharmacy.

Extraction and separation. Dried fruits of *C. cujete* (300 g) were extracted with hot MeOH. After removal of the solvent by evapn, the extract (162 g) was partitioned between H_2O and Et_2O. The H_2O layer was subjected to CC on Diaion HP-20 eluted with H_2O, 25% MeOH, 50% MeOH and MeOH, successively. The 25% MeOH eluate (1.1 g) was sepd into eight frs by CC on silica gel using EtOAc–EtOH–H_2O (8:2:1). Frs 4–6 were subjected to MPLC with 18, 12 and 5% MeOH, respectively, and then purified by HPLC to afford **8** (210 mg) from fr. 4 with 18% MeOH, **3** (210 mg) and **5** (90 mg) from fr. 5 with 12% MeOH, **1** (240

Table 1. ^{13}C NMR data of compounds **1–8**, **1a**, **4a**, **8a** and **12** in D_2O

C	**1a***	**meso***	**R,R***	**1***	(δΔ)†	**1**	**2**	(δΔ)‡	**3**	(δΔ)§	**4a**	**4**	(δΔ)‖	**5**	**12**	**6**	**7**	**8**	**8a**¶
1	23.7	23.8	24.2	20.0	(−3.7)	18.7	18.7		18.8		29.8	29.7		29.7	67.1	67.2	67.2	120.4	127.0
2	67.4	67.4	65.5	74.2	(+6.8)	72.6	72.6		72.6		214.2	214.2		214.7	36.0	36.0	36.0	115.0	121.7
3	48.4	48.4	48.9	47.2	(−1.2)	44.6	44.6		44.7		50.5	50.0	(−0.5)	49.9	68.6	68.6	68.5	131.6	131.3
4	67.4	67.4	65.5	66.7		65.1	65.2		65.2		63.9	71.7	(+7.8)	71.7	35.7	35.8	35.8	160.6	154.5
5	23.7	23.8	24.2	23.6		21.7	21.8		21.8		21.8	18.9	(−2.9)	18.9	24.3	24.3	24.2	131.6	131.3
6															31.1	31.0	31.1	115.0	121.7
7															21.8	21.8	21.8	167.8	165.2
8															13.2	13.2	13.2		
				β-Glc		*β*-Glc	*β*-Glc		*β*-Glc			*β*-Glc		*β*-Glc	*β*-Glc	*β*-Glc	*β*-Glc	α-Glc, *β*-Glc	*β*-Glc
1				102.1		99.9	100.0		99.9			100.1		100.0	100.0	101.0	100.0	91.7, 95.6	91.7
2				74.9		72.6	72.7		72.6			72.6		72.6	73.7	78.7	72.6	69.3, 73.2	70.3
3				77.9		75.5	75.5		75.5			75.5		75.4	75.6	75.8	75.5	72.2, 75.1	72.7
4				71.6		69.3	69.1		68.9			69.1		69.1	69.3	69.5	69.0	69.0, 69.2	68.1
5				77.8		75.4	74.5	(−0.9)	74.5	(−0.9)		75.3		74.3	75.4	75.7	74.5	71.0, 73.6	72.7
6				62.8		60.3	68.2	(+7.9)	68.3	(+8.0)		60.2		68.3	60.2	60.7	68.3	63.1, 63.1	62.2
							β-Glc		*β*-Xyl					*β*-Glc		*β*-Api	*β*-Glc		
1							102.4		103.2					102.4		109.2	102.4		
2							73.9		73.8					73.9		76.7	73.8		
3							75.4		75.2					75.5		79.3	75.4		
4							69.2		69.2					69.2		73.6	69.1		
5							75.2		64.7					75.3		63.7	75.2		
6							60.3							60.3			60.3		

* In CD_3OD. † δ of **1**–δ of **1a**. ‡ δ of **2**–δ of **1**. § δ of **3**–δ of **1**. ‖ δ of **4**–δ of **4a**. **meso**: Meso-isomer. **R,R**: 2*R*,3*R*-Isomer. ¶ In $CDCl_3$.

