

## Terpenoids and Phenols from *Taiwania flousiana*

XIANG Ying, YANG Sheng-Ping, ZHAN Zha-Jun, YUE Jian-Min\*

(State Key Laboratory of Drug Research, Institute of Materia Medica, Shanghai Institutes for Biological Sciences, The Chinese Academy of Sciences, Shanghai 201203, China)

**Abstract:** Two new terpenoids, namely taiwaniatriol (**1**) and senecrassidiol-9-O- $\beta$ -D-glucopyranoside (**8**), along with fifteen known compounds including five triterpenoids (**2-6**), one diterpene (**7**) and nine phenols (**9-17**), were isolated from the root bark of *Taiwania flousiana* Gaussen. Taiwaniatriol was elucidated as (24S)-3 $\beta$ -methoxy-5 $\alpha$ -lanost-9(11)-ene-7 $\beta$ , 24, 25-triol. Their structures were established mainly by spectral methods.

**Key words:** *Taiwania flousiana*; Taxodiaceae; triterpenoids; sesquiterpene glycoside; phenols

The genus *Taiwania* belonging to the family Taxodiaceae has only two species. A number of sesquiterpenes (Cheng *et al.*, 1967; Kuo *et al.*, 1969; He *et al.*, 1997), diterpenes (Lin *et al.*, 1995; Lin *et al.*, 1996; Lin *et al.*, 1998a), cycloadducts of diterpenes (Lin *et al.*, 1996; Lin *et al.*, 1997), sterols (Lin *et al.*, 1998a), lignans (Lin *et al.*, 1967; Lin *et al.*, 1998b) and biflavones (Kamil *et al.*, 1977; Kamil *et al.*, 1981) were isolated from *Taiwania cryptomerioides*. Among these compounds,  $\alpha$ -cadinol showed selectively cytotoxic activity against the human colon adenocarcinoma (HT-29) cell line with an ED<sub>50</sub> value of 0.778  $\mu$ g/mL (He *et al.*, 1997). Ferruginol and taiwanin C exhibited significant antifungal activity (Chang *et al.*, 1999).

*T. flousiana* Gaussen, an evergreen tree with linear-triangular leaves mainly distributed in China and northern Burma, has not been previously investigated chemically. In an effort to understand the chemical constituents of this plant, seventeen compounds, including six triterpenoids, one sesquiterpene glycoside, one diterpenoid, and nine phenols were isolated from the root bark of *T. flousiana*. Two of them are new compounds, namely (24S)-3 $\beta$ -methoxy-5 $\alpha$ -lanost-9(11)-ene-7 $\beta$ ,24,25-triol (**1**) and senecrassidiol-9-O- $\beta$ -D-glucopyranoside (**5**). A trivial name taiwaniatriol was given to compound **1**. Their structures were established mainly by spectral methods. Herein, we present the isolation and structural elucidation of these compounds (Fig. 1).

### 1 Results and Discussion

(24S)-3 $\beta$ -Methoxy-5 $\alpha$ -lanost-9(11)-ene-7 $\beta$ ,24,25-triol (**1**), obtained as white powder,  $[\alpha]_D^{20} + 42.0^\circ$  (*c* 0.14, CHCl<sub>3</sub>). The molecular formula C<sub>31</sub>H<sub>54</sub>O<sub>4</sub> was determined by HR-

EI-MS at *m/z* 490.400 8 [M]<sup>+</sup> (calcd. 490.402 2). Its IR spectrum showed absorption bands at 3 547 cm<sup>-1</sup> and 3 452 cm<sup>-1</sup> ascribable to hydroxyl groups, and a medium absorption band at 1 628 cm<sup>-1</sup> assignable to a double bond. In the <sup>1</sup>H-NMR (see **Experimental**) and <sup>13</sup>C-NMR spectra (Table 1), it exhibited signals for one secondary methyl, seven tertiary methyls, one methoxyl group, three oxygenated tertiary carbons, one oxygenated quaternary carbon, and one trisubstituted double bond. The spectral data of compound **1** were remarkably similar to those of compound **2** except for the presence of one more hydroxyl group attached to a tertiary carbon. Compared with compound **2**, the carbon signals of C-6, C-7 and C-8 in compound **1** resonating at  $\delta$  31.9, 72.5 and 50.4 were down-field shifted  $D\delta$  10.7, 44.5 and 8.6, respectively, indicating the presence of a C-7-OH (Fig. 1). The C-5 signal ( $\delta$  49.2) of compound **1** was up-field shifted  $D\delta$  3.8 compared with that of compound **2** caused by a typical  $\gamma$ -gauche effect of the C-7-OH, suggesting that the C-7-OH took a  $\beta$ -orientation, which was confirmed by the large coupling constants of H-7 (dt, *J* = 10.6, 4.9 Hz) taking an axial position. Compared with the known compound vietchiolide (Tanaka and Matshunaga, 1990) with a 7 $\beta$ -OH, the carbon signals of the B-ring and the coupling constants of 7 $\alpha$ -H in compound **1** were dramatically matched with those reported for vietchiolide. 2D-NMR experiment (HMQC and HMBC) further confirmed the structure of compound **1** (Fig. 2). The structure of compound **1** was thus elucidated to be (24S)-3 $\beta$ -methoxy-5 $\alpha$ -lanost-9(11)-en-7 $\beta$ , 24, 25-triol.

Senecrassidiol-9-O- $\beta$ -D-glucopyranoside (**8**) obtained as pale gum,  $[\alpha]_D^{20} - 34.0^\circ$  (*c* 0.18, CH<sub>3</sub>OH), has the molecular formula C<sub>21</sub>H<sub>36</sub>O<sub>7</sub> determined by HR-EI-MS at *m/z*

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\* Author for correspondence. Tel.: +86 (0)21 50806718; Fax: +86 (0)21 50807088; E-mail: <jmyue@mail.shnc.ac.cn>.

