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IRIDOIDAL GLYCOSIDES FROM *JASMINUM SAMBAC*

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Key Word Index—*Jasminum sambac*; Oleaceae; flower; iridoidal glycosides; molihuasides A–E.

Abstract—Besides a known trimeric iridoidal glycoside, sambacoside A, five new oligomeric iridoidal glycosides, molihuasides A–E were isolated from the flowers of *Jasminum sambac*. Their structures were determined by spectral and chemical evidence. Among them, molihuasides A and C–E are new dimeric iridoidal glycosides and molihuaside B is a new trimeric iridoidal glycoside.

INTRODUCTION

Jasminum sambac (L.) Ait., is a famous oleaceous plant originating in India. As a fragrant plant, it is now widely cultivated in tropical, subtropical and temperate zones of the whole world, and its flowers are used for the preparation of an essential oil and for making jasmine tea (or Mo-Li-Hua-Cha). In addition, the flower can be used as a drug for the treatment of diarrhoea, abdominal pain, conjuctivitis and dermatitis. The leaves and roots of this plant are used for treating diarrhoea and fever, and as an anaesthestic and an analgesic, respectively [1, 2]. Some chemical studies that have been reported on this plant: from its leaves and stems, triterpenoids [3], flavonoids [4] and iridoidal glycosides [5–7] have been isolated, and the constituents of the essential oil of its flowers have been determined by GC-MS [8]. In China, besides infusing 'jasmine tea' with the flower fragrance, it is common to mix the flowers with tea in boiling water to drink. We investigated further the water-soluble fraction of the flowers of *J. sambac* and isolated six oligomeric iridoidal glycosides. We now report on the structure elucidation of these compounds.

RESULTS AND DISCUSSION

Five new oligomeric iridoidal glycosides (**1**–**5**) and sambacoside A (**6**) the *n*-butanol-soluble fraction of a methanol extract from the flowers of *J. sambac*. Sambacoside A was identified by comparing its physical data (FAB-MS, ^{1}H and ^{13}C NMR) with the reported values [7].

Compound **1** was assigned the molecular formula $C_{44}H_{64}O_{24}$ (negative FAB-MS: $[M-H]^-$ *m/z* 975). Comparison of the ^{13}C NMR spectrum of **1** with that of **6** revealed that it possessed the same basic skeleton as **6**. The difference between them was the absence of an iridoidal glycoside unit (**A**: oleoside methyl ester unit) at the C-10″ position of the tetraol part in **1**, causing the downfield shift of the C-8″ signal of the tetraol part from δ44.4 in **6** to δ47.5 in **1**, and the upfield shift of the C-10″ signal of the tetraol part from δ64.4 in **6** to δ61.9 in **1**. The absence of an oleoside methyl ester unit at the C-10″ position of the tetraol part of **1** was further confirmed by the demonstration that on alkaline hydrolysis **6** gave rise to **1** and **11**. Comparison of the ^{1}H and ^{13}C NMR spectra of **11** with that of **6** revealed that **11** had only one unit of **A** linked to the C-5″ position of the tetraol part, causing the downfield shift of the C-2″ signal from δ49.4 in **6** δ52.3 in **11** and of the C-8″ signal from δ44.4 in **6** to δ47.9 in **11**, and the upfield shift of the C-7″ signal from δ68.1 in **6** to δ65.8 in **11** and of the C-10″ signal from δ64.4 in **6** to δ62.3 in **11**, determining the structure of **11**. Therefore, the structure of **1** was established, and named molihuaside A. Compound **1** is a new iridoidal glycoside that has not been reported before.

