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SECOIRIDOID AND FLAVONOID GLYCOSIDES FROM *GONOCARYUM CALLERYANUM*

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Key Word Index—*Gonocaryum calleryanum*; Icacinaceae; leaves; gonocaryosides A–D; secoiridoid glycosides; apigenin glycoside; flavonoid glycoside.

Abstract—The leaves of *Gonocaryum calleryanum* afforded four new secoiridoid glycosides acylated with 2,3-dihydroxy-2-methylbutanoic acid, three of which have a novel 10-membered dilactone-ring. From this plant, we also isolated a new flavonoid glycoside, apigenin 7-*O*-β-apiofuranosyl (1 → 6)-β-D-glucopyranoside, along with six known flavonoids and flavonoid glycosides, apigenin, apigenin-5,7-dimethyl ether, apigenin trimethyl ether, apigenin 7-*O*-glucoside, apigenin 7-*O*-neohesperidoside, and vitexin. The structure of the new glycosides was elucidated by chemical and spectral means.

INTRODUCTION

Gonocaryum calleryanum (Baill.) Becc. is distributed from Indonesia to Taiwan. Its leaves are used in Philippine folk medicine for the treatment of stomach disease [1]. From the leaves of this plant, we have isolated four new secoiridoid glycosides, named gonocaryosides A (**1**), B (**2**), C (**3**) and D (**4**), and a new flavonoid glycoside (**5**), together with six known flavonoids and flavonoid glycosides: apigenin (**6**) [2], apigenin-5,7-dimethyl ether (**7**) [3], apigenin trimethyl ether (**8**) [3], apigenin 7-*O*-glucoside (apigetrin) (**9**) [4], apigenin 7-*O*-neohesperidoside (rhoifolin) (**10**) [5] and vitexin (**11**) [6]. This paper deals with the structural elucidation of these new glycosides.

RESULTS AND DISCUSSION

The methanolic extract of *G. calleryanum* was worked-up as described in the Experimental to give the new glycosides (**1**–**5**) and known compounds (**6**–**11**). The identification of **6**–**11** was confirmed by the agreement between their NMR spectral data and the reported data for apigenin [2], apigenin-5, 7-dimethyl ether [3], apigenin trimethyl ether [3], apigenin 7-*O*-glucoside [4], apigenin 7-*O*-neohesperidoside [5] and vitexin [6], respectively.

Gonocaryoside A (**1**) was obtained as an amorphous powder. Its molecular formula was determined as $C_{22}H_{32}O_{14}$ by high-resolution FAB-mass spectrometry. The ^{13}C NMR spectrum of **1** showed the signals of a β-glucopyranosyl moiety, a trisubstituted double bond (δ153.7 and 111.3), a carbomethoxyl group (δ51.2 and 166.2) and a ketal carbon (δ96.0). The presence of these partial structures suggested that **1** was an iridoid or secoiridoid glycoside. Furthermore, two additional ester carbonyl carbon signals (δ172.2 and 175.4) were observed. On alkaline hydrolysis, glycoside **1** afforded two compounds **1a** and **b** (Scheme 1), the former of which was identified as a secoiridoid glucoside, kingisidic acid, a compound previously isolated from *Citronella gongonha* belonging to the same family (Icacinaceae) [7]. Accordingly, the secoiridoid glycoside moiety of **1** had to be the methyl ester of **1a**: kingiside, which has also been isolated from several *Lonicera* species (Caprifoliaceae) [8–11]. Compound **1b** was easily identified as 2,3-dihydroxy-2-methylbutanoic acid from its ^1H and ^{13}C NMR spectra. In order to the linkage sites between **1a** and **1b**, an HMBC experiment was performed. The result of this experiment is illustrated in Scheme 2. Thus, the glycoside **1** was designated as a unique compound having a 10-membered lactone-ring formed as a result of the two ester bonds between **1a** and **b**.