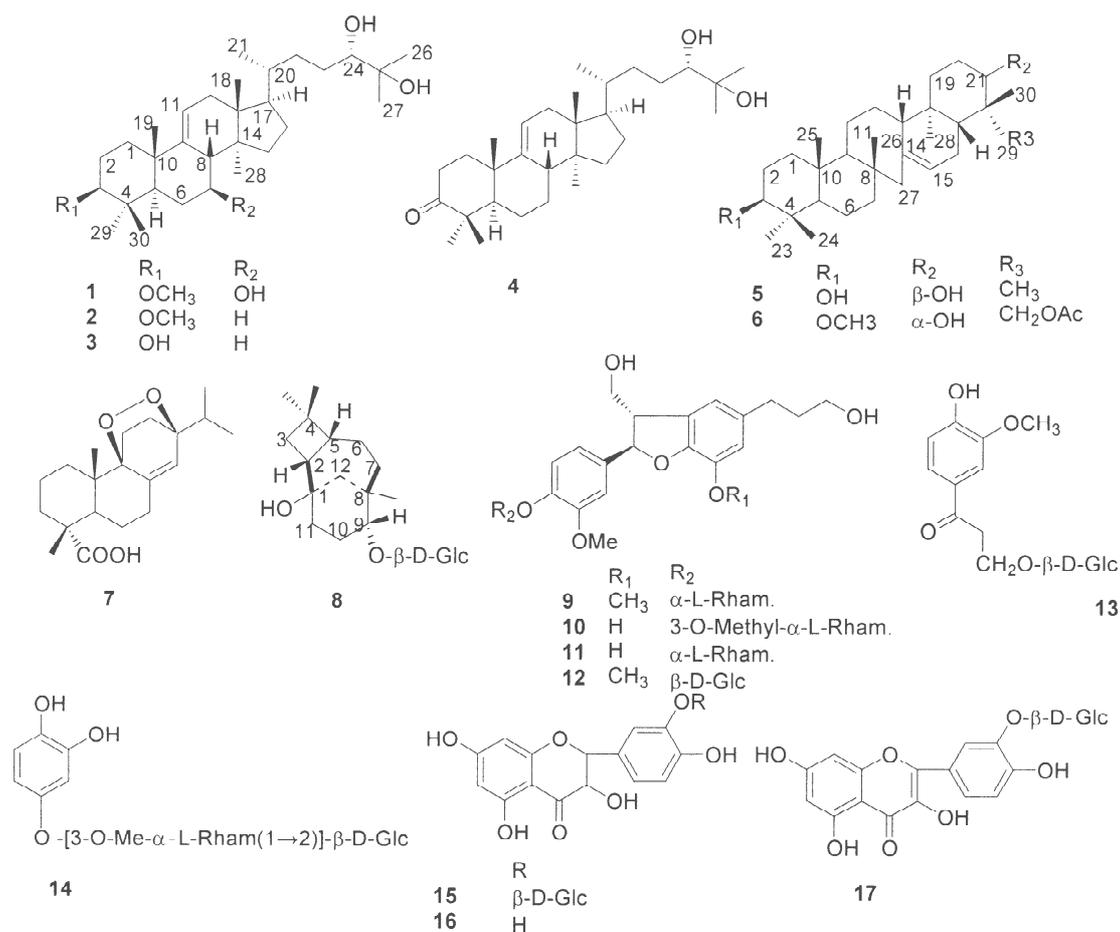


Fig.1. Structures of compounds 1-17.

Table 1 <sup>13</sup>C-NMR data of compounds 1-4 (CDCl<sub>3</sub>, 400 MHz)

No.	1	2	3	4	No.	1	2	3	4
1	36.2	36.0	36.1	36.7	17	50.2	51.0	51.0	50.9
2	28.6	28.1	29.7	33.6	18	14.3	14.4	14.4	14.4
3	88.4	88.6	78.9	217.3	19	22.0	22.2	22.2	22.0
4	38.9	39.0	39.1	47.7	20	36.4	36.4	36.4	36.4
5	49.2	53.0	52.5	53.4	21	18.6	18.5	18.5	18.5
6	31.9	21.2	21.4	22.5	22	33.7	33.9	33.9	34.9
7	72.5	28.0	28.1	28.0	23	28.8	28.7	28.7	27.7
8	50.4	41.8	41.8	41.9	24	79.6	79.6	79.6	79.6
9	146.3	148.7	148.5	147.1	25	73.3	73.2	73.2	73.2
10	39.1	39.4	39.4	39.1	26	26.6	26.5	26.5	25.6
11	117.2	114.7	114.9	116.2	27	23.3	23.2	23.2	23.2
12	36.9	37.2	37.1	37.2	28	18.3	18.5	18.5	18.5
13	45.1	44.3	44.3	44.3	29	28.2	28.2	28.1	26.5
14	46.5	47.0	47.0	47.0	30	16.3	16.4	15.6	21.8
15	36.7	33.6	33.9	33.9	OCH <sub>3</sub>	57.6	57.5		
16	22.6	22.5	28.1	28.7					

382.237 0 [M-H<sub>2</sub>O]<sup>+</sup> (calcd. 382.235 5) and the <sup>13</sup>C-NMR spectra. A broad IR absorption band at 3 415 cm<sup>-1</sup> was ascribed to hydroxyl groups. The <sup>1</sup>H-NMR spectrum showed three angular methyl signals at  $\delta$  0.87, 0.94 and 1.12

(each 3H, s). A typical fragmentation ion at  $m/z$  220 [M-62-H<sub>2</sub>O]<sup>+</sup> and <sup>13</sup>C-NMR spectral data suggested that the compound **8** was likely a sesquiterpenoid glucoside. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR (see **Experimental**) indicated the sugar