Compound **2** was assigned the molecular formula $C_{61}H_{86}O_{34}$ (negative ion FAB-MS: $[M-H]^- = m/z$ 1361). Comparison of the ^{13}C NMR spectrum with that of **6** revealed that they had the same basic skeleton, in which three iridoidal glycoside units were linked to a tetraol part and the linkage positions in the tetraol part in **2** were the same as those of **6**. The difference between them was that, besides two units of **A**, **2** had another iridoidal glycoside unit, a secoxyloganin unit (**B**), which was determined by comparing the ^{13}C NMR spectrum with that of the secoxyloganin [8]. On partial alkaline hydrolysis, **2** afforded compound tetraol (**7**) and **9**–**11**. The negative ion FAB-mass spectrum of **9** showed that its molecular formula was $C_{44}H_{64}O_{24}$, ($[M-H]^- = m/z$ 975). Comparison of the ^{1}H and ^{13}C NMR spectra of **9** with those of **1** revealed that **9** was very similar to **1**, i.e. two iridoidal glycoside units were linked to the C-5″ and

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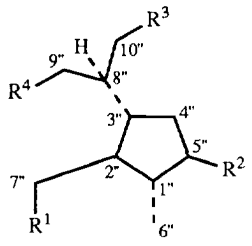
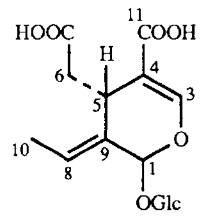


	R1	R2	R3	R4
1	A	A	OH	OH
2	B	A	A	OH
3	OH	A	A	OH
4	A	OH	A	OH
5	A	OH	OH	A
6	A	A	A	OH
7	OH	OH	OH	OH
9	B	A	OH	OH
10	B	A	OH	A
11	OH	A	OH	OH



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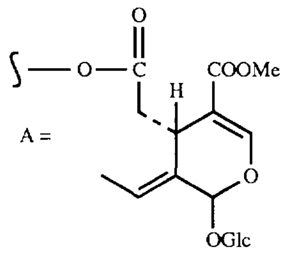

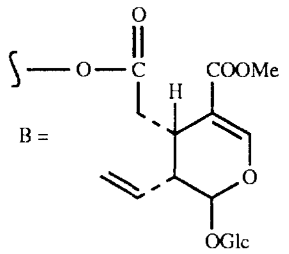

the C-7'' position of the tetraol part. The only difference between them was that **9** had two kinds of iridoidal glycoside unit (**A** and **B**). Since **11** only had 1 mol of **A** linked at C-5'', the unit of **B** in **9** should be linked at C-7''. Thus, the structure of **9** was established. The negative ion FAB-mass spectrum of **10** showed that its molecular formula was $C_{61}H_{86}O_{34}$, ($[M - H]^- = m/z$ 1361). The spectral data of this compound indicated that it was an epimer of **2**. On comparison of the ^{13}C NMR spectrum of **10** with that of a known compound, sambacoside F [7], which is an epimer of **6** and its three iridoidal glycoside units are linked to C-5'', C-7'' and C-9'' positions of the tetraol part, revealed that they had the same basic skeleton, and the linkage positions of three iridoidal glycoside units on the tetraol part in **10** and sambacoside F were the same. The difference between them was that besides two units of **A**, **10** had another iridoidal glycoside unit as **B**. Since **10** was the product of partial alkaline hydrolysis of **2**, the position of **B** in **10** was the same of that of **2**. From the above evidence, the structure of **2** was determined, and named molihuaside B. The structure of **10** was also determined. Both compounds **9** and **10** are new oligomeric iridoidal glycosides that have not been reported before.