The stereochemistry of C-2′ and C-3′ was determined as follows. Oxidation of methyl angelate (**12**) and methyl tiglate (**13**) with osmium tetroxide followed by treatment with alkali yielded angliceric acid (**14**) (a mixture of L- and D-*erythro*-compounds) and tigliceric acid (**15**) (a mixture of L- and D-*threo*-compounds), respectively (Scheme 1). The ^1H and ^{13}C NMR spectra of **1b** were in complete agreement with those of **14**.

It has been reported that the enantiomers of α-hydroxycarboxylic acids can be separated by HPLC (rever-

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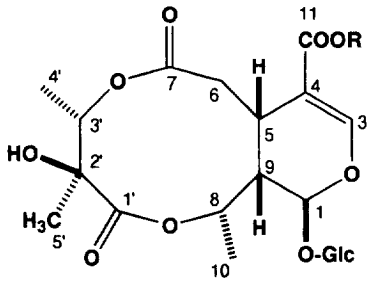
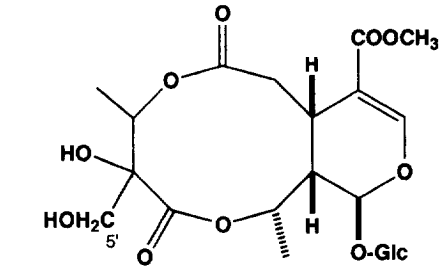


R

1: -CH_3

2: -H



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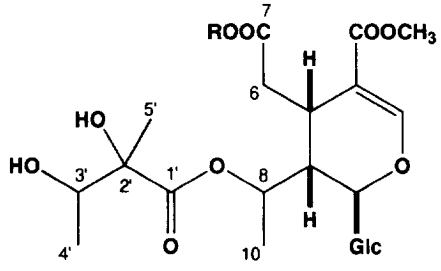
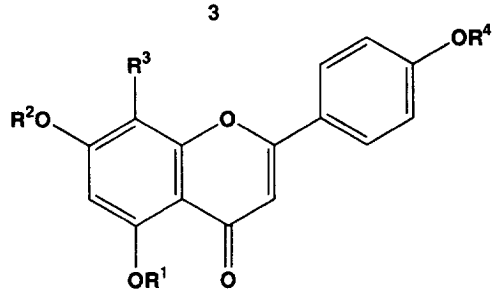


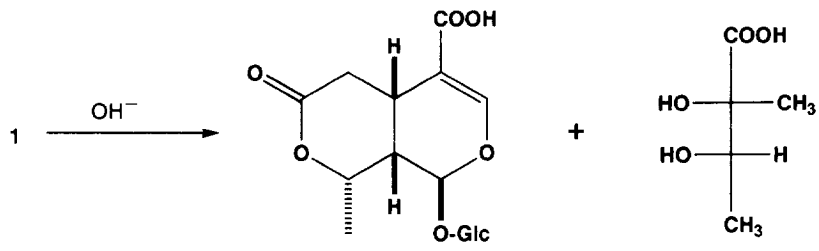
R

4: -H

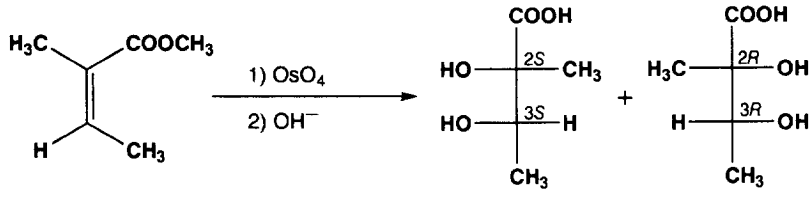
4M: -CH_3



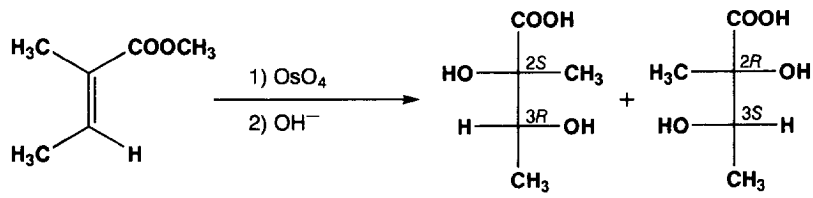
	R^1	R^2	R^3	R^4	
5:	-H	-Glc^6-Api	-H	-H	
6:	-H	-H	-H	-H	
7:	-CH_3	-CH_3	-H	-H	
8:	-CH_3	-CH_3	-H	-CH_3	
9:	-H	-Glc	-H	-H	
10:	-H	-Glc^2-Rha	-H	-H	
11:	-H	-H	-Glc	-H	(*C*-glucoside)