mg) and **11** (30 mg) from fr. 6 with 2% MeCN. The 50% MeOH eluate (1.2 g) was chromatographed on silica gel with EtOAc–EtOH–H_2O (40:5:1–8:2:1) to give seven frs. Fr. 4 was sepd into three frs by CC on silica gel with CH_2Cl_2–MeOH–H_2O (7:2:1, lower phase). Frs 4-1 and 4-2 were purified by HPLC with 20 and 18% MeOH to afford **10** (21 mg) and **12** (27 mg), respectively. Frs 5 and 6 were purified by MPLC with 30 and 40% MeOH, respectively, and then by HPLC to give **9** (15 mg) from fr. 5 with 35% MeOH, **6** (60 mg) and **7** (30 mg) from fr. 6 with 40% MeOH. The H_2O eluate was extracted with *n*-BuOH satd with H_2O. The BuOH extract (1.1 g) was sepd into five frs by CC on silica gel using EtOAc–EtOH–H_2O (8:2:1). Fr. 1 was sepd into five frs by MPLC using 5% MeOH. Compound **2** (18 mg) from fr. 1–2 and **4** (21 mg) from fr. 1–4 were obtained by HPLC with H_2O.

(2R,4S)-2-O-β-D-*Glucopyranosyl*-2,4-*pentanediol* (**1**). Oil, $[\alpha]_D$ −33° (MeOH; *c* 1.3). FAB-MS (negative): *m/z* 265.1284 $[M-H]^-$ ($C_{11}H_{21}O_7$ requires: *m/z* 265.1287); ^1H NMR (D_2O): δ 4.35 (1H, *d*, *J* = 8.1 Hz, Glc-1), 3.89 (1H, *ddq*, *J* = 7.3, 7.3, 6.3 Hz, H-2), 3.80 (1H, *ddq*, *J* = 7.3, 7.3, 6.3 Hz, H-4), 3.73 (1H, *dd*, *J* = 12.3, 2.1 Hz, Glc-6a), 3.54 (1H, *dd*, *J* = 12.3, 5.7 Hz, Glc-6b), 3.31 (1H, *dd*, *J* = 9.2, 9.2 Hz, Glc-3), 3.25 (1H, *ddd*, *J* = 9.2, 5.7, 2.1 Hz, Glc-5), 3.20 (1H, *dd*, *J* = 9.2, 9.2 Hz, Glc-4), 3.05 (1H, *dd*, *J* = 9.2, 8.1 Hz, Glc-2), 1.67 (1H, *ddd*, *J* = 14.1, 7.3, 7.3 Hz, H-3a), 1.41 (1H, *ddd*, *J* = 14.1, 7.3, 7.3 Hz, H-3b), 1.05 (3H, *d*, *J* = 6.3 Hz, H-5), 1.03 (3H, *d*, *J* = 6.3 Hz, H-1); ^{13}C NMR: Table 1.

Acid hydrolysis of **1**. A soln of **1** (50 mg) in 1 M HCl (dioxane–H_2O, 1:1, 5 ml) was refluxed for 1 hr under an Ar atmosphere. The reaction mixt. was extracted with Et_2O in a liquid–liquid extractor for 3 days. Then Et_2O phase was evapd off *in vacuo* to give **1a**. ^1H NMR (CD_3OD): δ 3.90 (2H, *ddq*, *J* = 9.5, 8.3, 6.1 Hz, H-2, 4), 1.60 (1H, *ddd*, *J* = 13.7, 8.3, 8.3 Hz, H-3a), 1.45 (1H, *ddd*, *J* = 13.7, 9.5, 9.5 Hz, H-3b), 1.16 (6H, *d*, *J* = 6.1 Hz, H-1 and H-5); ^{13}C NMR: Table 1.

