Triterpene Acids from the Leaves of *Planchonella duclitan* (Blanco) Bakhuizan

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From the methanolic extract of the leaves of *Planchonella duclitan*, 2α,3α,19α,23-tetrahydroxy-13,27-cyclours-11-en-28-oic acid (**1**), myrianthic acid (**2**), 2-hydroxyursolic acid (**3**), ursolic acid (**4**), pomolic acid (**5**), rotundic acid (**6**), and jacoumaric acid (**7**) were isolated, and their structures were elucidated on the basis of their spectroscopic analysis. Among them, compound **1** was a new cyclopropyl ursane-type triterpene acid. Additionally, compounds **4** and **7** showed significant cytotoxicity toward human colorectal carcinoma cell line HT29 and human breast carcinoma cell line MCF-7 with IC_{50} values ranging from 5.8 ± 1.4 to 6.5 ± 1.9 μM.

Keywords: *Planchonella duclitan*; Sapotaceae; Leaves; Triterpene acids; 2α,3α,19α,23-tetrahydroxy-13,27-cyclours-11-en-28-oic acid; HT29; MCF-7.

INTRODUCTION

Planchonella duclitan (Blanco) Bakhuizan, a tall tree belonging to the family Sapotaceae, is distributed only in the areas of Lanyu Island and South-East Asia.[1] It was used as firewood or for making the decks of ships locally, but not in folk medicines. Recently, it has been shown from our preliminary pharmacological experiments that the crude extracts of the leaves of this plant exhibited significant anti-proliferation activities toward breast cancer cell line MCF-7 and liver cancer cell line Hep 3B. The leaves may contain bioactive agents with anti-proliferation activities worth investigating phytochemically. Therefore, a series of phytochemical examinations on the leaf extracts of this plant was thus undertaken and has led to the isolation and characterization of seven triterpene acids **1**-**7**. This paper describes the isolation and structural elucidation of the new compound as well as their cytotoxicities.

RESULTS AND DISCUSSION

From the methanolic extract of the leaves of *P. duclitan* seven triterpene acids were identified. The compounds were isolated by a serial separation on Si-gravity column and reversed phase HPLC. Spectroscopic data of 2α,3α,19α,23-tetrahydroxy-12-en-28-oic acid (**2**) were interpreted by comparison with those reported in the literature, and reported as myrianthic acid.[2] The structure of **3** was determined to be 2α-hydroxyursolic acid, named as corosolic acid, having been isolated from callus tissue cultures of *Eriobotrya japonica*[3] and *Chaenomeles sinensis*.[4] Compound **4**, a major component, was obtained as a white powder whose spectral data were consistent with those of ursolic acid, having been isolated from *Ilex paraguariensis*[5] and *Baeckea gunniana*.[6] Both compounds **5** and **6** were ursolic acid analogues and were identified as pomolic acid (**5**), obtained previously from *Sanguisorba officinalis*,[7] and rotundic acid (**6**), isolated from the root bark of *Mussaenda macrophylla*.[8] Alkaline hydrolysis of compound **7** afforded corosolic acid (**3**) and *trans-p*-coumaric acid. This result and spectroscopic evidence showed **7** to be jacoumaric acid, which had been isolated from a Chinese Medicine, Goreishi (the feces of *Trogopterus xanthipes*),[9] and *Leptospermum scoparium*.[10]

Compound **1**, a white powder, had a molecular formula of $C_{30}H_{46}O_6$ based on the results of HRFABMS and ^{13}C-NMR experiments. It contained hydroxyl and carbonyl groups due to the IR absorption bands at 3441 and 1686 cm^{-1}, respectively. The ^{1}H-NMR data of **1** showed four singlet methyl groups (δ_H 0.85, 1.03, 1.16, and 1.59), one doublet methyl