1a **1b**

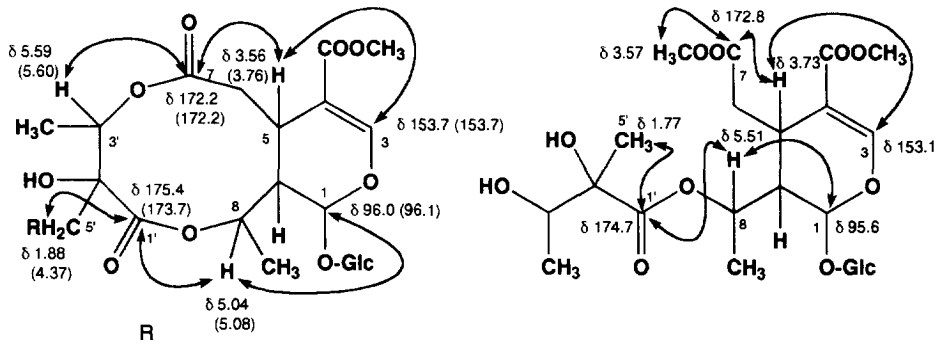


12 **14**



13 **15**

Scheme 1.



Scheme 2. C-H Long-range correlations of compounds **1**, **3** and **4M**.

sed-phase column) using an aqueous solution of *N*,*N*,-dimethyl-L-phenylalanine and copper sulphate as the mobile phase [12]. By this method, each isomer of **14** was clearly separated. The R_f of **1b** was in good agreement with that of the L-isomer of **14**. Therefore, **1b** is 2*S*,3*S*-angliceric acid. On the basis of these results, the structure of **1** was established as shown.

Gonocaryoside B (**2**) was obtained as a powder and had a molecular formula of $C_{21}H_{30}O_{14}$. The ^1H and ^{13}C NMR spectra of **2** were essentially similar to those of **1** except for the absence of the methyl signal due to the carbomethoxyl group δ_H 3.65 (3H, *s*) and δ_C 51.2 of **1**. This indicated that **1** is a methyl ester of **2**. The structure of **2** was proved by conversion of **2** to **1** on treatment with diazomethane.

By comparison of the NMR spectra, gonocaryoside C (**3**), $C_{22}H_{32}O_{15}$, was seen to be a derivative of **1**. Thus, the spectra were very similar except that the signal assigned to the C-5′ methyl group in **1** (δ_H 1.88 and δ_C 17.7) was replaced by the signals for a hydroxy-methylene group in **3** (δ_H 4.37 and δ_C 62.3). Therefore, **3** is the 5′-hydroxylated derivative of **1**. This was confirmed by the HMBC long-range correlations shown in Scheme 2.

Gonocaryoside D (**4**), $C_{22}H_{34}O_{15}$, was obtained as a powder. The ^{13}C NMR spectrum of **4** revealed the presence of the same secoiridoid and acyl moieties as in **1**. On treatment with diazomethane, glycoside **4** was converted to **4M** with an additional carbomethoxyl group. These data allowed us to propose that **4** was formed by fission of either the C-7/C-3′ or C-1′/C-8 ester bond of **1**. In the HMBC spectrum of **4M**, C–H long-range correlations were observed as illustrated in Scheme 2, demonstrating that the acyl moiety of **4** was attached to C-8. On the basis of these observations, the structure of **4** was identified as shown.

The configurations of the C-2′ and C-3′ of **3** and **4**, and C-8 of **4** seem to be the same as in **1**, but this was not confirmed because of a small amount of both samples available for analysis.