(2R,4S)-2-O-β-D-*Glucopyranosyl*-(1 → 6)-β-D-*glucopyranosyl*-2,4-*pentanediol* (**2**). Oil, $[\alpha]_D$ −43° (MeOH; *c* 0.2). FAB-MS (negative): *m/z* 427.1803 $[M-H]^-$ ($C_{17}H_{31}O_{12}$ requires: *m/z* 427.1815); ^1H NMR (D_2O): δ 4.38 (1H, *d*, *J* = 8.1 Hz, Glc-1′), 4.34 (1H, *d*, *J* = 8.1 Hz, Glc-1), 4.02 (1H, *dd*, *J* = 11.7, 1.7 Hz, Glc-6a), 3.91 (1H, *ddq*, *J* = 7.3, 7.3, 6.8 Hz, H-2), 3.82 (1H, *ddq*, *J* = 5.4, 7.3, 6.6 Hz, H-4), 3.75 (1H, *dd*, *J* = 12.2, 2.2 Hz, Glc-6a′), 3.69 (1H, *dd*, *J* = 12.2, 5.6 Hz, Glc-6b′), 3.56 (1H, *dd*, *J* = 11.7, 5.8 Hz, Glc-6b), 3.44 (1H, *m*, Glc-5), 3.22–3.35 (5H, Glc-2, Glc-3, Glc-2′, Glc-3′, Glc-5′), 3.14 (1H, *dd*, *J* = 9.0, 9.0 Hz, Glc-4), 3.07 (1H, *dd*, *J* = 9.0, 9.0 Hz, Glc-4′), 1.68 (1H, *ddd* *J* = 14.2, 7.3, 7.3 Hz, H-3a), 1.42 (1H, *ddd*, *J* = 14.2, 7.3, 5.4 Hz, H-3b), 1.06 (3H, *d*, *J* = 6.6 Hz, H-5), 1.04 (3H, *d*, *J* = 6.8 Hz, H-1); ^{13}C NMR: Table 1.

(2R,4S)-2-O-β-D-*Xylopyransyl*-(1 → 6)-β-D-*glucopyranosyl*-2,4-*pentanediol* (**3**). Oil, $[\alpha]_D$ −92° (MeOH; *c* 1.1). FAB-MS (negative): *m/z* 397.1721 $[M-H]^-$ ($C_{16}H_{29}O_{11}$ requires: *m/z* 397.1710); ^1H NMR (D_2O): δ 4.35 (1H, *d*, *J* = 8.0 Hz, Xyl-1), 4.28 (1H, *d*, *J* = 8.0 Hz, Glc-1), 4.02 (1H, *dd*, *J* = 11.7, 1.7 Hz, Glc-6a), 3.89 (1H, *ddq*, *J* = 7.3, 7.3, 6.8 Hz, H-2), 3.82 (1H, *ddq*, *J* = 7.3, 5.4, 6.3 Hz, H-4), 3.78 (1H, *dd*, *J* = 11.8, 6.8 Hz, Xyl-5a), 3.68 (1H, *dd*, *J* = 11.7, 5.6 Hz, Glc-6b), 3.47 (1H, *ddd*, *J* = 9.1, 6.8, 2.9 Hz, Xyl-4), 3.42 (1H, *ddd*, *J* = 9.2, 5.6, 1.7 Hz, Glc-5), 3.33 (1H, *dd*, *J* = 9.2, 9.2 Hz, Glc-3), 3.31 (1H, *dd*, *J* = 9.2, 9.2 Hz, Glc-4), 3.28 (1H, *dd*, *J* = 9.1, 9.1 Hz, Xyl-3), 3.23 (1H, *dd*, *J* = 11.8, 2.9 Hz, Xyl-5b), 3.20 (1H, *dd*, *J* = 9.1, 8.0 Hz, Xyl-2), 3.07 (1H, *dd*, *J* = 9.2, 8.0 Hz, Glc-2), 1.66 (1H, *ddd*, *J* = 14.2, 7.3, 7.3 Hz, H-3a), 1.42 (1H, *ddd*, *J* = 14.2, 7.3, 5.4 Hz, H-3b), 1.05 (3H, *d*, *J* = 6.3 Hz, H-5), 1.03 (3H, *d*, *J* = 6.8 Hz, H-1); ^{13}C NMR: Table 1.

