Pergamon 0031-9422(95)00747-4 Phytochemistry, Vol. 41, No. 5, pp. 1341–1345, 1996

0031-9422/96 $15.00 + 0.00

TWO DIMERIC SECOIRIDOID GLUCOSIDES FROM *JASMINUM POLYANTHUM*

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(*Received in revised form* 12 *September* 1995)

Key Word Index—*Jasminum polyanthum*; Oleaceae; secoiridoid glucosides; jaspolyoside; jaspolyanthoside; structure elucidation.

Abstract—Investigation of the crude drug 'Ye su xin', the dried flowers of *Jasminum polyanthum*, led to the isolation of two new secoiridoid glucosides, jaspolyoside and jaspolyanthoside, together with the known secoiridoid glucosides, oleuropein, ligstroside and Gl 5. The structures of the new compounds were elucidated as [2*S*-(2α,3*E*,4β)]-3-ethylidene-2-[6-*O*-([2*S*-(2α,3*E*,4β)]-{[3-ethylidene-2-(β-D-glucopyranosyloxy)-3,4-dihydro-5-(methoxycarbonyl)-2*H*-pyran-4-yl]acetyloxy})-β-D-glucopyranosyl]-3,4-dihydro-5-(methoxycarbonyl)-2*H*-pyran-4-acetic acid 2-(3,4-dihydroxyphenyl)ethyl ester and [2*S*-(2α,3*E*,4β)]-3-([2*S*-(2α,3*E*,4β)]-{[3-ethylidene-2-(β-D-glucopyranosyloxy)-3,4-dihydro-5-(methoxycarbonyl)-2*H*-pyran-4-yl]acetyloxy}) ethylidene-2-(β-D-glucopyranosyloxy)-3,4-dihydro-5-(methoxycarbonyl)-2*H*-pyran-4-acetic acid methyl ester on the basis of chemical and spectroscopic data.

INTRODUCTION

Jasminum polyanthum Franch. is a shrub with a wide distribution in China. The dried flowers of this plant have been used as a crude drug, 'Ye su xin', in Chinese folk medicine for the treatment of orchitis, menorrhalgia and stomachalgia [1]. No phytochemical investigation on this plant material has been reported to date. In the course of our chemical studies on the secoiridoid glucosides from the family Oleaceae [2], we examined the constituents of this crude drug and isolated five secoiridoid glucosides, two of which were new compounds. We describe here the structural elucidation of the novel compounds.

RESULTS AND DISCUSSION

Dried flowers of *J. polyanthum* were extracted with hot MeOH. The MeOH extract was fractionated by column chromatography on ODS and then purified by preparative HPLC, yielding five secoiridoid glucosides (**1**–**5**). Compounds **1**, **2** and **3** were identified as oleuropein [3,4], ligstroside [4,5] and Gl 5 [6], by comparison of their spectral data with those described in the literature and/or direct comparison with the authentic samples.