Glycoside **5**, $C_{26}H_{28}O_{14}$, was obtained as a yellow powder. Inspection of the ^{13}C NMR spectrum suggested that **5** was a flavone glycoside having two monosaccharide units. The ^{13}C NMR values of the aglycone were found to be consistent with those of **10** (and **9**), showing that **5** is a 7-*O*-glycoside of **6**. This was supported by the UV spectra of **5** in the presence of the usual shift reagents (Experimental) [13]. The signals attributable to the sugar moiety of **5** closely corresponded to those reported for the lignan glycoside, vomifoliol 3′-*O*-β-apiofuranosyl (1 → 6)-β-D-glucopyranoside (**16**) [14]. In addition, the chromatographic mobility (TLC and HPLC of **5** was different from that of apiin, apigenin 7-*O*-apiofuranosyl (1 → 2)-glucopyranoside [15] (Experimental). Thus, the structure of **5** was established as shown.

EXPERIMENTAL

General. ^1H (400 MHz) and ^{13}C (100 MHz) NMR: TMS or dioxane as int. standard; CC: silica gel (Kieselgel 60, 70–230 mesh, Merck), highly porous polymer resin (Diaion HP-20, Mitsubishi Chem. Ind., Japan) and Sephadex LH-20 (Pharamacia Fine Chem.); MPLC: ODS-AQ 120-S50 (23 mm × 42 cm, YMC, Japan); HPLC: R-ODS-10 S-10 120A, R-ODS-5 S-5 120A (4.6 mm × 25 cm, YMC, Japan) or LiChroprep RP-18 (25 mm × 25 cm, Merck). All solvent systems for chromatography were homogeneous.

Plant material. Leaves of *G. calleryanum* (BAILL.) BECC. were collected in the Makiling Plant Garden, University of Philippines, Los Baños in 1990. The plant was identified by Dr Juan V. Pancho of this university. A voucher specimen is deposited in the Institute of Pharmaceutical Sciences, Hiroshima University (No. Ica-9002).

Extraction and separation. Dried and powdered leaves (1.0 kg) were extracted with hot MeOH. After removal of the solvent by evapn, the extract (160 g) was partitioned between H_2O and Et_2O. The H_2O layer was subjected to CC on the highly porous polymer resin eluted with H_2O, MeOH and Me_2CO, successively. The MeOH eluate (48 g) was sepd into two frs, 1 and 2, by CC on silica gel using EtOAc–EtOH–H_2O (12:2:1–4:2:1). Fr. 1 was

purified by CC of Sephadex LH-20 with MeOH to give **6** (3.1 g, 0.3% from dried leaves), **7** (115 mg, 0.01%), **8** (65 mg, 0.007%), **9** (980 mg, 0.1%) and **11** (265 mg, 0.03%). Fr. 2 yielded **5** (1.1 g, 0.1%), **10** (99 mg, 0.01%) and a crude secoiridoid glycosides fr. by CC on Sephadex LH-20 with 50% MeOH. The crude fr. was purified by HPLC to afford **1** (2.8 g, 0.3%) using 40% MeOH, and **2** (118 mg, 0.1%), **3** (22 mg, 0.002%) and **4** (31 mg, 0.003%) using 22–33% MeOH.

Compound **1**. Powder; $[\alpha]_D^{28}$ −17.1° (MeOH; *c* 1.00); FAB-MS (negative): *m/z* 519.1698 $[M-H]^-$ ($C_{22}H_{31}O_{14}$ requires: *m/z* 519.1714); ^{1}H NMR (pyridine-d_5): δ7.67 (1H, *s*, H-3), 6.41 (1H, *d*, *J* = 9.9 Hz, H-1), 5.59 (1H, *q*, *J* = 6.6 Hz, H-3'), 5.45 (1H, *d*, *J* = 7.9 Hz, Glc-1), 5.04 (1H, *q*, *J* = 6.8 Hz, H-8), 4.49 (1H, *dd*, *J* = 11.7, 2.8 Hz, Glc-6a), 4.32 (1H, *dd*, *J* = 11.7, 4.9 Hz, Glc-6b), 4.31 (1H, *t*, *J* = 9.2 Hz, Glc-4), 4.24 (1H, *t*, *J* = 9.2 Hz, Glc-3), 4.07 (1H, *dd*, *J* = 9.2, 7.9 Hz, Glc-2), 4.01 (1H, *ddd*, *J* = 9.2, 4.9, 2.8 Hz, Glc-5), 3.65 (3H, *s*, OMe), 3.56 (1H, *m*, H-5), 2.76 (1H, *br d*, *J* = 13.8 Hz, H-6a), 2.55 (1H, *br d*, *J* = 13.8 Hz, H-6b), 2.15 (1H, *m*, H-9), 1.88 (3H, *s*, H-5'), 1.67 (3H, *d*, *J* = 6.8 Hz, H-10), 1.45 (3H, *d*, *J* = 6.6 Hz, H-4'); ^{13}C NMR: Table 1.