Compounds **4** and **5** were both assigned the molecular formula $C_{44}H_{64}O_{24}$ (negative FAB-MS: $[M-Me]^- = m/z$ 961 for **4** and $[M - H]^- = m/z$ 975 for **5**). Alkaline hydrolysis of **5** afforded tetraol (**7**) and oleoside (**8**) which were identified by comparison of their spectral data with those of the reported values, indicating that **5** was composed of tetraol and oleoside methyl ester moieties. The UV, IR ^{1}H and ^{13}C NMR spectral features of **4** and **5** were closely similar, but their $[\alpha]_D$ values and R_f values on reverse phase TLC (Rp-8) were different. Comparison of their ^{13}C NMR spectra with that of **6** revealed that both **4** and **5** lacked 1 mol of **A** at the C-5'' position of the tetraol part, causing the signals of C-1'' and C-4'' of the tetraol part to shift downfield and the signal of C-5'' of the tetraol part to shift upfield. Thus, **4** and **5** had 1 mol of **A** linked at the C-7'' position of the tetraol part, and 1 mol of **A** attached to the C-9'' or 10'' position of the tetraol part, which was the difference between glycosides **4** and **5**. The absolute configuration of C-8'' was different in **4** and **5**. Thus **4** and **5** are epimers. The CD spectra of **4** and **6** were very similar, indicating that **4** was like **6**, and the absolute configuration of all the chiral carbons (C-1'', C-2'', C-3'', C-5'', C-8'', etc.) were the same as those of **6**. Thus, one of the iridoidal glycoside moieties (**A**) was linked at the C-10'' position of the tetraol part. Accordingly, the structure of **4** was determined, and named as molihuaside D. Since 1 mol of **A** was linked at C-10'' in **4**, the mol of **A** in **5** was linked at the C-9'' position of the tetraol part. The CD spectrum of **5** was different with those of **4** and **6** and indicated that the absolute configuration of C-8'' of the tetraol part was of the opposite configuration. Thus, the mol of **A** was determined to be linked at the C-9″ position of the tetraol part in **5**. Accordingly, the structure of **5** was established, and named as molihuaside E.

Compound **3** was assigned the molecular formula $C_{44}H_{64}O_{24}$ (negative FAB-MS: $[M-Me]^- = m/z$ 961). The spectral data of this compound indicated that it was an isomer of **1**, **4** and **5**. Comparison of the ^{13}C NMR spectrum of **3** with that of **6** revealed that they possessed the same basic skeleton. The difference between them was the absence of an iridoidal glycoside unit (**A**) at the C-7″ position of the tetraol part in **3**, causing the downfield shift of the signal of C-2″ of the tetraol part from δ49.7 in **6** to δ52.2 in **3** and the upfield shift of the signal of C-7″ of the tetraol part from δ68.1 in **6** to δ65.2 in **3**. Thus, the 2 mol of **A** were linked at C-5″ and the C-10″ or C-9″ position of the tetraol part in **3**. Comparing the CD spectrum of **3** with that of **6** revealed that **3** was like **6**, and, therefore the absolute configuration of all the chiral carbons (C-1″, C-2″, C-3″, C-5″, C-8″, etc.) were the same as those of **6**. Thus, one of the iridoidal glycoside moieties (**A**) was linked at the C-10″ position of the tetraol part. Accordingly, the structure of **3** was established, and named molihuaside C.

EXPERIMENTAL

MPs: uncorr.; UV: EtOH; IR: KBr; ^{1}H (400 MHz) and ^{13}NMR: CD_3OD with TMS as int. standard; FAB-MS: JAB-HS mass spectrometer.

Extraction and isolation. Dried flowers of *Jasminum sambac* (2.18 kg) were refluxed with MeOH. After removal of the solvent *in vacuo*, the residue (500 g) was suspended in H_2O and then successively extracted with petrol, $CHCl_3$ and *n*-BuOH. The *n*-BuOH layer was concd *in vacuo* to give a viscous residue (126.5 g), of which 80 g was chromatographed on a silica gel column, eluting with $CHCl_3$-MeOH-H_2O (40:10:1–10:10:1) to give 6 frs (1–6). Fr. 3 (19.5 g) was chromatographed on a silica gel column, eluting with $CHCl_3$-MeOH (9:1–7:3) and then repeatedly chromatographed on a reverse phase column of RP-8, eluting with aq. MeOH (63 or 43%) to give **6** (3.208 g), **1** (4.739 g) and **3** (1.017 g). Fr. 4 (5 g) was chromatographed on a Sephadex column eluting with aq. MeOH (57%) and then repeatedly chromatographed on a reverse phase column of RP-8 eluting with aq. MeOH (57 or 43%) to afford **2** (90 mg), **4** (80 mg) and **5** (200 mg).