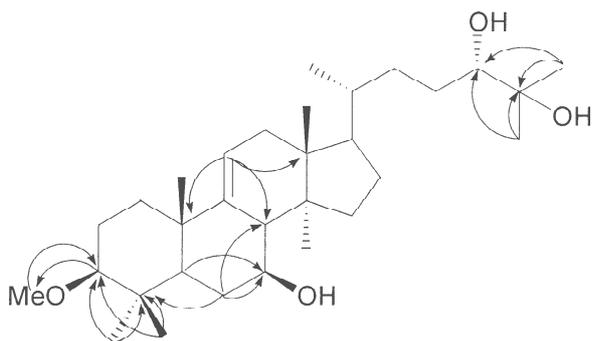


Fig.2. Selected HMBC correlations of compound 1.

moiety was glucose. The proton and carbon signals of the anomeric center of the glucose ( $\delta_{\text{H}} 4.31$ , 1H, d,  $J = 7.9$  Hz;  $\delta_{\text{C}} 100.7$ ) suggested a  $\beta$ -configuration. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  data of the aglycone moiety of compound **8** were closely matched with those of senecrassidiol (Bohlman and Ziesche, 1981; Iwabuchi *et al.*, 1990), except for the C-9 at  $\delta$  79.0 and the C-10 at  $\delta$  22.8, the former was down-field shifted ca.  $\Delta\delta$  5, and the latter was up-field shifted ca.  $\Delta\delta$  4 compared with those of senecrassidiol resulting from glycosylation, indicating that the sugar moiety was definitely linked to C-9. The structure of compound **8** was thus elucidated as senecrassidiol-9-O- $\beta$ -D-glucopyranoside.

Compounds **2** and **3** were respectively identified as (24*S*)-3 $\beta$ -methoxy-5 $\alpha$ -lanost-9(11)-ene-24,25-diol and (24*S*)-5 $\alpha$ -lanost-9(11)-ene-3 $\beta$ ,24,25-triol on the basis of spectral data (Kutney *et al.*, 1981). As no  $^{13}\text{C-NMR}$  spectral data have been reported for compounds **2** and **3** before, the detail assignments of  $^{13}\text{C-NMR}$  data for compounds **2** and **3** were thus made for the first time (Table 1). Compound **4** was identified as 3-oxo-lanost-9(11)-ene-24*S*,25-diol (Wada *et al.*, 2001). The known serratene triterpenes, serrat-14-en-3 $\beta$ ,21 $\beta$ -diol (**5**) (Fang *et al.*, 1991) and 29-acetoxy-3 $\beta$ -methoxyserrat-14-en-21 $\alpha$ -ol (**6**) (Wada *et al.*, 2001) were identified by comparison of the spectral data with those reported. The known diterpenoid was identified as 9 $\beta$ ,13 $\beta$ -endoperoxide-abieta-8(14)-en-18-oic acid (**7**) by comparison of its  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectral data with those reported values of its methyl ester (Monaco *et al.*, 1987; Barrero *et al.*, 1991). This paper deals with the spectral data in its original form (see experimental).

The known lignans, icariside E4 (**9**) (Miyase *et al.*, 1989), (2*R*,3*R*)-2,3-dihydro-7-hydroxy-2-(4'-hydroxy-3'-methoxyphenyl)-3-hydroxymethyl-5-benzofuranpropanol 4'-O-(3-O-methyl- $\alpha$ -L-rhamnopyranoside) (**10**) (Pan and Lundgren, 1995), (2*R*,3*R*)-2,3-dihydro-7-hydroxy-2-(4'-hydroxy-3'-methoxyphenyl)-3-hydroxymethyl-5-

benzofuranpropanol-4'-O- $\alpha$ -L-rhamnopyranoside (**11**) (Popoff and Theander, 1975), and dihydrodehydrodiconiferyl alcohol 4'-O- $\beta$ -D-glucoside (**12**) (Abe and Yamauchi, 1986) were identified by spectral data.

The known compounds, monoaryl glycosides  $\beta$ -hydroxypropiovanillone 3-O- $\beta$ -D-glucopyranoside (**13**) (Anderson and Lundgren, 1988), 3,4-dimethoxyphenyl-2-O-(3-O-methyl- $\alpha$ -L-rhamnopyranosyl)- $\beta$ -D-glucopyranoside (**14**) (Pan and Lundgren, 1995), and three known flavonoids taxifolin 3'-O- $\beta$ -D-glucopyranoside (**15**), taxifolin (**16**) (Shen and Theander, 1985), and quercetin-3'-O- $\beta$ -D-glucopyranoside (**17**) were also identified by comparison of their spectral data with those reported.

## 2 Experimental

### 2.1 General

Optical rotations were measured on a Perkin-Elmer 341 polarimeter (Na filter,  $\lambda = 589$  nm). IR spectra were recorded on a Perkin-Elmer 577 spectrometer. NMR spectra were recorded on a Bruker AM-400 (400 MHz) spectrometer with TMS as internal standard. Mass spectra including high-resolution mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. All solvents used were of analytical grade (Shanghai Chemical Plant). Silica gel (200–300 mesh) was used for column chromatography, and pre-coated silica gel GF254 plates (Qingdao Marine Chemical Plant) were used for TLC. C-18 reversed-phase silica gel (150–200 mesh, Merck) and MCI GEL CHP20P (75–150  $\mu$ ) (Mitsubishi Chemical Industry Ltd.) were also used for column chromatography.

### 2.2 Plant material

The root bark of *Taiwania flosiana* Gaussen was collected in Lichuan, Hubei, China (May, 2001) and was authenticated by Prof. ZHANG Chang-Gong (Tongji Medical College, Huazhong University of Sciences and Technology, Wuhan, China). A voucher specimen (20010102) has been deposited in the Faculty of Pharmacognosy, Tongji Medical College, Huazhong University of Sciences and Technology.