Compound **4** was analysed for $C_{42}H_{54}O_{23}$ from its HR-SIMS. Its UV spectrum, in addition to showing the typical absorption at 234.5 nm (log ε 4.41) of an iridoidic enol ether system conjugated with a carbonyl group, revealed an additional absorption at 282 nm due to a phenolic function. It showed IR bands at 3425 (OH), 1732 (esters), 1717 and 1636 (α,β-unsaturated esters), and 1506 (aromatic ring) cm^{-1}. Its ^1H NMR spectrum exhibited two sets of signals both assignable to an oleoside (**6**) moiety together with a set of signals arising from a 3,4-dihydroxyphenethyl group (Table 1). Conventional acetylation of the glucoside **4** yielded the acetate **7**, which exhibited ^1H NMR signals of nine acetyl groups at δ2.00–2.08 (7 × Ac), 2.28 and 2.29, supporting the presence in **4** of seven alcoholic and two phenolic hydroxyl groups. In accord with the above findings, the ^{13}C NMR signals of **4** (Table 1) showed duplicated carbon signals corresponding to oleoside methyl ester together with the resonances of a 3,4-dihydroxyphenethoxyl group. The methoxyl groups were situated at C-11 in each of the two oleoside moieties based upon the HMBC experiments with **4**, where ^3J interaction was observed between the methoxyl signals at δ3.67 and 3.71 and conjugated carbonyl carbons at δ168.67 and 168.64, although one of the two methoxyls resonated at a slightly higher frequency than the 11-carbomethoxyl group in the usual oleoside-type secoiridoid glucoside [7]. The shielding could be accounted for by the conformation in which the methoxyl group is influenced by the aromatic ring. Another important ^3J correlation, observed between H_2-1″ at δ4.08 and δ4.17 and a saturated carbonyl carbon at δ173.01 (or 172.96), was indicative of an ester linkage of C-7 of an oleoside unit with the hydroxyl of the 3,4-dihydroxyphenethoxyl group. All these results allowed us to depict the structure of **4** as an ester of oleuropein (**1**, a part) with oleoside-11-methyl ester (**8**, b part). The position of the ester linkage of both parts was determined by comparative studies of the ^{13}C NMR spectra of **1*** and **4** [8]. The chemical shifts of carbon signals

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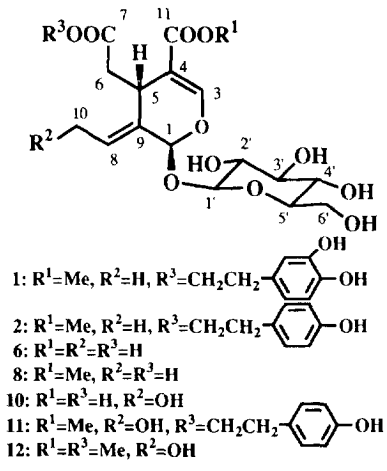

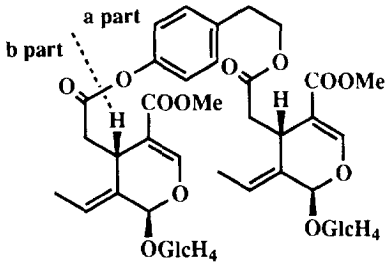

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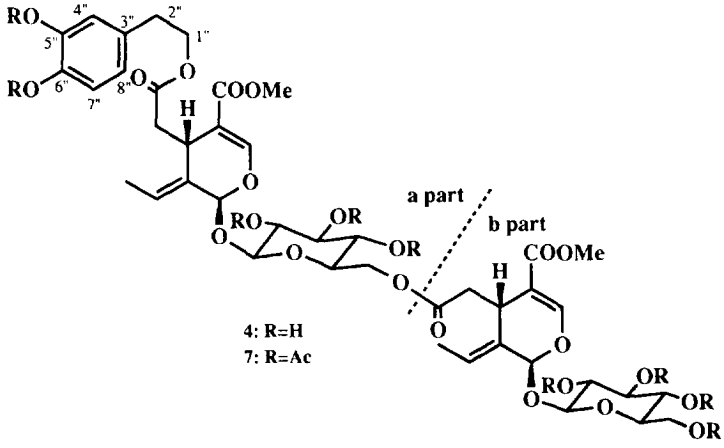
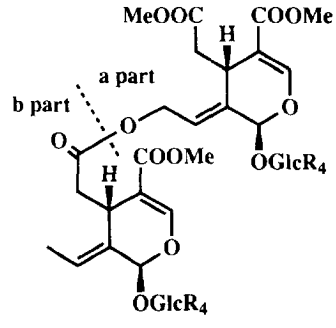


4: R=H
7: R=Ac



5: R=H
9: R=Ac

ascribable to the oleuropein portion in **4** were superimposable on those of **1**, except for the signals arising from the glucose moiety. The downfield shift of C-6'a ($\Delta\delta$ + 2.1 ppm) and upfield shift of C-5'a ($\Delta\delta$ − 2.8 ppm) of **4**, when compared with the corresponding signals of **1**, were ascribed to an acylation effect, and suggested that the hydroxy group at C-6'a was esterified. This was further confirmed by HMBC experiments with **4**, which showed a cross-peak between H-6'a at δ4.22 and C-7b at δ172.96 (or 173.01). Accordingly, compound **4** was formulated as shown and designated jaspolyoside.