Molihuaside A (**1**). A yellowish powder from MeOH, mp 121–124°; $[\alpha]_D^{25}$ −203.4° (MeOH; *c* 0.23); UV λ_{max} nm (log ε): 238 (4.29), 201 (3.76); IR ν_{max} cm^{-1}: 3400, 1705, 1625, 1435, 1305, 1075; FAB-MS *m/z*: 975 $[M-H]^-$; ^{1}H NMR (CD_3OD): 1.05 (3H, *d*, *J* = 7.0 Hz, H-6″), 1.75 (6H, *br d*, *J* = 7.0 Hz, H-10 × 2), 3.72 (6H, *s*, OMe × 2), 4.81 (2H, *d*, *J* = 8.0 Hz, H-1′ × 2), 5.93 (2H, *br s*, H-1 × 2), 6.11 (2H, *br q*, *J* = 7.0 Hz, H-8 × 2), 7.53 (2H, *s*, H-3 × 2); ^{13}C NMR: Table 1.

Molihuaside B (**2**). An amorphous powder from MeOH, mp 128–131°; $[\alpha]_D^{25}$ −176.2° (MeOH; *c* 0.32); UV λ_{max} nm (log ε): 233 (4.35), 202 (4.09); IR ν_{max} cm^{-1}: 3400, 1705, 1625, 1435, 1305, 1705; FAB-MS *m/z*: 1361 $[M-H]^-$; ^{1}H NMR (CD_3OD): δ1.06 (3H, *d*, *J* = 7.0 Hz, H-6″), part **A**: δ1.75 (6H, *d*, *J* = 7.0 Hz, H-10 × 2), 3.72 (6H, *s*, OMe × 2), 4.82, 4.81 (each 1H, *d*, *J* = 8.0 Hz, H-1′), 5.94, 5.93 (each 1H, *s*, H-1), 6.11 (2H, *br q*, *J* = 7.0 Hz, H-8 × 2), 7.54, 7.53 (each 1H, *s*, H-3); part **B**: δ3.68 (3H, *s*, OMe), 4.66 (1H, *d*, *J* = 8.0 Hz, H-1′), 5.25 (2H, *dd*, *J* = 18, 10 Hz, H-10), 5.48 (1H, *d*, *J* = 4.0 Hz, H-1), 5.64 (1H, *m*, H-8), 7.48 (1H, *d*, *J* = 1.6 Hz, H-3); ^{13}C NMR: Table 1.

Molihuaside C (**3**). An amorphous powder from MeOH, mp 140–143°; $[\alpha]_D^{25}$ − 180.9° (MeOH; *c* 0.28); IR ν_{max} cm^{-1}: 3400, 1700, 1625, 1432, 1300, 1075; FAB-MS *m/z*: 961 $[M-Me]^-$; CD: $[\theta]_{195}$ -4.88×10^7, $[\theta]_{255}$ -7.59×10^7 (MeOH; *c* 0.074%); ^{1}H NMR (CD_3OD): 1.04 (3H, *d*, *J* = 7.0 Hz, H-6″), 1.74 (6H, *br s*, H-10 × 2), 3.72 (6H, *s*, OMe × 2), 4.81 (2H, *br d*, *J* = 7.0 Hz, H-1′ × 2), 5.94, 5.90 (each 1H, *br s*, H-1), 6.09 (2H, *m*, H-8 × 2), 7.53, 7.48 (each 1H, *s*, H-3); ^{13}C NMR: Table 1.

Molihuaside D (**4**). A yellowish amorphous powder from MeOH, mp 151–154°; $[\alpha]_D^{25}$ −153.3° (MeOH; *c* 0.26); UV λ_{max} nm (log ε): 235 (4.24), 200 (4.11); IR ν_{max} cm^{-1}: 3400, 1700, 1625, 1430, 1300, 1075; FAB-MS *m/z*: 971 $[M-Me]^-$; CD: $[\theta]_{198}$ -4.96×10^7, $[\theta]_{227}$ -6.77×10^7, $[\theta]_{231}$ -6.81×10^7 (MeOH; *c* 0.06%); ^{1}H NMR (CD_3OD): 1.04 (3H, *d*, *J* = 6.0 Hz, H-6″), 1.75 (6H, *br d*, *J* = 7.0 Hz, H-10 × 2), 3.71 (6H, *s*, OMe × 2), 4.81 (2H, *d*, *J* = 8.0 Hz, H-1′ × 2), 5.93 (2H, *br s*, H-1 × 2), 6.10 (2H, *m*, *J* = 7.0 Hz, H-8 × 2), 7.53, 7.52 (each 1H, *s*, H-3); ^{13}C NMR; Table 1.