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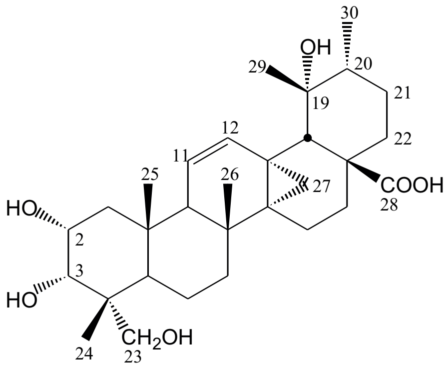

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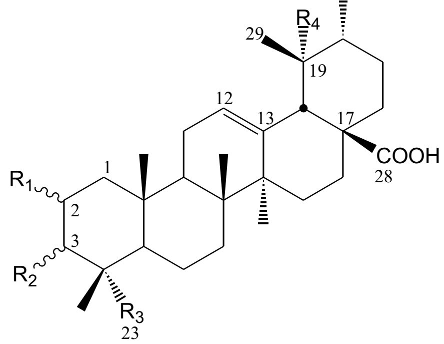

	R_1	R_2	R_3	R_4
2	α-OH	α-OH	CH_2OH	OH
3	α-OH	β-OH	CH_3	H
4	H	β-OH	CH_3	H
5	H	β-OH	CH_3	OH
6	H	β-OH	CH_2OH	OH
7	α-OH	β-*O*-*trans*-coumaroyl	CH_3	H

group [δ_H 1.08 (J = 6.5 Hz)], two oxygenated methine protons [δ_H 4.17 (br s, H-3), 4.34 (br d, J = 11.5 Hz, H-2)], two oxygenated methylene protons [δ_H 3.75 (d, J = 11.0 Hz, H_a-23), 3.90 (d, J = 11.0 Hz, H_b-23)], two olefinic protons [δ_H 5.44 (dd, J = 1.5, 9.5 Hz, H-11), 6.30 (dd, J = 1.5, 9.5 Hz, H-12)] at the low field region (Table 1). The ^{13}C-NMR and DEPT data showed four oxygenated carbons (δ_C 66.6, 71.7, 75.9, and 79.5), a disubstituted double bond (δ_C 119.6 and 142.1), and an acid carbonyl functional group (δ_C 181.2). On account of the molecular formula $C_{30}H_{46}O_6$, the index of hydrogen deficiency (IHD) of **1** was eight including one acid carbonyl and one olefinic functionalities. Thus, the number of rings of **1** should be six. HSQC and HMBC of **1** showed that two cyclopropyl protons at δ_H 1.52 and 2.35 had long-range correlations with one of the olefinic carbons (δ_C 142.1, C-12), three quaternary carbons [δ_C 28.2 (C-13), 33.6 (C-14), and 34.5 (C-8)], one tertiary carbon (δ_C 47.8, C-18), and one secondary carbon (δ_C 22.8, C-15). All these data suggested that compound **1** was a 13,27-cycloursane-type triterpene acid with four hydroxyl groups at C-2, -3, -19, and -23, one acid group at C-17, and one double bond at C-11 and -12. The NOESY spectrum of **1** exhibited mutual correlations between H-2, H_3-24, and H_3-25, confirming H-2 to be β-oriented. H-3 was also deduced to be β-oriented to fit the small axial-equatorial coupling constant between H-2 and H-3. Further analysis of all the 2D NMR data allowed the complete assignment of ^{1}H- and ^{13}C-NMR spectra of **1**, and these results are listed in Table 1. Accordingly, compound **1** was established as 2α,3α,19α,23-tetrahydroxy-13,27-cyclours-11-en-28-oic acid. Although ursane triterpenes are commonly found in higher plants, 13,27-cycloursane-type triterpenes such as **1** are rare. To our knowledge, the other three analogues of the 13,27-cycloursane triterpene were isolated from *Phylanthus engleri*,[11] and *Ficus microcarpa*.[12]