The second new glucoside **5**, named jaspolyanthoside, on HR-SIMS exhibited a peak at *m/z* 843.2551 ($[M + Na]^+$) consistent with a molecular formula of $C_{35}H_{48}O_{22}$. On acetylation, the glucoside provided the acetate **9** with eight aliphatic acetoxyl groups. The molar absorption coefficient (log ε 4.33) at 236 nm and ^{1}H NMR spectral features of **5** [H-3a and H-3b (δ7.54, 7.52), H-1a and H-1b (δ5.99, 5.93), two anomeric protons (δ4.81, 4.82) and three methoxyls (δ3.72, 3.71, 3.66)] suggested it to be a dimeric secoiridoid glucoside like jaspolyoside (**4**). However, its ^{1}H NMR spectrum showed only one set of signals corresponding to an ethylidene group at δ6.12 (1H, *qd*) and 1.73 (3H, *dd*), but exhibited the signals for an olefinic proton at δ6.10 (*ddd*) and coupled methylene protons at δ4.73 and 4.82, suggesting that the glucoside **5** was composed of one 10-hydroxyoleoside (**10**, a part) and one oleoside (**6**, b part) unit. From the ^{1}H NMR chemical shifts, each of the methoxyl groups at δ3.71 and δ3.72 was deduced to be esterified with an α,β-unsaturated acid, i.e. C-11a of a 10-hydroxyoleoside unit and C-11b of an oleoside moiety, while the residual one at δ3.66 was assigned to a saturated carbomethoxyl group [7]. The downfield shifts of H_2-10a ($\Delta\delta$ + 0.61, + 0.55 ppm) and C-10a ($\Delta\delta$ + 2.8 ppm) in **5** relative to the corresponding signals in 10-hydroxyligstroside (**11**) showed an acylation of the 10-hydroxyl group in the 10-hydroxyoleoside unit [9]. These findings led us to conclude that in the structure of jaspolyoside, the C-7b carboxyl group of the oleoside-11-methyl ester (**8**) unit was linked to the C-10a hydroxy group of the 10-hydroxyoleoside-7,11-dimethyl ester (**12**) portion. To confirm this elucidation, extensive NMR studies including ^{1}H–^{1}H COSY, DEPT, HMQC and HMBC experiments were performed on compound **5**, allowing us to assign almost all of the significant proton and carbon signals. The HMBC technique revealed cross peaks between H_2-6a (δ2.54 and δ2.80) and C-7a (δ173.35) as well as between H_2-6b (δ2.46 and δ2.76) and C-7b (δ172.83), confirming the assignment of C-7a and C-7b and showed ^3J interactions between H-10a (δ4.73) and C-7b and between OCH_3 (δ3.66) and C-7a as well as

*On the basis of a comparison with data for related compounds [9], the earlier assignments [8] were revised as follows: 35.3 (C-2''), 66.8 (C-1''), 77.9 (C-3') and 78.3 (C-5').