Molihuaside E (**5**). A yellowish amorphous powder from MeOH, mp 123–126; $[\alpha]_D^{25}$ −190.8° (MeOH; *c* 0.26); UV λ_{max} nm (log ε): 237 (4.36), 201 (3.88); IR ν_{max} cm^{-1}: 3400, 1705, 1625, 1435, 1305, 1075; FAB-MS *m/z*: 975 $[M-H]^-$; CD: $[\theta]_{208}$ -2.60×10^7, $[\theta]_{250}$ -8.4×10^6, $[\theta]_{256}$ -1.10×10^7 (MeOH; *c* 0.05%); ^{1}H NMR (CD_3OD): 1.04 (3H, *d*, *J* = 6.0 Hz, H-6″), 1.75 (6H, *br d*, *J* = 7.0 Hz, H-10 × 2), 2.49 (2H, *dd*, *J* = 9.0, 14.0 Hz, H_A-6 × 2), 2.72 (2H, *dd*, *J* = 4.0, 14.0 Hz, H_B-6 × 2), 3.72 (6H, *s*, OMe × 2), 4.81 (2H, *d*, *J* = 8.0 Hz, H-1′ × 2), 5.93 (2H, *br s*, H-1 × 2), 6.11 (2H, *br q*, *J* = 7.0 Hz, H-8 × 2), 7.53 (2H, *s*, H-3 × 2); ^{13}C NMR: Table 1.

Sambacoside A (**6**). An amorphous powder from MeOH, mp 145–147°; $[\alpha]_D^{28}$ −187.8° (MeOH; *c* 0.82); UV λ_{max} nm (log ε): 237 (4.54), 201 (4.00); IR ν_{max} cm^{-1}: 3400, 1705, 1625, 1435, 1302, 1705; FAB-MS *m/z*: 1361 $[M-H]^-$; CD: $[\theta]_{195}$ -9.90×10^7, $[\theta]_{229}$ -1.41×10^8, $[\theta]_{233}$ -1.41×10^8 (MeOH; *c* 0.06%); ^{1}H NMR (CD_3OD): 1.06 (3H, *d*, *J* = 7.0 Hz, H-6″), 1.75 (9H, *br d*, *J* = 7.0 Hz, H-10 × 3), 3.72 (9H, *s*, OMe × 3), 4.82 (3H, *d*, *J* = 8.0 Hz, H-1′ × 3), 5.93 (3H, *br s*, H-1 × 3), 6.09 (3H, *br q*, *J* = 7.0 Hz, H-8 × 3), 7.54 (3H, *s*, H-3 × 3); ^{13}C NMR: Table 1.

Partial alkaline hydrolysis of **2**. A soln of **2** (84 mg) in 0.5 ml diethyl amine/100 ml MeOH (3 ml) was heated at 60° for 28 hr, and then neutralized with Amberlite MB-3. The resulting residue, after concn *in vacuo*, was subjected to a reverse phase of RP-8 column, eluting with aq. MeOH (57%) to give **9** (10 mg), **10** (12 mg) and **2** (20 mg).

Compound **9**. Powder, mp 122–124°; $[\alpha]_D^{25}$ −161.8° (MeOH; *c* 0.22); FAB-MS *m/z*: 975 $[M-H]^-$; ^{1}H NMR (CD_3OD): δ1.04 (3H, *d*, *J* = 7.0 Hz, H-6″); part *A*: δ1.75

Table 1. ^{13}C NMR spectral data of **1**–**11** (in CD_3OD)