Alkaline hydrolysis of compound **1**. A soln of **1** (200 mg) in 5% aq. KOH (5 ml) was allowed to stand for 12 hr at room temp. The reaction mixture was neutralized with Dowex 50W-X8 ion-exchange resin. After removal of the solvent, the residue was dissolved in H_2O satd with NaCl, and then 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 **1b** (34 mg). From the H_2O layer, **1a** (79 mg) was obtained by silica gel CC with EtOAc–EtOH–H_2O (8:2:1). Compound **1a**: powder; FAB-MS (negative): *m/z* 389 $[M-H]^-$; ^{1}H NMR (D_2O, 50°): δ7.61 (1H, *s*, H-3), 5.83 (1H, *d*, *J* = 4.8 Hz, H-1), 5.02 (1H, *dd*, *J* = 6.8, 4.8 Hz, H-8), 4.97 (1H, *d*, *J* = 7.9 Hz, Glc-1), 4.09 (1H, *dd*, *J* = 12.4, 2.3 Hz, Glc-6a), 3.91 (1H, *dd*, *J* = 12.4, 5.6 Hz, Glc-6b), 3.69 (1H, *t*, *J* = 8.8 Hz, Glc-3), 3.64 (1H, *ddd*, *J* = 8.8, 5.6, 2.3 Hz, Glc-5), 3.61 (1H, *t*, *J* = 8.8 Hz, Glc-4), 3.59 (1H, *dd*, *J* = 8.8, 7.9 Hz, Glc-2), 3.50 (1H, *ddd*, *J* = 8.3, 7.1, 5.0 Hz, H-5), 3.24 (1H, *dd*, *J* = 16.9, 7.1 Hz, H-6a), 2.90 (1H, *dd*, *J* = 16.9, 5.0 Hz, H-6b), 2.78 (1H, *ddd*, *J* = 8.3, 5.0, 4.8 Hz, H-9), 1.69 (3H, *d*, *J* = 6.8 Hz, H-10); ^{13}C NMR: Table 1. Compound **1b**: powder. ^{1}H NMR (CD_3OD): δ3.84 (1H, *q*, *J* = 6.6 Hz, H-3), 1.39 (3H, *s*, H-5), 1.16 (3H, *d*, *J* = 6.6 Hz, H-4); ^{13}C NMR: Table 1.

Synthesis of angliceric acid (**14**). A soln of methyl angelate (**12**, 4.0 g), barium chlorate (3.2 g) and OsO_4 (20 mg) in H_2O (325 ml) was kept at room temp. for 3 days under stirring. The reaction mixture was adjusted to pH 4 with 2 M HCl, and then washed with benzene. After concn to a vol. of 100 ml, the aq. layer was satd with NaCl, and then extracted with Et_2O in a liquid–liquid extractor for 2 days. The Et_2O layer was concd, and the residue saponified with 5% aq. KOH and then worked-up as usual to give **14** (3.2 g). Methyl tiglate (**13**, 4.0 g) was converted to **15** (3.2 g) by the same procedure. Powder;

Table 1. ^{13}C NMR spectral data of compounds **1**–**4**, **1a**, **1b**, **15** and **4M** (pyridine-d_5)