Compounds **1**-**7** were evaluated for their cytotoxic activities against two cell lines which were named human colorectal carcinoma HT29 and human breast carcinoma MCF-7. After 72 h of treatment, the relative polar compounds **1** and **2**, both bearing four hydroxyl groups at their C-2, -3, -19, -23 and one acid functionality at C-17, and with IC_{50} values higher than 40 μM, seemed to be less cytotoxic than compounds **3**-**7** toward the two cell lines (Table 2). Compounds **3**-**7** exhibited IC_{50} values ranging from 5.8 ± 1.4 to 32.4 ± 3.8 μM, and among them, **4** and **7** were the most toxic. Concerning the structure and activity relationships, pentacyclic triterpenes bearing a carboxylic acid functionality at their C-17 were found to exhibit potent cytotoxicity in the literature.[13] However, **1** and **2** exerted comparably low cytotoxic effect toward HT29 and MCF-7 in our results. The reason why **1** and **2** exhibited less potency toward these two cell lines remains to be studied. In addition, it was shown that pentacyclic triterpenes with an (*E*)- or (*Z*)-coumaroyl functionality at C-3 or -23 would display significant cytotoxic effects.[14] This was also observed in **7** which possessed an (*E*)-coumaroyl at its C-3, and exhibited an IC_{50} value similar to the positive control, the clinically used anticancer drug etoposide (VP-16, IC_{50} = 3.6 ± 1.7 ~ 8.2 ± 3.8 μM).

EXPERIMENTAL SECTION

General Methods

Optical rotation was measured on a Jasco P-1020 polarimeter (Tokyo, Japan). IR spectra were recorded on a Thermo

Table 1. ^{13}C- and ^{1}H-NMR spectral data of compound **1** (500 MHz, pyridine-d_5)

position	δ_C (ppm) mult.[a]	δ_H mult. (J/Hz)[b]	position	δ_C (ppm) mult.[a]	δ_H mult. (J/Hz)[b]
1	43.4 t	1.80	16	26.9 t	2.02 m
		2.19			2.72 m
2	66.6 d	4.34 br d (11.5)	17	47.5 s	
3	79.5 d	4.17 br s	18	47.8 d	2.85 s
4	42.4 s		19	75.9 s	
5	44.1 d	2.15	20	42.9 d	1.48
6	18.9 t	2.00	21	27.4 t	1.40
		1.70			1.96
7	37.7 t	1.49	22	38.0 t	2.07
		1.92			2.18
8	34.5 s		23	71.7 t	3.75 d (11.0)
9	53.8 d	2.17			3.90 d (11.0)
10	38.3 s		24	17.6 q	0.85 s
11	119.6 d	5.44 dd (1.5, 9.5)	25	19.4 q	1.03 s
12	142.1 d	6.30 dd (1.5, 9.5)	26	16.9 q	1.16 s
13	28.2 s		27	16.5 t	1.52 d (4.6)
14	33.6 s				2.35 d (4.6)
15	22.8 t	1.75 m	28	181.2 s	
		2.54 m	29	27.4 q	1.59 s
			30	16.3 q	1.08 d (6.5)

[a] Multiplicities were obtained from DEPT experiments.
[b] Signals without multiplicity were picked up from COSY or HMQC spectra.

Table 2. IC_{50} values of compounds **1**-**7** against human HT29 and MCF-7 cancer cell lines

Compound	IC_{50} (μM)[a]	
	HT29[b]	MCF-7[c]
1	> 40	> 40
2	> 40	> 40
3	6.9 ± 2.3	15.1 ± 2.1
4	5.8 ± 1.4	6.3 ± 0.5
5	24.1 ± 4.2	32.4 ± 3.8
6	21.8 ± 3.6	9.5 ± 2.5
7	6.5 ± 1.9	6.3 ± 1.7
VP-16[d]	3.6 ± 1.7	8.2 ± 3.8

[a] Cells were treated with various concentrations of tested compounds for 3 days. Cell growth was determined by methylene blue dye assay. The IC_{50} value resulting from 50% inhibition of cell growth was calculated. Each value represents the mean of three independent experiments.
[b] HT29 as human colorectal carcinoma cell line.
[c] MCF-7 as human breast carcinoma cell line.
[d] VP-16, a chemotherarpeutic drug, as reference compound in this study.