C	**1**	**3**	**4**	**5**	**6**	**7**	**8**	**11**	**2**		**9**		**10**	
Tetraol														
1″	44.3	44.8	46.6	46.5	44.1	46.2		43.6	44.2		44.2		44.2	
2″	49.6	52.2	49.6	49.4	49.4	52.0		52.3	49.7		49.8		49.6	
3″	39.7	39.4	39.0	38.9	39.9	38.2		39.4	40.0		39.7		40.2	
4″	34.8	35.1	36.9	36.8	34.7	37.7		35.3	34.7		34.9		34.9	
5″	83.4	83.3	79.6	79.5	83.2	79.6		83.7	83.2		83.4		83.1	
6″	19.1	19.0	18.4	18.4	19.0	18.6		19.0	18.9		18.9		18.8	
7″	68.5	62.3	68.4	68.3	68.1	66.1		65.8	67.6		68.0		67.8	
8″	47.5	43.3	44.9	44.8	44.4	48.4		47.9	44.1		47.3		44.3	
9″	62.8	65.2	64.5	62.4	62.4	63.1		63.2	62.6		63.4		65.8	
10″	61.9	64.5	62.6	64.4	64.4	62.5		62.3	64.4		62.1		61.0	
Iridoidal part									part **A**	part **B**	part **A**	part **B**	part **A**	part **B**
1	95.1	95.2	95.2	95.1	95.1		95.3	95.3	95.2	97.6	95.2	97.6	95.3	97.6
3	155.2	155.1	155.1	155.1	155.2		153.9	155.1	155.1	153.7	155.1	153.7	155.1	153.7
4	109.4	109.4	109.5	109.4	109.4		111.7	109.5	109.5	110.0	109.5	110.0	109.5	110.0
5	31.9	31.9	31.9	31.9	31.9		32.5	31.9	32.0	29.1	31.9	29.1	31.8	29.1
6	41.3	41.3	41.3	41.3	41.3		42.8	41.3	41.3	35.6	41.4	35.6	41.4	35.6
7	173.1	173.1	173.4	173.2	173.2		177.1	173.1	173.0	174.3	173.0	174.3	173.2	174.3
8	124.9	124.9	124.9	124.8	124.8		124.0	124.7	124.9	135.6	124.7	135.6	125.0	135.6
9	130.8	130.8	130.8	130.6	130.8		131.5	130.9	130.8	45.4	130.4	45.4	130.7	45.4
10	13.8	13.7	13.7	13.8	13.8		13.7	13.9	13.8	120.7	13.7	120.7	13.8	120.7
11	168.7	168.6	168.7	168.6	168.0		171.4	168.7	168.8	168.8	168.8	168.8	168.8	168.7
OMe	52.0	52.0	52.0	52.0	52.0			51.9	52.0	51.8	52.0	51.8	52.0	51.8
Glucose														
1′	100.8	100.8	100.9	100.8	100.8		101.0	100.9	100.9	100.1	100.9	100.1	100.9	100.1
2′	74.8	74.8	74.8	74.7	74.7		74.8	74.8	74.6	74.8	74.7	74.8	74.6	74.8
3′	78.4	78.4	78.4	78.4	78.4		78.3	78.5	78.4	78.4	78.4	78.4	78.4	78.4
4′	71.4	71.5	71.5	71.4	71.5		71.5	71.5	71.6	71.6	71.6	71.6	71.6	71.6
5′	77.9	78.0	78.0	77.9	77.9		77.9	78.0	78.0	78.0	78.0	78.0	78.0	78.0
6′	62.8	62.7	62.8	62.7	62.8		62.7	62.8	62.8	62.9	62.9	62.9	62.8	62.8

(3H, *d*, $J = 6.0$ Hz, H-10), 3.71 (3H, *s*, OMe), 4.80 (1H, *d*, $J = 8.0$ Hz, H-1′), 5.92 (1H, *br s*, H-1), 6.10 (1H, *br q*, $J = 7.0$ Hz, H-8), 7.52 (1H, *s*, H-3); part **B**: δ3.67 (3H, *s*, OMe), 4.65 (1H, *d*, $J = 8.0$ Hz, H-1′), 5.24 (2H, *dd*, $J = 17$, 10 Hz, H-10), 5.48 (1H, *d*, $J = 4.0$ Hz, H-1), 5.61 (1H, *m*, H-8), 7.48 (1H, *d*, $J = 1.6$ Hz, H-3); ^{13}C NMR: Table 1.