Table 1. ^1H and ^{13}C NMR spectral data of compounds **4** and **5** in CD_3OD

	4						**5**			
	δ_H				δ_C		δ_H		δ_C	
H/C	a part			b part	a part	b part	a part	b part	a part	b part
1	5.88	*br s*	5.84	*br s*	95.20[b,x]	95.37[b,y]	5.99 *br s*	5.93 *br s*	94.34	95.25
3	7.49	*s*	7.52	*s*	155.19[b]	155.15[b]	7.54 *s*	7.52 *s*	154.98	155.23
4	—		—		109.40	109.49	—	—	109.13	109.39
5	3.98	*dd* (9.0, 4.5)	3.96	*dd* (9.0, 4.5)	31.80 [b,x]	31.84 [b,y]	4.01 *dd* (9.0, 4.5)	4.00 *dd* (9.0, 4.5)	32.50	31.88
6	2.41	*dd* (15.0, 9.0)	2.38	*dd* (15.0, 9.0)	41.28	41.40	2.54 *dd* (15.0, 9.0)	2.46 *dd* (14.5, 9.0)	40.82	41.17
	2.70	*dd* (15.0, 4.5)	2.69	*dd* 15.0, 4.5)			2.80 *dd* (15.0, 4.5)	2.76 *dd* (14.5, 4.5)		
7	— [a,x]		— [a,y]		173.01[b]	172.96[b]	—	—	173.35	172.83
8	6.08	*qd* (7.0, 0.9)	6.07	*qd* (7.0, 0.9)	124.92 [b,x]	125.16 [b,y]	6.10 *ddd* (7.0, 6.0, 1.0)	6.12 *qd* (7.0, 1.0)	124.40	125.12
9	—		—		130.50	130.29	—	—	133.95	130.42
10	1.71	*dd* (7.0, 1.0)	1.65	*dd* (7.0, 1.0)	13.80	13.62	4.73 *ddd* (13.5, 6.0, 2.0)	1.73 *dd* (7.0, 1.5)	62.13	13.84
							4.82 *br dd* (13.5, 7.0)			
11	—		—		168.67[b]	168.64[b]		—	168.31[d]	168.66[d]
OMe	3.67	*s*	3.71	*s*	51.98[b]	52.01[b]	3.71[c] *s*	3.72[c] *s*	52.00	52.00
	—						3.66 *s*	—	52.44	
1′	4.81[a]	*d* (7.5)	4.83[a]	*d* (7.5)	101.05[b]	100.91[b]	4.81[c] *d* (8.0)	4.82[c] *d* (7.5)	100.97	100.97
2′					74.66[b]	74.76[b]			74.74	74.74
3′	3.27–3.57 *m*		3.27–3.57 *m*		77.81[b]	77.97[b]	3.25–3.44 *m*	3.25—3.44 *m*	77.96	77.96
4′					71.36	71.48			71.43[d]	71.51[d]
5′					75.47	78.37			78.43[d]	78.53[d]
6′	4.22	*dd* (12.0, 6.0)	3.68	*dd* (12.0, 5.5)	64.83	62.72	3.66–3.72[c] *m*	3.67[c] *dd* (12.0, 5.0)	62.79	62.79
	4.33	*dd* (12.0, 1.5)	3.89	*dd* (12.0, 1.5)			3.90[c] *dd* (12.0, 2.0)	3.88[c] *br d* (12.0)		
1″	4.08	*dt* (11.0, 7.0)			66.86					
	4.17	*dt* (11.0, 7.0)								
2″	2.72	*t* (7.0)			35.45					
3″	—				130.77					
4″	6.63	*d* (2.0)			116.55					
5″					146.20					
6″					144.89					
7″	6.68	*d* (8.0)			117.09					
8″	6.52	*dd* (8.0, 2.0)			121.40					

Values in parentheses are coupling constants in Hz.

[a–d]Assignments may be reversed horizontally.

[x,y]Signals with the same superscript were ascribable to the same part in the structure.

between OCH_3(a)/OCH_3(b) and C-11a/11b. Thus, the structure of jaspolyanthoside was represented by **5**.

Oligomeric secoiridoid glucosides with oleoside or 10-hydroxyoleoside moieties have only been isolated from oleaceous plants [9–11]. The isolation of jaspolyanthoside (**5**) constitutes the first instance of a dimeric secoiridoid glucoside, which possesses both oleoside and 10-hydroxyoleoside units in its structure.