(R)-4-O-β-D-*Glucopyranosyl*-4-*hydroxy*-2-*pentanone* (**4**). Oil, $[\alpha]_D$ −21° (MeOH; *c* 0.2). FAB-MS (negative): *m/z* 263.1138 $[M-H]^-$ ($C_{11}H_{19}O_7$ requires: *m/z* 263.1131); ^1H NMR (D_2O): δ 4.43 (1H, *d*, *J* = 7.8 Hz, Glc-1), 4.32 (1H, *ddq*, *J* = 7.3, 4.9, 6.1 Hz, H-4), 3.97 (1H, *dd*, *J* = 11.7, 1.7 Hz, Glc-6a), 3.63 (1H, *dd*, *J* = 11.7, 4.9 Hz, Glc-6b), 3.38 (1H, *d*, *J* = 8.7, 8.7 Hz, Glc-3), 3.33 (1H, *ddd*, *J* = 8.7, 4.9, 1.7 Hz, Glc-5), 3.28 (1H, *dd*, *J* = 8.7, 7.8 Hz, Glc-2), 3.11 (1H, *dd*, *J* = 8.7, 8.7 Hz, Glc-4), 2.82 (1H, *dd*, *J* = 16.4, 7.3 Hz, H-3a), 2.65 (1H, *dd*, *J* = 16.4, 4.9 Hz, H-3b), 2.19 (3H, *s*, H-1), 1.16 (3H, *d*, *J* = 6.1 Hz, H-5); ^{13}C NMR: Table 1.

Synthesis of 4-*hydroxy*-2-*pentanone*. A soln of Me_2CO and acetaldehyde in 0.01% aq. NaOH was allowed to stand for 5 hr at room temp. The reaction mixt. was extracted with Et_2O in a liquid–liquid extractor for 2 days. The Et_2O-soluble compound was purified by silica gel CC with EtOAc to give 4-hydroxy-2-pentanone: Oil, ^1H NMR (D_2O): δ 4.18 (1H, *dq*, *J* = 6.1, 6.1 Hz, H-4), 2.61 (2H, *d*, *J* = 6.1 Hz, H-3), 2.14 (3H, *s*, H-1), 1.11 (3H, *d*, *J* = 6.1 Hz, H-5); ^{13}C NMR: Table 1.

(R)-4-O-β-D-*Glucopyranosyl*-(1 → 6)-β-D-*glucopyranosyl*-4-*hydroxy*-2-*pentanone* (**5**). Oil, $[\alpha]_D$ −12° (MeOH; *c* 0.4). FAB-MS (negative): *m/z* 425.1655 $[M-H]^-$ ($C_{17}H_{29}O_{12}$ requires: *m/z* 425.1659); ^1H NMR (D_2O): δ 4.43 (1H, *d*, *J* = 7.8 Hz, Glc-1′), 4.40 (1H, *d*, *J* = 7.8, Glc-1), 4.32 (1H, *ddq*, *J* = 7.3, 4.9, 6.1 Hz, H-4), 3.96 (1H, *dd*, *J* = 11.9, 2.0 Hz, Glc-6a), 3.78 (1H, *dd*, *J* = 12.4, 1.7 Hz, Glc-6a′), 3.74 (1H, *dd*, *J* = 11.9, 5.1 Hz, Glc-6b), 3.63 (1H, *dd*, *J* = 12.4, 4.9 Hz, Glc-6b′), 3.50 (1H, *m*, Glc-5), 3.25–3.39 (5H, Glc-2, 3, 2′, 3′, 5′), 3.18 (1H, *dd*, *J* = 9.0, 9.0 Hz, Glc-4′), 3.11 (1H, *dd*, *J* = 9.0, 9.0 Hz, Glc-4), 2.82 (1H, *dd*, *J* = 16.4, 7.3 Hz, H-3a), 2.65 (1H, *dd*, *J* = 16.4, 4.9 Hz, H-3b), 2.19 (3H, *s*, H-1), 1.16 (3H, *d*, *J* = 6.1 Hz, H-5); ^{13}C NMR: Table 1.