### 2.3 Extraction and isolation

The dried root bark (1.15 kg) was powdered and extracted with 95% ethanol to give crude extract (270 g). The crude was dissolved in  $\text{H}_2\text{O}$  and partitioned with petroleum ether and EtOAc successively to afford petroleum ether and EtOAc soluble fractions, respectively. The petroleum ether soluble part (21 g) was subjected to silica gel chromatography using a gradient mixture of petroleum ether- $\text{Me}_2\text{CO}$  (from 1:0 to 1:1) as eluting solvent to give four fractions. Fraction 1 was mainly composed of waxy materials.

Fraction 2 was separated by CC on silica gel with a gradient mixture of petroleum ether-CHCl<sub>3</sub> (1:1 to CHCl<sub>3</sub>) to give compound **5** (55 mg), and two sub-fractions 2a and 2b. Sub-fraction 2a was subjected to a C-18 reversed-phase silica gel CC using a gradient solvent H<sub>2</sub>O-Me<sub>2</sub>CO to give compound **6** (2.3 mg). Sub-fraction 2b was separated by CC on silica gel with mixture of petroleum ether-Me<sub>2</sub>CO (4:1) to give compounds **2** (42 mg) and **4** (49 mg). Fraction 3 was subjected to silica gel CC using petroleum ether with increasing amount of *iso*-PrOH as solvent to give two sub-fractions 3a and 3b, which were then subjected to C-18 reversed-phase silica gel CC to yield compounds **3** (8 mg) and **7** (12 mg), respectively. Fraction 4 was subjected to silica gel CC using petroleum ether with increasing amount of *iso*-PrOH as solvent to give a major fraction, which was further purified by C-18 reversed-phase silica gel CC to obtain compound **1** (4.3 mg).

The ethyl acetate soluble part (42 g) was subjected to silica gel CC using a gradient mixture of petroleum ether-Me<sub>2</sub>CO (3:1 to Me<sub>2</sub>CO) as solvent to give eight fractions. Fraction 4 was chromatographed over MCI-gel and silica gel columns to give compound **16** (40 mg). Fraction 7 was separated on column of MCI-gel, and then to column of C-18 reversed-phase silica gel to give compounds **10** (80 mg), **15** (650 mg) and **17** (120 mg). Fraction 8 was separated by column of MCI-gel and then silica gel CC with a gradient mixture of CHCl<sub>3</sub>-MeOH to give eight sub-fractions (8a to 8h). Sub-fraction 8b was purified over column of C-18 reversed-phase silica gel to give compound **9** (10 mg). Sub-fraction 8c was separated by silica gel CC to give a mixture of two compounds, which were then purified by preparative TLC to obtain compounds **11** (90 mg) and **12** (20 mg). Sub-fractions 8e, 8f and 8h were purified by Sephadex LH-20 to give compounds **8** (2.2 mg), **13** (9 mg) and **14** (15 mg), respectively.

## 2.4 Identification

**Compound 1** White powder, C<sub>31</sub>H<sub>54</sub>O<sub>4</sub>, [ $\alpha$ ]<sub>D</sub><sup>20</sup>+42.0° (c 0.14, CHCl<sub>3</sub>). <sup>1</sup>H-NMR  $\delta$  (in CDCl<sub>3</sub>): 0.68 (3H, s, Me-18), 0.81 (3H, s, Me-30), 0.84 (3H, s, Me-28), 0.88 (1H, t, *J*=6.9 Hz, H-5), 0.92 (3H, d, *J*=6.5 Hz, Me-21), 0.98 (3H, s, Me-29), 1.07 (3H, s, Me-19), 1.11 (1H, m, H-23), 1.17 (3H, s, Me-26), 1.22 (3H, s, Me-27), 1.30 (1H, m, H-16), 1.31 (1H, m, H-2), 1.32 (1H, m, H-1), 1.40 (2H, m, H-15), 1.53 (1H, br d, *J*=12.6 Hz, H-6), 1.63 (1H, m, H-20), 1.66 (1H, m, H-17), 1.79 (1H, m, H-23), 1.94 (1H, m, H-1), 1.98 (2H, m, H-16 and H-6), 1.99 (1H, m, H-2), 2.11 (1H, br d, *J*=9.5 Hz, H-12), 2.17 (1H, br d, *J*=10.6 Hz, H-8), 2.20 (1H, m, H-12), 2.34 (2H, m, H-22), 2.65 (1H, dd, *J*=11.7, 4.1 Hz, H-3), 3.29 (1H, dd, *J*=10.0, 1.7 Hz, H-24), 3.37 (3H, s, OMe), 3.69 (1H, dt, *J*=10.6, 4.9 Hz, H-7), 5.30 (1H, d,

*J*=6.2 Hz, H-11). <sup>13</sup>C-NMR: see Table 1. IR (KBr)  $\nu_{\max}$ : 3547, 3452, 2918, 1716, 1628, 1464, 1371, 1159, 1097, 1070, 978. EI-MS *m/z*: 490 (M<sup>+</sup>, 2), 472 (23), 457 (54), 454 (62), 439 (53), 425 (18), 414 (26), 407 (40), 399 (26), 367 (25), 343 (100), 327 (31), 285 (21), 260 (22), 225 (23), 183 (38), 173 (49), 159 (34), 151 (33), 147 (32), 145 (38), 133 (45), 123 (45), 121 (68), 109 (63). HR-EI-MS: 490.400 8 [M<sup>+</sup>] (calcd. 490.402 2 for C<sub>31</sub>H<sub>54</sub>O<sub>4</sub>).