C	1	2	1a*	1b†	15†	3‡	4	4M
1	96.0	95.9	93.9			96.1	95.8	95.6
3	153.7	153.0	152.7			153.7	152.9	153.1
4	111.3	112.8	113.0			111.5	110.5	109.8
5	33.7	34.3	26.5			33.8	30.8	30.9
6	36.5	36.8	33.6			36.4	36.4	35.8
7	172.2	172.5	177.0			172.2	175.3	172.8
8	75.2	75.4	76.4			75.4	71.0	70.7
9	45.2	45.5	38.9			45.3	43.9	43.7
10	20.3	20.5	17.2			20.2	20.1	20.2
11	166.2	168.4	171.7			166.3	167.1	166.9
OMe	51.2					51.2	51.0	51.1
OMe								51.6
1'	175.4	175.6		179.0	178.9	173.7	174.7	174.7
2'	75.4	75.6		78.7	78.4	79.7	78.8	78.8
3'	73.6	73.6		73.1	72.7	72.6	72.4	72.3
4'	12.9	13.1		18.2	16.8	13.8	18.3	18.3
5'	17.7	17.8		23.0	22.3	62.3	22.1	21.9
G-1	100.4	100.6	98.9			100.3	100.6	100.5
-2	74.9	75.0	73.3			74.6	74.8	74.8
-3	78.7	78.7	76.2			78.4	79.0	79.0
-4	71.6	71.8	70.2			70.1	71.2	71.1
-5	78.3	78.4	76.9			78.0	78.5	78.5
-6	62.8	63.0	61.3			61.5	62.2	62.1

*Measured in D_2O.
†Measured in methanol-d_4.
‡Measured in pyridine-d_5 and D_2O.

Table 2. ^{13}C NMR spectral data of compounds **5**, **6**, **10** and the sugar moiety of **16*** (DMSO-d_6)

C	5	6	10	16
2	164.4	163.8	164.2	
3	103.0	102.8	103.1	
4	182.0	180.8	181.8	
5	161.6	161.1	161.1	
6	99.6	98.8	99.6	
7	162.9	164.1	162.6	
8	94.8	94.0	94.7	
9	157.0	157.3	157.9	
10	105.5	103.7	105.6	
1′	120.9	121.3	121.1	
2′	128.7	128.4	128.5	
3′	116.1	116.0	115.9	
4′	161.2	161.5	161.4	
5′	116.1	116.0	115.9	
6′	128.7	128.4	128.5	
Glc-1	99.9		98.6	99.6
2	73.4		77.1	73.7
3	76.3		77.0	76.7
4	69.8		70.6	70.0
5	76.1		77.4	75.9
6	67.4		61.0	67.5
Api-1	109.3			109.3
2	75.6			75.5
3	78.8			78.9
4	73.1			73.3
5	63.4			63.3
Rha-1			100.5	
2			70.2	
3			70.6	
4			72.3	
5			68.6	
6			18.1	

*Data taken from ref. [14].

^{1}H NMR (CD_3OD): δ3.94 (1H, *q*, *J* = 6.4 Hz, H-3), 1.29 (3H, *s*, H-5), 1.19 (3H, *d*, *J* = 6.4 Hz, H-4); ^{13}C NMR: Table 1.

Separation of the enantiomers of compound **14** [12]. Column: ODS AQ-312 (6 mm × 15 cm, YMC, Japan); mobile phase: aq. soln. of 0.8 mM $CuSO_4$ and 1.5 mM *N*,*N*-dimethyl-L-phenylalanine, which was adjusted to pH 4.5 with NH_4OAc; flow rate: 1.0 ml min^{-1}; detection: UV (230 nm); column temp: ambient; R_t: D-epimer (2*R*, 3*R*) 12.7 min, L-epimer (2*S*, 3*S*) 15.5 min.