(R)-1-O-β-D-*Apiofuranosyl*-(1 → 2)-β-D-*glucopyransoyl*-1,3-*octanediol* (**6**). Oil, $[\alpha]_D$ −40° (MeOH; *c* 0.5). FAB-MS (negative): *m/z* 409.2059 $[M-H]^-$ ($C_{19}H_{35}O_{11}$ requires: *m/z* 409.2072); ^1H NMR (D_2O): δ 5.20 (1H, *d*, *J* = 2.7 Hz, Api-1), 4.37 (1H, *d*, *J* =

7.8 Hz, Glc-1), 0.74 (3H, *t*, $J = 6.6$ Hz, H-8); ^{13}C NMR: Table 1.

(R)-1-O-*β*-D-*Glucopyranosyl*-(1 → 6)-*β*-D-*glucopyranosyl*-1,3-*octanediol* (**7**). Oil, $[\alpha]_D$ −21° (MeOH; *c* 0.3). FAB-MS (negative): *m/z* 469.2266 $[M-H]^-$ ($C_{20}H_{37}O_{12}$ requires: *m/z* 469.2284); ^1H NMR (D_2O): *δ* 4.37 (1H, *d*, $J = 8.0$ Hz, Glc-1′), 4.32 (1H, *d*, $J = 8.0$ Hz, Glc-1), 0.75 (3H, *t*, $J = 6.6$ Hz, H-8); ^{13}C NMR: Table 1.

6-O-(p-*hydroxybenzoyl*)-D-*Glucose* (**8**). Powder, FAB-MS (negative): *m/z* 299.0778 $[M-H]^-$ ($C_{13}H_{15}O_8$ requires: *m/z* 299.0766); ^1H NMR (D_2O): *δ* 4.76 (1H, *d*, $J = 8.1$ Hz, *β*-anomeric H of Glc), 5.91 (1H, *d*, $J = 3.7$ Hz, α-anomeric H of Glc); ^{13}C NMR: Table 1.

Acetyl 6-O-(p-*acetoxybenzoyl*)-2,3,4-*tri*-O-*acetyl*-*β*-*D*-*glucoside* (**8a**). Powder. ^1H NMR ($CDCl_3$): *δ* 8.08 (2H, *d*, $J = 8.8$ Hz, H-2, 6), 7.19 (2H, *d*, $J = 8.8$ Hz, H-3, 5), 5.76 (1H *d*, $J = 8.1$ Hz, Glc-1), 5.29 (1H, *t*, $J = 9.3$ Hz, Glc-3), 5.22 (1H, *t*, $J = 9.3$ Hz, Glc-4), 5.16 (1H, *dd*, $J = 9.3$, 8.1 Hz, Glc-2), 4.49 (1H, *dd*, $J = 12.4$, 2.2 Hz, Glc-6a), 4.36 (1H, *dd*, $J = 12.4$, 4.6 Hz, Glc-6b), 3.98 (1H, *ddd*, $J = 9.3$, 4.6, 2.2 Hz, H-5), 2.32, 2.11, 2.04, 2.03, 2.02 (each 3H, *s*, Ac); ^{13}C NMR: Table 1.

Acanthoside D (**9**). Powder, $[\alpha]_D$ −44° (pyridine; *c* 0.6). FAB-MS (negative): *m/z* 739 $[M-H]^-$; ^{13}C NMR (DMSO-d_6): *δ* 152.7 (C-3, 3′, 5, 5′), 137.1 (C-4, 4′), 133.7 (C-1, 1′), 104.3 (C-2, 2′, 6, 6′), 102.5 (Glc-1, 1′), 85.0 (C-7, 7′), 77.0 (Glc-3, 3′), 76.5 (Glc-5, 5′), 74.2 (Glc-2, 2′), 71.4 (C-9, 9′), 69.9 (Glc-4, 4′), 61.0 (Glc-6, 6′), 56.5 ($OCH_3 \times 4$), 53.5 (C-8, 8′).