Mattson IR300 spectrometer (Califonia, USA). ^{1}H, ^{13}C and 2D NMR spectra were acquired on a Bruker DMX-500SB spectrometer. LR/HRFABMS and EIMS were obtained on a Finnigan/Thermo Quest MAT-95XL spectrometer (Bremen, Germany). HPLC was performed on a Hitachi L-7000 liquid chromatograph with a Bischoff RI detector (Leonberg, Germany).

Plant Material

The leaves of *P. duclitan* were collected from the National Museum of Natural Science in Taichung in December, 2003, and were identified by Dr. Chen Chang, an assistant researcher in Department of Botany, National Museum of Natural Science. A voucher specimen (No. 12292003) has been deposited at the Graduate Institute of Pharmacognosy Science, Taipei Medical University, Taipei, Taiwan.

Extraction and Isolation

Fresh leaves (3.0 kg) of *P. duclitan* were extracted three times with 10 L MeOH at room temperature for two weeks. The methanolic extract was concentrated in vacuum to give a black residue (200 g), which was re-dissolved in 85% aqueous methanol and then partitioned with *n*-hexane to generate two fractions: the aqueous methanol soluble fraction and the *n*-hexane soluble fraction. Subsequently the *n*-hexane fraction was vacuum-evaporated to dryness (50 g), which was pre-adsorbed with 75 g of silica gel, then loaded into a Si-open column (8 × 26 cm) with mixtures of *n*-hexane and EtOAc as eluents in a step-wise elution mode. Every 300 mL of eluent was collected as one fraction and each was analyzed by thin layer chromatography using plates of Silica gel 60, F_{254}, 0.2 mm thickness (Merck, Germany), and a solution of EtOAc/*n*-hexane (2:1) for development. Vanillin-sulfuric acid charring to form purple or blue spots was used to detect the triterpene acids. A total of 78 fractions was collected, and all the fractions were combined into nine major portions according to the TLC results. Portion VI (#fr.41~50) eluted by EtOAc/*n*-hexane (3:7) was further purified by repetitive HPLC on a Hypersil ODS semi-preparative column (10 × 250 mm, Thermo Electron Corp., Bellefonte, USA) with MeCN/H_2O (85:15) containing 0.1% trifluoroacetic acid (TFA) as eluent to afford **4** (68 mg) and **5** (14 mg). Portion VII (#fr.51~58) eluted by EtOAc/hexane (1:1) was further purified by HPLC using the same column with MeCN/H_2O (80:20) containing 0.1% TFA as eluent to afford **3** (37 mg) and **7** (8 mg). Portion VIII (#fr.59~70) eluted by EtOAc was further purified using the same chromatograph with MeCN/H_2O (65:35) containing 0.1% TFA as eluent to afford **6** (5 mg), and with MeCN/H_2O (45:55) containing 0.1% TFA as eluent to afford **1** (16 mg) and **2** (14 mg).

Cell Culture

Human colorectal carcinoma HT29 cells and breast carcinoma MCF-7 cells were maintained in RPMI-1640 medium supplied with 5% fetal bovine serum, 100 units/mL penicillin and 100 μg/mL streptomycin.

Growth Inhibition Assay

Cells in logarithmic growth phase were cultured at a density of 1×10^4 cells/mL/well in a 24-well plate. The cells were exposed to various concentrations of the test drugs for 3 days. At the end of the incubation period, cells were fixed and stained with 50% ethanol containing 0.5% methylene blue for 30 min. The plates were washed five times with water and allowed to air dry. The resulting colored residue was dissolved in 1% *N*-lauroyl-sarcosine, and optical density was read at 570 nm using a Bio-Rad microplate reader (Model 2550). Each point represents the average of at least two independent experiments run in triplicate.