Compound **2**. Powder; $[\alpha]_D^{28}$ − 21.8° (H_2O; *c* 1.00); FAB-MS (negative): *m/z* 505.1593 $[M - H]^-$ ($C_{21}H_{29}O_{14}$ requires: *m/z* 505.1557); ^{1}H NMR (pyridine-d_5): δ7.60 (1H, *s*, H-3), 6.42 (1H, *d*, *J* = 9.5 Hz, H-1), 5.60 (1H, *q*, *J* = 6.6 Hz, H-3′), 5.48 (1H, *d*, *J* = 7.9 Hz, Glc-1), 5.08 (1H, *q*, *J* = 6.4 Hz, H-8), 4.50 (1H, *dd*, *J* = 11.4, 2.1 Hz, Glc-6a), 4.35 (1H, *dd*, *J* = 11.4, 5.1 Hz, Glc-6b), 4.31 (1H, *t*, *J* = 9.0 Hz, Glc-4), 4.27 (1H, *t*, 9.0 Hz, Glc-3), 4.08 (1H, *dd*, *J* = 9.0, 7.9 Hz, Glc-2), 4.04 (1H, *ddd*, *J* = 9.0, 5.1, 2.1 Hz, Glc-5), 3.76 (1H, *m*, H-5), 2.97 (1H, *br d*, *J* = 13.5 Hz, H-6a), 2.58 (1H, *br d*, *J* = 13.5 Hz, H-6b), 2.17 (1H, *m*, H-9), 1.90 (3H, *s*, H-5′), 1.67 (3H, *d*, *J* = 6.4 Hz, H-10), 1.45 (3H, *d*, *J* = 6.6 Hz, H-4′); ^{13}C NMR: Table 1.

Methylation of compound **2**. An excess of an ethereal soln of CH_2N_2 was added to a soln of **2** (50 mg) in MeOH, and the mixture allowed to stand for 2 hr. The reaction mixture was evapd *in vacuo* to give **1**, quantitatively.

Compound **3**. Powder; $[\alpha]_D^{17}$ + 8.2° (pyridine; *c* 0.73); FAB-MS (negative): *m/z* 535.1691 $[M - H]^-$ ($C_{22}H_{31}O_{15}$ requires; *m/z* 535.1663); ^{1}H NMR (pyridine-d_5 added one drop of D_2O): δ7.66 (1H, *s*, H-3), 6.45 (1H, *d*, *J* = 9.3 Hz, H-1), 5.58 (1H, *q*, *J* = 6.8 Hz, H-3′), 5.45 (1H, *d*, *J* = 7.1 Hz, Glc-1), 5.05 (1H, *q*, *J* = 6.6 Hz, H-8), 4.58 (1H, *dd*, *J* = 10.8, 2.2 Hz, Glc-6a), 4.47 (1H, *dd*, *J* = 10.8, 5.3 Hz, Glc-6b), 4.37 (2H, *br s*, H-5′), 4.35 (1H, *t*, *J* = 8.1 Hz, Glc-4), 4.22 (1H, *t*, *J* = 8.1 Hz, Glc-3), 4.04 (1H, *dd*, *J* = 8.1, 7.1 Hz, Glc-2), 3.86 (1H, *m*, Glc-5), 3.62 (3H, *s*, OMe), 3.56 (1H, *m*, H-5), 2.75 (1H, *br d*, *J* = 13.7 Hz, H-6a), 2.63 (1H, *br d*, *J* = 13.7 Hz, H-6b), 2.14 (1H, *m*, H-9), 1.71 (3H, *d*, *J* = 6.6 Hz, H-10), 1.42 (3H, *d*, *J* = 6.8 Hz, H-4′); ^{13}C NMR: Table 1.