β-D-*Glucopyranosyl benzoate* (**10**). Powder. ^1H NMR (pyridine-d_5): *δ* 8.17 (2H, *d*, $J = 8.3$ Hz, H-2, 6), 7.49 (1H, *t*, $J = 8.3$ Hz, H-4), 7.34 (2H, *dd*, $J = 8.3$, 8.3 Hz, H-3, 5), 6.60 (1H, *d*, $J = 6.8$ Hz, Glc-1, characteristic chemical shift of ester linked Glc), 4.51–4.12 (6H, *m*, Glc-2, 3, 4, 5, 6a, 6b); ^{13}C NMR (pyridine-d_5): *δ* 165.7 (C-7), 133.6 (C-4), 130.4 (C-1), 130.2 (C-2, 6), 128.8 (C-3, 5), 96.7 (Glc-1, characteristic chemical shift of ester linked Glc), 79.4 (Glc-3), 78.5 (Glc-5), 74.3 (Glc-2), 71.0 (Glc-4), 62.2 (Glc-6).

(R)-1-O-*β*-D-*Glucopyransoyl*-1,3-*octanediol* (**11**). Oil. FAB-MS (negative): *m/z* 307 $[M-H]^-$; ^1H NMR (D_2O): *δ* 4.35 (1H, *d*, $J = 7.8$ Hz, Glc-1), 0.74 (3H, *t*, $J = 6.6$ Hz, H-8); ^{13}C NMR: *δ* 100.0 (Glc-1), 75.6 (Glc-3), 75.4 (Glc-5), 73.7 (Glc-2), 69.3 (Glc-4), 68.6 (C-3), 67.1 (C-1), 60.2 (Glc-6), 36.0 (C-2), 35.7 (C-4), 31.1 (C-6), 24.3 (C-5), 21.8 (C-7), 13.2 (C-8).

β-D-*Fructofuranosyl* 6-O-(p-*hydroxybenzoyl*(-α-D-*glucopyranoside* (**12**). Powder, $[\alpha]_D$ +22° (MeOH; *c* 0.5). FAB-MS (negative): *m/z* 461 $[M-H]^-$; ^1H NMR (DMSO-d_6): *δ* 7.80 (2H, *d*, $J = 8.8$ Hz, H-2, 6), 6.83 (2H, *d*, $J = 8.8$ Hz, H-3, 5), 5.20 (1H, *d*, $J = 3.7$ Hz, Glc-1), 4.36 (1H, *dd*, $J = 12.0$, 2.0 Hz, Glc-6a), 4.25 (1H, *dd*, $J = 12.0$, 4.9 Hz, Glc-6b), 4.03 (1H, *ddd*, $J = 9.0$, 4.9, 2.0 Hz, Glc-5), 3.90 (1H, *d*, $J = 8.0$ Hz, Fru-3), 3.80 (1H, *dd*, $J = 8.0$, 8.0 Hz, Fru-4), 3.58 (1H, *ddd*, $J = 8.0$, 6.5, 3.0 Hz, Fru-5), 3.55 (1H, *dd*, $J = 9.0$, 9.0 Hz, Glc-3), 3.53 (1H, *dd*, $J = 11.3$, 6.5, Hz, Fru-6a), 3.45 (1H, *dd*, $J = 11.3$, 3.0 Hz, Fru-6b), 3.42 (1H, *d*, $J = 12.5$ Hz, Fru-1a), 3.40 (1H, *d*, $J = 12.5$ Hz, Fru-1b), 3.25 (1H, *dd*, $J = 9.0$, 3.7 Hz, Glc-2), 3.22 (1H, *dd*, $J = 9.0$, 9.0 Hz, Glc-4); ^{13}C NMR (DMSO-d_6): *δ* 165.5 (C-7), 162.8 (C-4), 131.4 (C-2, 6), 120.0 (C-1), 115.5 (C-3, 5), 103.9 (Fru-2), 91.5 (Glc-1), 82.4 (Fru-5), 77.0 (Fru-3), 74.3 (Fru-4), 72.5 (Glc-3), 71.3 (Glc-2), 70.1 (Glc-4), 69.8 (Glc-5), 63.5 (Glc-6), 62.4 (Fru-6), 61.9 (Fru-1).

Acknowledgement—We wish to thank Dr Nguyen Thoi Nham of The Science Production Centre of Vietnamese Ginseng for encouragement, and the Research Centre for Molecular Medicine, Hiroshima University School of Medicine for the use of its NMR facilities.

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