2α,3α,19α,23-Tetrahydroxy-13,27-cyclours-11-en-28-oic acid (1)

Amorphous white powder; $[\alpha]_D^{25}$ -6.5° (*c* 1.0, MeOH); IR ν_{max} (KBr) 3441, 2929, 1686 cm^{-1}; ^1H- and ^{13}C-NMR data see Table 1; FABMS *m/z* 503 $[M + H]^+$; HRFABMS *m/z* 503.3376 $[M + H]^+$ (Calcd. for $C_{30}H_{47}O_6$ 503.3373).

Myrianthic acid (2)

Amorphous white powder; $[\alpha]_D^{25}$ +22.1° (*c* 1.0, MeOH); IR ν_{max} (KBr) 3570, 3387, 2935, 1686 cm^{-1}; ^1H-NMR (pyridine-d_5) δ 4.65 (1H, br d, *J* = 11.5 Hz, H-2), 4.38 (1H, br s, H-3), 5.62 (1H, br s, H-12), 3.05 (1H, s, H-18), 3.72 (1H, d, *J* = 11.0 Hz, H_a-23), 3.92 (1H, d, *J* = 11.0 Hz, H_b-23), 0.88 (3H, s, H-24), 1.04 (3H, s, H-25), 1.14 (3H, s, H-26), 1.70 (3H, s, H-27), 1.42 (3H, s, H-29), 1.13 (3H, d, *J* = 6.0 Hz, H-30); ^{13}C-NMR (pyridine-d_5) δ 42.8 (C-1), 66.7 (C-2), 79.5 (C-3), 43.1 (C-4), 48.2 (C-5), 18.9 (C-6), 33.7 (C-7), 41.0 (C-8), 44.0 (C-9), 39.0 (C-10), 24.6 (C-11), 128.4 (C-12), 140.5 (C-13), 42.7 (C-14), 29.7 (C-15), 26.8 (C-16), 48.7 (C-17), 55.1 (C-18), 73.1 (C-19), 42.3 (C-20), 27.4 (C-21), 38.9 (C-22), 71.7 (C-23), 17.5 (C-24), 17.8 (C-25), 18.2 (C-26), 25.1 (C-27), 181.2 (C-28), 27.5 (C-29), 17.2 (C-30); FABMS *m/z* 527 $[M + Na]^+$.

Corosolic acid (3)

Amorphous white powder; $[\alpha]_D^{25}$ +38.5° (*c* 1.0, MeOH); IR ν_{max} (KBr) 3423, 2926, 1688 cm^{-1}; ^1H-NMR (pyridine-d_5) δ 4.11 (1H, ddd, *J* = 4.0, 9.5, 11.0 Hz, H-2), 3.43 (1H, d, *J* = 9.5 Hz, H-3), 5.48 (1H, br s, H-12), 2.65 (1H, d, *J* = 11.0 Hz, H-18), 1.30 (3H, s, H-23), 1.10 (3H, s, H-24), 1.01 (3H, s, H-25), 1.07 (3H, s, H-26), 1.23 (3H, s, H-27), 1.00 (3H, d, *J* = 6.0 Hz, H-29), 0.97 (3H, d, *J* = 6.0 Hz, H-30); ^{13}C-NMR (pyridine-d_5) δ 48.5 (C-1), 69.1 (C-2), 84.3 (C-3), 40.3 (C-4), 56.4 (C-5), 19.3 (C-6), 34.0 (C-7), 40.5 (C-8), 48.5 (C-9), 38.9 (C-10), 24.2 (C-11), 126.0 (C-12), 139.8 (C-13), 43.0 (C-14), 29.1 (C-15), 25.4 (C-16), 48.6 (C-17), 54.0 (C-18), 39.9 (C-19), 40.0 (C-20), 31.5 (C-21), 37.9 (C-22), 29.8 (C-23), 18.2 (C-24), 17.4 (C-25), 17.9 (C-26), 24.4 (C-27), 180.4 (C-28), 18.0 (C-29), 21.9 (C-30); EIMS *m/z* (rel. int.) (%) 472 (M^+, 1), 248 (100), 203 (19), 133 (14).