Compound **10**. Powder, mp 137–140°; $[\alpha]_D^{25}$ −152.2° (MeOH; *c* 0.38); FAB-MS *m/z*: 1361 $[M-H]^-$; ^{1}H NMR (CD_3OD): δ1.06 (3H, *d*, $J = 7.0$ Hz, H-6″); part **A**: δ1.75 (6H, *d*, $J = 7.0$ Hz, H-10 × 2), 3.71 (6H, *s*, OMe × 2), 4.81, 4.80 (each 1H, *d*, $J = 8.0$ Hz, H-1′), 5.94, 5.92 (each 1H, *s*, H-1), 6.10 (2H, *br q*, $J = 7.0$ Hz, H-8 × 2), 7.53, 7.52 (each 1H, *s*, H-3); part **B**: δ3.67 (3H, *s*, OMe), 4.65 (1H, *d*, $J = 8.0$ Hz, H-1′), 5.23 (2H, *m*, H-10), 5.48 (1H, *d*, $J = 4.0$ Hz, H-1), 5.61 (1H, *m*, H-8), 7.48 (1H, *d*, $J = 1.5$ Hz, H-3); ^{13}C NMR: Table 1.

Alternative partial alkaline hydrolysis of **2**. A soln of **2** (50 mg) in 0.5% K_2CO_3–100 ml MeOH (4 ml) was heated at 60° for 5 hr, and then neutralized with Amberlite MB-3. The resulting residue, after concn *in vacuo*, was subjected to a silica gel column, eluting with $CHCl_3$–MeOH–H_2O (7 : 3 : 1, lower phase) and a reverse phase of RP-8 column, eluting with 42% aq. MeOH to give **7** (2 mg) and **11** (8 mg).

Tetraol (**7**). ^{1}H NMR (CD_3OD): δ1.04 (3H, *d*, $J = 7.0$ Hz, H-6″); ^{13}C NMR data see Table 1.

Compound **11**. Powder. ^{1}H NMR (CD_3OD): δ1.03 (3H, *d*, $J = 7.0$ Hz, H-6″), 1.74 (3H, *d*, $J = 7.0$ Hz, H-10), 2.47 (1H, *dd*, $J = 9.0$, 1.4 Hz, H_A-6), 2.66 (1H, *dd*, $J = 4.0$, 14 Hz, H_B-6), 3.71 (3H, *s*, OMe), 4.80 (1H, *d*, $J = 8.0$ Hz, H-1′), 5.93 (1H, *s*, H-1), 6.10 (1H, *q*, $J = 7.0$ Hz, H-8), 7.52 (1H, *s*, H-3); ^{13}C NMR: Table 1.

Alkaline hydrolysis of **5**. A soln of **5** (100 mg) in 0.5 M NaOH (2.5 ml) was stirred for 16 hr at room temp. and then neutralized with Amberlite MB-3. The resulting residue (110 mg), after concn *in vacuo*, was subjected to prep. TLC (CH_3Cl–MeOH, 4:1) to give tetraol (**7**) (28 mg) and oleoside (**8**) (45 mg).

Oleoside (**8**). ^{1}H NMR (CD_3OD): δ1.76 (3H, *br d*, $J = 6.0$ Hz, H-10), 2.30 (1H, *dd*, $J = 10.0$, 14.0 Hz, H_A-6), 2.78 (1H, *dd*, $J = 4.0$, 14.0 Hz, H_B-6), 5.93 (1H, *s*, H-1), 6.08 (1H, *q*, H-8), 7.47 (1H, *s*, H-3); ^{13}C NMR: Table 1.

Partial alkaline hydrolysis of **6**. A soln of **6** (200 mg) in 0.5% K_2CO_3/100 ml MeOH (5 ml) was heated at 60° for 1 hr, and then neutralized with Amberlite MB-3. The resulting residue, after concn *in vacuo*, was subjected to a silica gel column (eluting with $CHCl_3$–MeOH–H_2O, 7:3:1 lower phase) and a reverse phase of RP-8 column (eluting with 57% aq. MeOH) to give **2** (12 mg) and **11** (9 mg).

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