**Compound 2** White powder, C<sub>31</sub>H<sub>54</sub>O<sub>3</sub>, <sup>1</sup>H-NMR  $\delta$  (in CDCl<sub>3</sub>): 0.64 (3H, s, Me-18), 0.73 (3H, s, Me-28), 0.79 (3H, s, Me-30), 0.89 (3H, d, *J*=6.4 Hz, Me-21), 0.96 (3H, s, Me-29), 1.02 (3H, s, Me-19), 1.13 (3H, s, Me-26), 1.21 (3H, s, Me-27), 2.64 (1H, dd, *J*=11.4, 4.1 Hz, H-3), 3.28 (1H, dd, *J*=10.1, 1.8 Hz, H-24), 3.36 (3H, s, OMe), 5.21 (1H, d, *J*=6.0 Hz, H-11). <sup>13</sup>C-NMR: see Table 1.

**Compound 3** White powder, C<sub>30</sub>H<sub>52</sub>O<sub>3</sub>, <sup>1</sup>H-NMR  $\delta$  (in CDCl<sub>3</sub>): 0.65 (3H, s, Me-18), 0.74 (3H, s, Me-28), 0.82 (3H, s, Me-30), 0.90 (3H, d, *J*=6.5 Hz, Me-21), 0.98 (3H, s, Me-29), 1.04 (3H, s, Me-19), 1.16 (3H, s, Me-26), 1.22 (3H, s, Me-27), 3.22 (1H, dd, *J*=11.4, 4.2 Hz, H-3), 3.29 (1H, dd, *J*=10.2, 2.1 Hz, H-24), 5.22 (1H, d, *J*=6.2 Hz, H-11). <sup>13</sup>C-NMR: see Table 1.

**Compound 4** White powder, C<sub>30</sub>H<sub>50</sub>O<sub>3</sub>, <sup>1</sup>H-NMR  $\delta$  (in CDCl<sub>3</sub>): 0.65 (3H, s, Me-18), 0.74 (3H, s, Me-28), 0.90 (3H, d, *J*=6.4 Hz, Me-21), 1.06 (3H, s, Me-30), 1.07 (3H, s, Me-29), 1.22 (3H, s, Me-26), 1.22 (3H, s, Me-27), 3.29 (1H, br d, *J*=9.3 Hz, H-24), 5.28 (1H, d, *J*=5.9 Hz, H-11). <sup>13</sup>C-NMR: see Table 1.

**Compound 5** White powder, C<sub>30</sub>H<sub>50</sub>O<sub>2</sub>, <sup>1</sup>H-NMR  $\delta$  (in CDCl<sub>3</sub>): 0.67 (3H, s, Me-28), 0.74 (3H, s, Me-24), 0.77 (3H, s, Me-25), 0.81 (3H, s, Me-26), 0.86 (3H, s, Me-29), 0.91 (3H, s, Me-30), 0.95 (3H, s, Me-23), 3.17 (1H, dd, *J*=11.8, 4.9 Hz, H-3), 3.43 (1H, dd, *J*=2.9, 2.4 Hz, H-21), 5.30 (1H, br s, H-15). <sup>13</sup>C-NMR  $\delta$  (in CDCl<sub>3</sub>): 13.3 (C-28), 15.4 (C-26), 15.7 (C-23), 18.9 (C-6), 19.8 (C-24), 21.8 (C-30), 24.0 (C-16), 25.2 (C-2), 25.4 (C-11), 27.2 (C-12), 27.6 (C-20), 27.7 (C-29), 28.1 (C-25), 31.2 (C-19), 35.9 (C-10), 37.1 (C-18), 37.5 (C-22), 38.2 (C-4), 38.6 (C-1), 39.0 (C-8), 43.4 (C-17), 45.2 (C-7), 55.8 (C-5), 56.3 (C-27), 56.9 (C-13), 62.9 (C-9), 76.2 (C-21), 78.9 (C-3), 122.1 (C-15), 138.5 (C-14).

**Compound 6** White powder, C<sub>33</sub>H<sub>54</sub>O<sub>4</sub>, <sup>1</sup>H-NMR  $\delta$  (in CDCl<sub>3</sub>): 0.65 (3H, s, Me-18), 0.74 (3H, s, Me-28), 0.82 (3H, s, Me-30), 0.90 (3H, d, *J*=6.5 Hz, Me-21), 0.98 (3H, s, Me-29), 1.04 (3H, s, Me-19), 1.16 (3H, s, Me-26), 1.22 (3H, s, Me-27), 3.22 (1H, dd, *J*=11.4, 4.2 Hz, H-3), 3.29 (1H, dd, *J*=10.2, 2.1 Hz, H-24), 5.22 (1H, d, *J*=6.2 Hz, H-11). <sup>13</sup>C-NMR  $\delta$  (in CDCl<sub>3</sub>): 14.0 (C-28), 15.7 (C-25), 16.2 (C-24), 18.8 (C-6), 19.8 (C-26), 21.1 (OAc), 21.6 (C-30), 22.4 (C-2), 24.3 (C-16), 25.5 (C-11), 27.2 (C-12), 27.8 (C-20), 28.1 (C-23), 35.9 (C-18), 37.2

(C-8), 37.3 (C-19), 38.2 (C-10), 38.5 (C-1), 38.9 (C-4), 42.0 (C-22), 45.2 (C-7), 50.6 (C-17), 56.0 (C-27), 56.3 (C-5), 57.1 (C-13), 57.5 (OMe), 62.8 (C-9), 64.7 (C-29), 79.4 (C-21), 88.5 (C-3), 121.6 (C-15), 138.3 (C-14), 171.0 (OAc).

**Compound 7** White powder,  $C_{20}H_{30}O_4$ ,  $^1H$ -NMR  $\delta$  (in  $Me_2CO-d_6$ ): 0.93 (3H, d,  $J = 6.9$  Hz, H-16), 0.95 (3H, d,  $J = 6.9$  Hz, H-17), 1.08 (3H, s, H-20), 1.30 (3H, s, H-19), 6.17 (1H, t,  $J = 2.2$  Hz, H-14).  $^{13}C$ -NMR  $\delta$  (in  $Me_2CO-d_6$ ): 17.1 (C-17), 17.3 (C-16), 17.6 (C-19), 18.0 (C-2), 18.1 (C-20), 21.0 (C-6), 24.1 (C-11), 25.6 (C-12), 28.5 (C-7), 32.6 (C-15), 34.1 (C-1), 37.8 (C-3), 38.9 (C-10), 40.7 (C-5), 47.1 (C-4), 79.6 (C-13), 82.0 (C-9), 127.1 (C-14), 144.4 (C-8), 179.3 (C-18).