Ursolic acid (4)

Amorphous white powder; $[\alpha]_D^{25}$ +78.2° (*c* 1.0, MeOH); IR ν_{max} (KBr) 3419, 2925, 1687 cm^{-1}; ^1H-NMR (pyridine-d_5) δ 3.49 (1H, dd, *J* = 6.0, 10.0 Hz, H-3), 5.52 (1H, br s, H-12), 2.68 (1H, d, *J* = 11.0 Hz, H-18), 1.27 (3H, s, H-23), 0.91 (3H, s, H-24), 1.08 (3H, s, H-25), 1.05 (3H, s, H-26), 1.25 (3H, s, H-27), 1.03 (3H, d, *J* = 6.0 Hz, H-29), 0.98 (3H, d, *J* = 6.0 Hz, H-30); ^{13}C-NMR (pyridine-d_5) δ 39.9 (C-1), 28.6 (C-2), 78.6 (C-3), 39.5 (C-4), 56.3 (C-5), 19.3 (C-6), 34.1 (C-7), 40.0 (C-8), 48.5 (C-9), 37.9 (C-10), 24.1 (C-11), 126.1 (C-12), 139.8 (C-13), 43.0 (C-14), 29.2 (C-15), 25.4 (C-16), 48.5 (C-17), 54.0 (C-18), 40.4 (C-19), 39.9 (C-20), 31.5 (C-21), 37.8 (C-22), 29.3 (C-23), 17.1 (C-24), 16.2 (C-25), 18.0 (C-

26), 24.4 (C-27), 180.4 (C-28), 17.9 (C-29), 21.9 (C-30); FABMS *m/z* 457 $[M + H]^+$.

Pomolic acid (5)

Amorphous white powder; $[\alpha]_D^{25}$ +21.9° (*c* 1.0, MeOH); IR ν_{max} (KBr) 3445, 2931, 1688 cm^{-1}; ^{1}H-NMR (pyridine-d_5) δ 3.46 (1H, dd, *J* = 4.5, 10.0 Hz, H-3), 5.64 (1H, br s, H-12), 3.09 (1H, s, H-18), 1.05 (3H, s, H-23), 1.26 (3H, s, H-24), 0.94 (3H, s, H-25), 1.13 (3H, s, H-26), 1.76 (3H, s, H-27), 1.48 (3H, s, H-29), 1.15 (3H, d, *J* = 6.0 Hz, H-30); ^{13}C-NMR (pyridine-d_5) δ 39.5 (C-1), 28.6 (C-2), 78.7 (C-3), 39.9 (C-4), 56.3 (C-5), 19.4 (C-6), 34.1 (C-7), 40.8 (C-8), 48.3 (C-9), 37.8 (C-10), 24.5 (C-11), 128.5 (C-12), 140.4 (C-13), 42.6 (C-14), 29.8 (C-15), 26.9 (C-16), 48.8 (C-17), 55.1 (C-18), 73.2 (C-19), 42.8 (C-20), 27.4 (C-21), 39.0 (C-22), 17.0 (C-23), 29.3 (C-24), 16.0 (C-25), 17.2 (C-26), 25.2 (C-27), 181.1 (C-28), 27.6 (C-29), 17.4 (C-30); EIMS *m/z* (rel. int.) (%) 472 (M^+, 18), 427 (48), 248 (54), 146 (100).