EXPERIMENTAL

Mp: uncorr.; ^{1}H (200, 300 or 500 MHz) and ^{13}C (125 MHz) NMR: TMS as int. standard; SIMS: glycerol or 3-nitrobenzyl alcohol as matrix; TLC: silica gel.

Plant material. The crude drug, identified as 'Ye su xin', the dried flowers of *J. polyanthum*, was obtained from Sunstar Bai Yunshan Co., Ltd., in Guangzhou, China. Voucher specimen (KPFY-862) are deposited in the laboratory of Kobe Pharmaceutical University.

Isolation of glucosides. The crude drug (124 g) was extracted with hot MeOH. The MeOH extracts were concentrated *in vacuo* to give a residue (47.1 g), a part (5.7 g) of which was chromatographed on a Wakogel LP-40C18 column. Elution with MeOH–H_2O mixts of the indicated MeOH content gave four frs, I (0–5%, 4.376 g), II (10%, 360 mg), III (20%, 259 mg), IV (30%, 91 mg). Fr. I was further purified by prep. HPLC (μBondasphere 5μ C18–100 Å, MeOH–H_2O, 23:27), giving oleuropein (**1**) (601 mg), ligstroside (**2**) (39.1 mg) and jaspolyanthoside (**5**) (37.2 mg), in order of elution. The following frs were also purified by prep. HPLC (μBondasphere 5μ C18–100 Å, MeOH–H_2O, 49:51 or 1:1). Fr. II yielded **1** (208 mg), **2** (23.1 mg), jaspolyanthoside (**4**) (15.1 mg) and **5** (10.3 mg); fr. III: **1** (25.1 mg), **2** (22.3 mg), **3** (15.0 mg) and **4** (40.1 mg); fr. IV: **1** (6.5 mg), **3** (6.9 mg) and **4** (3.6 mg).

Oleuropein (**1**). Amorphous powder, $[\alpha]_D^{26}$ −164° (*c* 1.26, MeOH); UV λ_{max}^{MeOH} nm (log ε): 232.5 (4.19), 282.5 (3.47); IR ν_{max}^{KBr} cm^{-1}: 3425, 1738, 1713, 1634, 1521, 1076, 816; ^{1}H NMR as in ref. [4]; SIMS *m/z*: 563 $[M + Na]^+$, 541 $[M + H]^+$, 361, 165, 137.

Ligstroside (**2**). Amorphous powder, $[\alpha]_D^{28}$ −161° (*c* 0.72, MeOH); UV λ_{max}^{MeOH} nm (log ε): 227 (4.19), 239sh (4.07), 277 (3.24), 285sh (3.14); IR ν_{max}^{KBr} cm^{-1}: 3419, 1731, 1715, 1634, 1518, 1076, 818; ^{1}H NMR as in ref. [4]; SIMS *m/z*: 547 $[M + Na]^+$, 345, 165, 121, 115.