Compound **4**. Powder; $[\alpha]_D^{17}$ − 5.8° (pyridine; *c* 0.84); FAB-MS (negative): *m/z* 537.1833 $[M - H]^-$ ($C_{22}H_{33}O_{15}$ requires; *m/z* 537.1819); ^{1}H NMR (pyridine-d_5, 50°): δ7.73 (1H, *s*, H-3), 6.29 (1H, *d*, *J* = 7.3 Hz, H-1), 5.45 (1H, *d*, *J* = 7.8 Hz, Glc-1), 5.20 (1H, *q*, *J* = 6.3 Hz, H-8), 4.53 (1H, *dd*, *J* = 11.7, 2.2 Hz, Glc-6a), 4.46 (1H, *dd*, *J* = 11.7, 5.1 Hz, Glc-6b), 4.30 (1H, *t*, *J* = 8.8 Hz, Glc-4), 4.26 (1H, *t*, *J* = 8.8 Hz, Glc-3), 4.08 (1H, *dd*, *J* = 8.8, 7.8 Hz, Glc-2), 3.94 (1H, *m*, Glc-5), 3.88 (1H, *q*, *J* = 6.3 Hz, H-3′), 3.65 (3H, *s*, OMe), 3.62 (1H, *m*, H-5), 3.08 (1H, *dd*, *J* = 16.4, 4.8 Hz, H-6a), 3.01 (1H, *dd*, *J* = 16.4, 7.6 Hz, H-6b), 2.49 (1H, *m*, H-9), 1.83 (3H, *s*, H-5′), 1.54 (3H, *d*, *J* = 6.3 Hz, H-4′), 1.41 (3H, *d*, *J* = 6.3 Hz, H-10); ^{13}C NMR: Table 1.

Methylation of compound **4**. Compound **4** was methylated with CH_2N_2 to give **4M**: powder; ^{1}H NMR (pyridine-d_5, 40°): δ7.66 (1H, *s*, H-3), 6.13 (1H, *d*, *J* = 7.6 Hz, H-1), 5.51 (1H, *q*, *J* = 6.6 Hz, H-8), 5.40 (1H, *d*, *J* = 7.8 Hz, Glc-1), 4.51 (1H, *dd*, *J* = 12.6, 2.1 Hz, Glc-6a), 4.40 (1H, *dd*, *J* = 12.6, 5.1 Hz, Glc-6b), 4.27 (1H, *t*, *J* = 8.9 Hz, Glc-4), 4.23 (1H, *t*, *J* = 8.9 Hz, Glc-3), 4.04 (1H, *dd*, *J* = 8.9, 7.8 Hz, Glc-2), 3.97 (1H, *m*, Glc-5), 3.89 (1H, *q*, *J* = 6.4 Hz, H-3′), 3.73 (1H, *m*, H-5), 3.59 (3H, *s*, OMe-11), 3.57 (3H, *s*, OMe-7), 2.84 (2H, *m*, H-6), 2.29 (1H, *m*, H-9), 1.77 (3H, *s*, H-5′), 1.50 (3H, *d*, *J* = 6.4 Hz, H-4′), 1.44 (3H, *d*, *J* = 6.6 Hz, H-10); ^{13}C NMR: Table 1.

Compound **5**. Yellow powder; $[\alpha]_D^{16}$ + 8.8° (pyridine; *c* 0.85); UV λ_{max}^{MeOH} nm: 268, 331; + NaOMe: 268, 388, + $AlCl_3$ 275, 344, 386; + NaOAc 269, 333. TLC (silica gel, EtOAc–HCO_2H–HOAc–H_2O, 100:11:11:27): **5** R_f = 0.28, apiin (purchased, Carl Roth KG, No. 5635) R_f = 0.32. HPLC [R-ODS-5 S-5 120A (4.6 mm × 25 cm), 50% aq. MeOH, 1 ml min^{-1}, UV (254 nm)]: **5** R_t = 11.4 min, apiin R_t = 14.0 min. FAB-MS (negative): *m/z* 563.1381 $[M - H]^-$ ($C_{26}H_{27}O_{14}$ requires: *m/z* 563.1401); ^{1}H NMR (DMSO-d_6): δ7.95 (2H, *d*, *J* = 8.8 Hz, H-2′ and H-6′), 6.94 (2H, *d*, *J* = 8.8 Hz, H-3′ and H-5′), 6.85 (1H, *s*, H-3), 6.79 (1H, *d*, *J* = 2.0 Hz, H-8), 6.45 (1H, *d*, *J* = 2.0 Hz, H-6), 5.06 (1H, *d*, *J* = 7.3 Hz,

Glc-1), 4.82 (1H, *d*, $J = 2.9$ Hz, Api-1); ^{13}C NMR: Table 2.

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