**Compound 8** Pale gum,  $C_{21}H_{36}O_7$ ,  $[\alpha]_D^{20} -34.0^\circ$  ( $c$  0.18,  $CH_3OH$ ).  $^1H$ -NMR  $\delta$  (in  $CD_3OD$ ): 0.87 (3H, s, Me-13), 0.94 (3H, s, Me-15), 1.03 (1H, dd,  $J = 13.9, 12.6$  Hz, H-8), 1.12 (3H, s, Me-14), 1.29 (1H, m, H-11), 1.37 (1H, br d,  $J = 13.6$  Hz, H-12), 1.38 (2H, m, H-6), 1.45 (1H, m, H-8), 1.57 (1H, m, H-3), 1.63 (1H, m, H-10), 1.77 (1H, m, H-5), 1.78 (1H, m, H-12), 1.79 (1H, m, H-3), 1.80 (1H, m, H-10), 1.94 (1H, m, H-11), 2.42 (1H, dd,  $J = 11.4, 7.5, 4.2$  Hz, H-2), 3.19 (1H, m, H-2'), 3.26 (1H, m, H-3'), 3.30 (1H, m, H-4'), 3.37 (1H, m, H-9), 3.38 (1H, m, H-5'), 3.62 (1H, dd,  $J = 11.6, 5.4$  Hz, H-6'), 3.78 (1H, dd,  $J = 11.6, 2.6$  Hz, H-6'), 4.31 (1H, d,  $J = 7.9$  Hz, H-1').  $^{13}C$ -NMR  $\delta$  (in  $CD_3OD$ ): 22.6 (C-6), 22.8 (C-10), 24.6 (C-13), 29.0 (C-14), 31.0 (C-15), 34.2 (C-4), 35.5 (C-3), 36.6 (C-11), 37.0 (C-7), 37.4 (C-8), 38.8 (C-12), 42.6 (C-2), 49.7 (C-5), 62.8 (C-6'), 71.7 (C-4'), 72.4 (C-1), 74.7 (C-2'), 77.1 (C-3'), 77.7 (C-5'), 79.0 (C-9), 100.7 (C-1'). IR (KBr)  $\nu_{max}$ : 3415, 2926, 1464, 1383, 1078, 1041. EI-MS  $m/z$ : 382 ( $[M-H_2O]^+$ , 7), 327 (12), 220 (12), 203 (100), 182 (24), 165 (35), 147 (46), 123 (86), 119 (24), 107 (36). HR-EI-MS: 382.237 0 (calcd. 382.235 5 for  $C_{21}H_{34}O_6$  ( $[M-H_2O]^+$ )).

**Compound 9** White powder,  $C_{26}H_{34}O_{10}$ ,  $^1H$ -NMR  $\delta$  (in  $CD_3OD$ ): 1.05 (3H, d,  $J = 6.2$  Hz, Me-6''), 1.64 (2H, m, H-8), 2.45 (2H, dd,  $J = 8.1, 7.3$  Hz, H-7), 3.62 (3H, s, OMe), 3.68 (3H, s, OMe), 5.17 (1H, d,  $J = 1.5$  Hz, H-1''), 5.38 (1H, d,  $J = 5.9$  Hz, H-7'), 6.54 (1H, s, H-6), 6.56 (1H, s, H-2), 6.74 (1H, dd,  $J = 8.4, 1.8$  Hz, H-6'), 6.86 (1H, d,  $J = 1.8$  Hz, H-2'), 6.91 (1H, d,  $J = 8.4$  Hz, H-5').  $^{13}C$ -NMR  $\delta$  (in  $CD_3OD$ ): 18.4 (C-6''), 33.4 (C-7), 36.3 (C-8), 56.1 (C-8'), 56.9 (OMe), 57.2 (OMe), 62.7 (C-9), 65.5 (C-9'), 71.3 (C-5''), 72.5 (C-2''), 72.6 (C-3''), 74.3 (C-4''), 89.0 (C-7'), 101.8 (C-1''), 111.7 (C-2'), 114.5 (C-2), 118.4 (C-6), 119.6 (C-6'), 120.0 (C-5'), 130.0 (C-1), 137.5 (C-5), 139.2 (C-1'), 145.7 (C-3), 147.0 (C-4), 147.9 (C-4'), 152.5 (C-3').

**Compound 10** White powder,  $C_{26}H_{34}O_{10}$ ,  $^1H$ -NMR  $\delta$  (in  $Me_2CO-d_6$ ): 1.16 (2H, d,  $J = 6.2$  Hz, Me-6''), 1.74 (2H, m, H-8), 2.52 (2H, dd,  $J = 8.1, 7.3$  Hz, H-7), 3.44 (3H, s, 3'-OMe), 3.81 (3H, s, 3'-OMe), 4.27 (1H, t,  $J = 2.2$  Hz, H-2''), 5.39 (1H,

d,  $J = 1.5$  Hz, H-1''), 5.57 (1H, d,  $J = 5.9$  Hz, H-7'), 6.59 (1H, s, H-6), 6.61 (1H, d,  $J = 1.5$  Hz, H-2), 6.96 (1H, dd,  $J = 8.4, 1.8$  Hz, H-6'), 7.10 (1H, d,  $J = 8.4$  Hz, H-5'), 7.12 (1H, d,  $J = 1.8$  Hz, H-2').  $^{13}C$ -NMR  $\delta$  (in  $Me_2CO-d_6$ ): 17.7 (C-6''), 31.9 (C-7), 35.2 (C-8), 55.0 (C-8'), 55.9 (3'-OMe), 56.8 (3''-OMe), 61.3 (C-9), 64.4 (C-9'), 67.1 (C-2''), 69.9 (C-5''), 71.5 (C-4''), 81.3 (C-3''), 87.1 (C-7'), 100.6 (C-1''), 110.8 (C-2'), 115.8 (C-2), 116.4 (C-6), 118.3 (C-6'), 119.1 (C-5'), 129.0 (C-1), 136.0 (C-5), 138.4 (C-1'), 141.3 (C-3), 145.5 (C-4), 145.5 (C-4'), 151.2 (C-3').