Gl 5 (**3**). Amorphous powder, $[\alpha]_D^{25}$ −180° (*c* 0.47, MeOH); UV λ_{max}^{MeOH} nm (log ε): 235.5 (4.34); IR ν_{max}^{KBr} cm^{-1}: 3419, 1731, 1705, 1634, 1508, 1076, 818; ^{1}H NMR (CD_3OD): δ1.59 (3H, *dd*, *J* = 7.0, 1.5 Hz, H_3-10a), 1.76 (3H, *dd*, *J* = 7.0, 1.0 Hz, H_3-10b), 2.44 (1H, *dd*, *J* = 14.0, 9.5 Hz, H-6a), 2.70 (1H, *dd*, *J* = 14.0, 4.5 Hz, H-6a), 2.73 (1H, *dd*, *J* = 14.0, 9.5 Hz, H-6b), 2.93 (2H, *t*, *J* = 6.5 Hz, H_2-2″), 2.97 (1H, *dd*, *J* = 14.0, 4.5 Hz, H-6b), 3.29–3.44 (8H, *m*, H-2′a, 3′a, 4′a, 5′a and H-2′b, 3′b, 4′b, 5′b), 3.64, 3.66 (each 1H, *dd*, *J* = 12.0, 5.5 Hz, H-6′a, H-6′b), 3.71, 3.73 (each 3H, *s*, 2 × OMe), 3.83 (1H, *br d*, *J* = 12.0 Hz, H-6′a or H-6′b), 3.89 (1H, *dd*, *J* = 12.0, 1.5 Hz, H-6′b or H-6′a), 3.94 (1H, *dd*, *J* = 9.0, 4.5 Hz, H-5a), 4.12 (1H, *dd*, *J* = 9.0, 4.5 Hz, H-5b), 4.16, 4.29 (each 1H, *dt*, *J* = 11.0, 6.5 Hz, H_2-1″), 4.81 (1H, *d*, *J* = 7.5 Hz, H-1′a), 4.83 (1H, *d*, *J* = 7.5 Hz, H-1′b), 5.92 (1H, *br s*, H-1a), 6.04 (1H, *br s*, H-1b), 6.06 (1H, *qd*, *J* = 7.0, 1.0 Hz, H-8a), 6.18 (1H, *qd*, *J* = 7.0, 1.0 Hz, H-8b), 7.03 (2H, AA′BB′ pattern, *J* = 8.5 Hz, H-5″, H-7″), 7.28 (2H, AA′BB′ pattern, *J* = 8.5 Hz, H-4″, H-8″), 7.51 (1H, *s*, H-3a), 7.57 (1H, *s*, H-3b); ^{13}C NMR (CD_3OD): δ13.58 (C-10a), 13.84 (C-10b), 31.83, (C-5b), 31.91 (C-5a), 35.35 (C-2″), 41.14 (C-6b), 41.25 (C-6a), 51.97, 52.02 (2 × OCH_3), 62.70, 62.85 (C-6′a, C-6′b), 66.44 (C-1″), 71.47, 71.59 (C-4′a, C-4′b), 74.81 × 2 (C-2′a, C-2′b), 77.96 × 2 (C-3′a, C-3′b), 78.44, 78.49 (C-5′a, C-5′b), 95.20 (C-1a), 95.40 (C-1b), 100.90 (C-1′a), 101.05 (C-1′b), 109.37 (C-4b), 109.41 (C-4a), 122.75 × 2 (C-5″, C-7″), 124.99 (C-8a), 125.18 (C-8b), 130.42 (C-9a), 130.67 (C-9b), 131.09 × 2 (C-4″, C-8″), 137.24 (C-3″), 150.83 (C-6″), 155.19 (C-3a), 155.32 (C-3b), 168.67, 168.70 (C-11a, C-11b), 171.63 (C-7b), 173.15 (C-7a); SIMS *m/z*: 933 $[M + Na]^+$, 911 $[M + H]^+$, 165, 137, 115.

Jaspolyoside: [2S-(2α,3E,4β)]-3-*ethylidene*-2-[6-O-([2S-(2α,3E,4β)]-{[3-*ethylidene*-2-(β-D-*glucopyranosyloxy*)-3,4-*dihydro*-5-(*methoxycarbonyl*)-2H-*pyran*-4-*yl*]*acetyloxy*}-β-D-*glucopyranosyl*]-3,4-*dihydro*-5-(*methoxycarbonyl*)-2H-*pyran*-4-*acetic acid* 2-(3,4-*dihydroxy phenyl*) *ethyl ester* **4**. Amorphous powder, $[\alpha]_D^{26}$ −198° (*c* 0.99, MeOH); UV λ_{max}^{MeOH} nm (log ε): 234.5 (4.41), 282 (3.46); IR ν_{max}^{KBr} cm^{-1}: 3425, 1732, 1717, 1636, 1506, 1076, 816; ^{1}H and ^{13}C NMR (CD_3OD): Table 1; HR-SIMS Found: 949.2979 $[M + Na]^+$; $C_{42}H_{54}O_{23}Na$ requires 949.2955.