Rotundic acid (6)

Amorphous white powder; $[\alpha]_D^{25}$ +35.9° (*c* 1.0, MeOH); IR ν_{max} (KBr) 3419, 2928, 1688 cm^{-1}; ^{1}H-NMR (pyridine-d_5) δ 4.24 (1H, dd, *J* = 4.5, 10.0 Hz, H-3), 5.64 (1H, br s, H-12), 3.08 (1H, s, H-18), 3.75 (1H, d, *J* = 10.0 Hz, H_a-23), 4.21 (1H, d, *J* = 10.0 Hz, H_b-23), 1.08 (3H, s, H-24), 1.01 (3H, s, H-25), 1.16 (3H, s, H-26), 1.71 (3H, s, H-27), 1.46 (3H, s, H-29), 1.13 (3H, d, *J* = 6.5 Hz, H-30); ^{13}C-NMR (pyridine-d_5) δ 39.2 (C-1), 28.2 (C-2), 73.5 (C-3), 43.4 (C-), 48.7 (C-5), 19.1 (C-6), 33.6 (C-7), 30.4 (C-8), 48.2 (C-9), 37.6 (C-10), 24.5 (C-11), 128.4 (C-12), 140.5 (C-13), 40.8 (C-14), 29.8 (C-15), 42.5 (C-16), 43.4 (C-17), 55.0 (C-18), 73.0 (C-19), 42.8 (C-20), 27.4 (C-21), 39.0 (C-22), 67.7 (C-23), 13.7 (C-24), 16.5 (C-25), 17.7 (C-26), 25.1 (C-27), 181.3 (C-28), 27.5 (C-29), 17.3 (C-30); EIMS *m/z* (rel. int.) (%) 488 (M^+, 6), 264 (54), 146 (100).

Jacoumaric acid (7)

Amorphous white powder; $[\alpha]_D^{25}$ +28.1° (*c* 1.0, MeOH); UV λ_{max} (log ε) (MeOH) 227 (3.5), 295 (3.8), 312 (4.0) nm; IR ν_{max} (KBr): 3446, 2928, 1688 cm^{-1}; ^{1}H-NMR (pyridine-d_5) δ 4.32 (1H, dt, *J* = 4.0, 10.0 Hz, H-2), 5.28 (1H, d, *J* = 10.0 Hz, H-3), 5.49 (1H, br s, H-12), 2.65 (1H, d, *J* = 11.0 Hz, H-18), 1.08 (3H, s, H-23), 1.06 (3H, s, H-24), 1.01 (3H, s, H-25), 1.06 (3H, s, H-26), 1.24 (3H, s, H-27), 1.06 (3H, d, *J* = 6.0 Hz, H-29), 0.98 (3H, d, *J* = 6.0 Hz, H-30), 6.69 (1H, d, *J* = 15.0 Hz, H-2′), 8.02 (1H, d, *J* = 15.0 Hz, H-3′), 7.57 (2H, d, *J* = 7.5 Hz, H-2″, 6″), 7.18 (2H, d, *J* = 7.5 Hz, H-3″, 5″); ^{13}C-NMR (pyridine-d_5) δ 48.3 (C-1), 66.7 (C-2), 85.4 (C-3), 40.2 (C-4), 55.9 (C-5), 19.0 (C-6), 33.7 (C-7), 40.3 (C-8), 48.9 (C-9), 38.7 (C-10), 24.1 (C-11), 125.8 (C-12), 139.9 (C-13), 42.9 (C-14), 29.0 (C-15), 25.3 (C-16), 48.4 (C-17), 53.9 (C-18), 39.9 (C-19), 39.8 (C-20), 31.5 (C-21), 37.9 (C-22), 29.4 (C-23), 18.7 (C-24), 17.3 (C-25), 18.0 (C-26), 24.4 (C-27), 180.5 (C-28), 17.8 (C-29), 21.9 (C-30), 168.4 (C-1′), 117.3 (C-2′), 145.3 (C-3′), 126.6 (C-1″), 131.1 (C-2″), 116.5 (C-3″), 161.8 (C-4″), 116.5 (C-5″), 131.1 (C-6″); FABMS *m/z* 641 $[M + Na]^+$.

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