**Compound 11** White powder,  $C_{25}H_{32}O_{10}$ ,  $^1H$ -NMR  $\delta$  (in  $Me_2CO-d_6$ ): 1.17 (3H, d,  $J = 6.2$  Hz, Me-6''), 1.74 (2H, m, H-8), 2.53 (2H, dd,  $J = 8.0, 7.3$  Hz, H-7), 3.80 (3H, s, 3'-OMe), 5.37 (1H, s, H-1''), 5.56 (1H, d,  $J = 5.9$  Hz, H-7), 6.60 (1H, s, H-6), 6.61 (1H, s, H-2), 6.95 (1H, d,  $J = 8.0$  Hz, H-6'), 7.10 (1H, d,  $J = 8.0$  Hz, H-5'), 7.11 (1H, s, H-2').  $^{13}C$ -NMR  $\delta$  (in  $Me_2CO-d_6$ ): 17.7 (C-6''), 32.1 (C-7), 35.5 (C-8), 55.0 (C-8'), 56.0 (3'-OMe), 61.5 (C-9), 64.6 (C-9'), 69.9 (C-5''), 71.4 (C-2''), 71.9 (C-3''), 73.2 (C-4''), 87.4 (C-7'), 100.5 (C-1''), 111.1 (C-2'), 116.0 (C-2), 116.6 (C-6), 118.6 (C-6'), 119.0 (C-5'), 129.2 (C-1), 136.1 (C-5), 138.1 (C-1'), 141.3 (C-3), 145.6 (C-4), 145.9 (C-4'), 151.3 (C-3').

**Compound 12** White powder,  $C_{25}H_{32}O_{11}$ ,  $^1H$ -NMR  $\delta$  (in  $CD_3OD$ ): 1.80 (2H, m, H-8), 2.62 (2H, dd,  $J = 8.1, 7.3$  Hz, H-7), 3.82 (3H, s, OMe), 3.85 (3H, s, OMe), 4.84 (1H, d,  $J = 7.2$  Hz, H-1''), 5.54 (1H, d,  $J = 5.9$  Hz, H-7'), 6.71 (1H, s, H-6), 6.73 (1H, s, H-2), 6.92 (1H, dd,  $J = 8.4, 1.8$  Hz, H-6'), 7.02 (1H, d,  $J = 1.8$  Hz, H-2'), 7.13 (1H, d,  $J = 8.4$  Hz, H-5').  $^{13}C$ -NMR  $\delta$  (in  $CD_3OD$ ): 33.4 (C-7), 36.3 (C-8), 56.1 (C-8'), 57.2 (OMe), 57.2 (OMe), 62.7 (C-9), 63.0 (C-6''), 65.5 (C-9'), 71.8 (C-4''), 75.4 (C-2''), 78.3 (C-5''), 78.6 (C-3''), 89.0 (C-7'), 103.2 (C-1''), 111.7 (C-2'), 114.6 (C-2), 118.4 (C-6), 118.4 (C-6'), 119.9 (C-5'), 130.1 (C-1), 137.6 (C-5), 138.8 (C-1'), 145.7 (C-3), 148.1 (C-4), 148.1 (C-4'), 151.4 (C-3').

**Compound 13** White powder,  $C_{16}H_{22}O_9$ ,  $^1H$ -NMR  $\delta$  (in  $CD_3OD$ ): 3.17 (1H, dd,  $J = 8.8, 8.1$  Hz, H-2''), 3.30 (overlapped with the signals of solvents, H-3'' and H-4''), 3.34 (2H, s, H-2), 3.38 (1H, m, H-5''), 3.68 (1H, dd,  $J = 13.2, 4.4$  Hz, H-6''), 3.85 (1H, dd,  $J = 13.2, 5.9$  Hz, H-6''), 3.89 (3H, s, OMe), 3.97 (1H, m, H-3), 4.26 (1H, m, H-3), 4.34 (1H, d,  $J = 8.1$  Hz, H-1''), 6.83 (1H, d,  $J = 8.4$  Hz, H-5'), 7.53 (1H, s, H-2'), 7.59 (1H, d,  $J = 8.4$  Hz, H-6').  $^{13}C$ -NMR  $\delta$  (in  $CD_3OD$ ): 39.6 (C-2), 56.8 (OMe), 63.9 (C-6''), 66.8 (C-3), 71.9 (C-4''), 75.4 (C-2''), 78.4 (C-5''), 78.4 (C-3''), 104.9 (C-1''), 112.3 (C-5'), 116.7 (C-2'), 125.7 (C-6'), 137.1 (C-1'), 150.0 (C-4'), 155.7 (C-3'), 199.9 (C-1).