Jaspolyanthoside: [2S-(2α,3E,4β)]-3-([2S-(2α,3E,4β)]-{[3-*ethylidene*-2-(β-D-*glucopyranosyloxy*)-3,4-*dihydro*-5-(*methoxycarbonyl*)-2H-*pyran*-4-*yl*]*acetyloxy*}) *ethylidene*-2-(β-D-*glucopyranosyloxy*)-3,4-*dihydro*-5-(*methoxycarbonyl*)-2H-*pyran*-4-*acetic acid methyl ester* **5**. Crystalline solid, mp 127–130° (MeOH–H_2O) $[\alpha]_D^{22}$ −197° (*c* 1.03, MeOH); UV λ_{max}^{MeOH} nm (log ε): 236 (4.33); IR ν_{max}^{KBr} cm^{-1}: 3427, 1733, 1715, 1634, 1074, 816; ^{1}H and ^{13}C NMR (CD_3OD): Table 1; SIMS *m/z*: 843 $[M + Na]^+$, 641, 255, 225, 165. HR-SIMS found: 843.2551 $[M + Na]^+$; $C_{35}H_{48}O_{22}Na$ requires 843.2536.

Acetylation of glucoside **4**. Glucoside **4** (18.0 mg) was acetylated with Ac_2O-pyridine and the crude acetate (27.4 mg) was purified by prep. TLC with Et_2O to yield **7** (22.3 mg) as an amorphous powder. $[\alpha]_D^{26}$ −138° (*c* 1.07, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 234 (4.31); IR ν_{max}^{KBr} cm^{-1}: 1759, 1709, 1636, 1506, 1070, 816; ^{1}H NMR ($CDCl_3$): δ1.68 (3H, *dd*, *J* = 7.0, 1.0 Hz, H_3-10a or H_3-10b), 1.75 (3H, *dd*, *J* = 7.0, 1.5 Hz, H_3-10b or H_3-10a), 2.00, 2.01, 2.021, 2.022, 2.026, 2.028, 2.08, 2.28, 2.29 (each 3H, *s*, 9 × Ac), 2.40 (1H, *dd*, *J* = 14.5, 8.0 Hz, H-6a or H-6b), 2.45 (1H, *dd*, *J* = 15.0, 8.0 Hz, H-6b or H-6a), 2.70 (1H, *dd*, *J* = 14.5, 5.0 Hz, H-6a or H-6b), 2.71 (1H, *dd*, *J* = 15.0, 5.0 Hz, H-6b or H-6a), 2.91 (2H, *t*, *J* = 7.0 Hz, H_2-2″), 3.70, 3.72 (each 3H, *s*, 2 × OMe), 3.76 (2H, *br ddd*, *J* = 9.5, 4.0, 2.0 Hz, H-5′a, H-5′b), 3.95 (2H, *br dd*, *J* = 8.0, 5.0 Hz, H-5a, H-5b), 4.11 (1H, *dd*, *J* = 12.5, 2.0 Hz, H-6′a or H-6′b), 4.12 (1H, *dd*, *J* = 12.5, 2.5 Hz, H-6′b or H-6′a), 4.18 (1H, *dt*, *J* = 11.0, 7.0 Hz, H-1″), 4.24 (1H, *dd*, *J* = 12.5, 4.5 Hz, H-6′a or H-6′b), 4.26 (1H, *dt*,