**Compound 14** White powder,  $C_{19}H_{28}O_{12}$ ,  $^1H$ -NMR  $\delta$  (in  $CD_3OD$ ): 1.30 (3H, d,  $J = 6.3$  Hz, Me-6''), 3.31 (1H, m, H-3'), 3.35 (1H, m, H-4'), 3.40 (3H, s, 3''-OMe), 3.41 (1H, m, H-

5'), 3.47 (1H, t,  $J=9.5$  Hz, H-4''), 3.58 (1H, dd,  $J=9.1, 8.4$  Hz, H-3'), 3.63 (1H, d,  $J=7.7$  Hz, H-2'), 3.68 (1H, br d,  $J=12.7$  Hz, H-6'), 3.77 (3H, s, 4-OMe), 3.81 (3H, s, 3-OMe), 3.90 (1H, dd, 12.1, 2.2 Hz, H-6'), 4.12 (1H, m, H-5''), 4.15 (1H, m, H-2''), 4.89 (1H, d,  $J=7.8$  Hz, H-1'), 5.32 (1H, d,  $J=1.8$  Hz, H-1''), 6.64 (1H, dd,  $J=8.8, 2.9$  Hz, H-6), 6.75 (1H, d,  $J=2.9$  Hz, H-2), 6.85 (1H, d,  $J=8.8$  Hz, H-5).  $^{13}\text{C-NMR } \delta$  (in  $\text{CD}_3\text{OD}$ ): 18.7 (C-6''), 56.9 (3-OMe), 57.7 (4-OMe), 57.7 (3'-OMe), 63.1 (C-6'), 68.5 (C-2''), 70.4 (C-5''), 72.1 (C-4'), 73.2 (C-4''), 78.6 (C-5'), 79.4 (C-2'), 79.7 (C-3'), 82.4 (C-3''), 102.0 (C-1'), 102.8 (C-1''), 104.0 (C-2), 108.9 (C-5), 114.5 (C-6), 146.4 (C-1), 151.7 (C-4), 154.2 (C-3).

**Compound 15** White powder,  $\text{C}_{21}\text{H}_{22}\text{O}_{12}$ ,  $^1\text{H-NMR } \delta$  (in  $\text{CD}_3\text{OD}$ ): 3.21–3.38 (4H, m, H-2''–H-5''), 3.50 (1H, dd,  $J=12.1, 5.9$  Hz, H-6''), 3.73 (1H, dd,  $J=12.1, 1.8$  Hz, H-6''), 4.41 (1H, d,  $J=11.7$  Hz, H-3), 4.67 (1H, d,  $J=7.3$  Hz, H-1''), 4.81 (1H, d,  $J=11.7$  Hz, H-2), 5.71 (1H, d,  $J=2.2$  Hz, H-6), 5.75 (1H, d,  $J=2.2$  Hz, H-8), 6.73 (1H, d,  $J=8.4$  Hz, H-5'), 6.93 (1H, dd,  $J=8.4, 1.8$  Hz, H-6'), 7.21 (1H, d,  $J=1.8$  Hz, H-2').  $^{13}\text{C-NMR } \delta$  (in  $\text{CD}_3\text{OD}$ ): 63.0 (C-6''), 71.9 (C-4''), 73.9 (C-3), 75.3 (C-2''), 78.0 (C-3''), 78.7 (C-5''), 85.3 (C-2), 96.8 (C-8), 97.8 (C-6), 102.3 (C-10), 104.4 (C-1''), 117.4 (C-5'), 118.6 (C-2'), 125.1 (C-6'), 130.4 (C-1'), 147.0 (C-3'), 149.4 (C-4'), 164.8 (C-9), 165.7 (C-7), 169.1 (C-5), 198.8 (C-4).

**Compound 16** White powder,  $\text{C}_{15}\text{H}_{12}\text{O}_7$ ,  $^1\text{H-NMR } \delta$  (in  $\text{Me}_2\text{CO}-d_6$ ): 4.59 (1H, d,  $J=11.4$  Hz, H-3) 4.99 (1H, d,  $J=11.4$  Hz, H-2), 5.92 (1H, d,  $J=1.8$  Hz, H-6), 5.97 (1H, d,  $J=1.8$  Hz, H-8), 6.87 (2H, m, H-5', H-6'), 7.05 (1H, d,  $J=1.1$  Hz, H-2').  $^{13}\text{C-NMR } \delta$  (in  $\text{DMCO}-d_6$ ): 72.6 (C-3), 84.1 (C-2), 95.6 (C-8), 96.6 (C-6), 100.9 (C-10), 115.4 (C-2'), 115.4 (C-5'), 120.3 (C-6'), 129.1 (C-1'), 145.4 (C-3'), 146.2 (C-4'), 163.6 (C-9), 164.2 (C-7), 167.7 (C-5), 197.7 (C-4).

**Compound 17** Yellow powder,  $\text{C}_{21}\text{H}_{20}\text{O}_{12}$ ,  $^1\text{H-NMR } \delta$  (in  $\text{CD}_3\text{OD}$ ): 3.33–3.46 (4H, m, H-2''–H-5''), 3.64 (1H, dd,  $J=11.7, 3.3$  Hz, H-6''), 3.81 (1H, br d,  $J=11.7$  Hz, H-6''), 4.71 (1H, d,  $J=7.0$  Hz, H-1''), 5.99 (1H, d,  $J=1.7$  Hz, H-6), 6.25 (1H, d,  $J=1.7$  Hz, H-8), 6.78 (1H, d,  $J=8.4$  Hz, H-5'), 7.69 (1H, d,  $J=8.4$  Hz, H-6'), 7.96 (1H, s, H-2').  $^{13}\text{C-NMR } \delta$  (in  $\text{CD}_3\text{OD}$ ): 62.9 (C-6''), 71.7 (C-4''), 75.3 (C-2''), 78.1 (C-3''), 78.9 (C-5''), 95.1 (C-8), 99.9 (C-6), 104.9 (C-1''), 104.9 (C-10), 117.6 (C-2'), 118.4 (C-5'), 124.8 (C-1'), 125.5 (C-6'), 138.0 (C-3), 147.2 (C-2), 147.8 (C-3'), 150.9 (C-4'), 158.7 (C-9), 163.0 (C-5), 166.5 (C-7), 177.9 (C-4).

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