J = 11.0, 7.0 Hz, H-1″), 4.31 (1H, *dd*, J = 12.5, 4.5 Hz, H-6′b or H-6′a), 5.02, 5.03 (each 1H, *d*, J = 8.0 Hz, H-1′a, H-1′b), 5.11 (2H, *dd*, J = 9.5, 8.0 Hz, H-2′a, H-2′b), 5.12, 5.13 (each 1H, *t*, J = 9.5 Hz, H-4′a, H-4′b), 5.26, 5.27 (each 1H, *t*, J = 9.5 Hz, H-3′a, H-3′b), 5.67, 5.70 (each 1H, *br s*, H-1a, H-1b), 5.97, 6.00 (each 1H, *qd*, J = 7.0, 0.5 Hz, H-8a, H-8b), 7.05 (1H, *d*, J = 2.0 Hz, H-4″), 7.09 (1H, *dd*, J = 8.0, 2.0 Hz, H-8″), 7.12 (1H, *d*, J = 8.0 Hz, H-7″), 7.445, 7.452 (each 1H, *s*, H-3a, H-3b); SIMS *m/z*: 1327 $[M + Na]^+$.

Acetylation of glucoside **5**. Conventional acetylation of glucoside **5** (19.2 mg) and subsequent purification of the crude acetate (26.3 mg) by prep. TLC with Et_2O yielded **9** (20.7 mg) as an amorphous powder. $[\alpha]_D^{25}$ − 162° (*c* 1.38, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 234.5 (4.36); IR ν_{max}^{KBr} cm^{-1}: 1759, 1747, 1709, 1636, 1072, 816; ^1H NMR ($CDCl_3$): δ1.75 (3H, *dd*, J = 7.0, 1.5 Hz, H_3-10b), 2.02, 2.03, 2.04, 2.09 (24H, each *s*, 8 × Ac), 2.43 (1H, *dd*, J = 15.5, 9.0 Hz, H-6a or H-6b), 2.45 (1H, *dd*, J = 15.0, 9.0 Hz, H-6b or H-6a), 2.75 (1H, *dd*, J = 15.0, 4.5 Hz, H-6b or H-6a), 2.80 (1H, *dd*, J = 15.5, 4.5 Hz, H-6a or H-6b), 3.63, 3.73, 3.74 (each 3H, *s*, 3 × OMe), 3.77 (2H, *m*, H-5′a, H-5′b), 3.95, 3.98 (each 1H, *dd*, J = 9.0, 4.5 Hz, H-5a, H-5b), 4.13 (2H, *dd*, J = 12.5, 1.5 Hz, H-6′a, H-6′b), 4.30 (1H, *dd*, J = 12.5, 5.0 Hz, H-6′a or H-6′b), 4.33 (1H, *d*, J = 12.5, 4.5 Hz, H-6′b or H-6′a), 4.71 (1H, *ddd*, J = 13.5, 6.0, 1.5 Hz, H-10a), 4.78 (1H, *br dd*, J = 13.5, 7.0 Hz, H-10a), 5.03, 5.04 (each 1H, *d*, J = 8.0 Hz, H-1′a, H-1′b), 5.11, 5.12 (each 1H, *dd*, J = 9.5, 8.0 Hz, H-2′a, H-2′b), 5.13, 5.14 (each 1H, *t*, J = 9.5 Hz, H-4′a, H-4′b), 5.271, 5.272 (each 1H, *t*, J = 9.5 Hz, H-3′a, H-3′b), 5.71 (2H, *br s*, H-1a, H-1b), 6.00 (1H, *br dd*, J = 7.0, 6.0 Hz, H-8a), 6.02 (1H, *br q*, J = 7.0 Hz, H-8b), 7.46 (2H, *s*, H-3a, H-3b); SIMS *m/z*; 1179 $[M + Na]^+$.

Acknowledgements—We are grateful to Dr H. Nayeshiro (Sunstar Inc., Osaka, Japan) for supply of the crude drug. Thanks are also due to Dr M. Sugiura (Kobe Pharmaceutical University) for ^1H and ^{13}C NMR spectra and to Dr K. Saiki (Kobe Pharmaceutical University) for mass spectra measurements.

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