5α-Steroidal Glycosides from *Parepigynum funingense*

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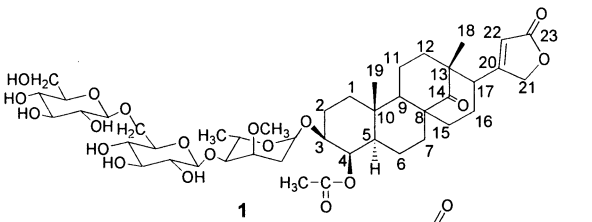
Received November 1, 2002

Four new 5α-steroidal glycosides with an unusual framework, funingenosides A (**1**), B (**2**), C (**3**), and D (**4**), were isolated from the roots of *Parepigynum funingense*. Their structures were elucidated on the basis of 1D and 2D NMR techniques. The structure and relative stereochemistry of compound **1** were demonstrated by X-ray crystallographic analysis.

Parepigynum funingense Tsiang et P. T. Li (Apocynaceae), a member of a monotypic genus, is distributed widely in Yunnan Province, People's Republic of China.[1] Due to the absence of any previous chemical studies on this species, we examined an extract of the roots from *Parepigynum funingense*. In this paper, we describe the isolation and structure elucidation of four new 5α-steroidal glycosides, namely, funingenosides A (**1**), B (**2**), C (**3**), and D (**4**). The relative configuration of **1** was determined by X-ray crystallographic analysis.



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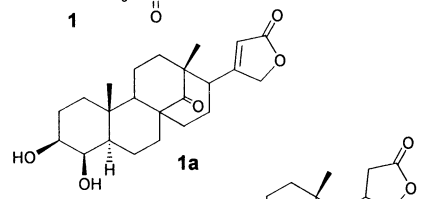
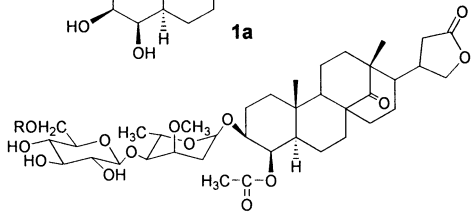


1a



2 R=β-D-glucopyranosyl
3 R=H
4 R=β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl

Funingenoside A (**1**) was obtained as colorless needles (MeOH) and analyzed for $C_{44}H_{66}O_{19}$ by negative-ion HR-FABMS. Its IR spectrum exhibited absorption bands for hydroxyl (3431 cm^{-1}), carbonyl (1742 and 1701 cm^{-1}), and olefinic groups (1627 cm^{-1}). The UV spectrum indicated the presence of an α,β-unsaturated carbonyl group (λ_{max} 211 nm). The ^1H and ^{13}C NMR spectra showed signals due to one acetyl group [δ_C 21.1 (q), 170.8 (s)], two carbonyl groups [δ_C 220.8 (s), 171.9 (s)], two olefinic carbons [δ_C 173.5 (s), 116.4 (d)], and two angular methyl groups [δ_C 16.1 (q), 23.3 (q)]. Also observed were signals of three anomeric carbons and their corresponding anomeric protons [δ_C 95.0 (d), 101.7 (d), 105.5 (d); δ_H 5.12 (1H, br s), 4.96 (1H, d, J = 7.6 Hz), 5.15 (1H, d, J = 7.8 Hz)]. In the negative FABMS, significant peaks occurred at *m/z* 736 [M − 162]$^-$, 573 [M − H − 162 − 162]$^-$, and 429 [M − H − 162 − 162 − 144]$^-$, and indicated the elimination of three hexosyl moieties.

Acid hydrolysis of **1** with 1 N HCl furnished two monosaccharides and an aglycon (**1a**). The two monosaccharides were determined to be D-glucose and L-cymarose by measuring their optical rotation values and TLC comparison with authentic samples. The EIMS of **1a** exhibited a $[M]^+$ ion at *m/z* 388, compatible with the molecular formula $C_{23}H_{32}O_5$. A careful comparison of the ^1H and ^{13}C NMR data of **1a** with those of oleagenin, (8*R*)-3β-hydroxy-14-oxo-5β-15(14→8)-*abeo*-card-20(22)-enolide,[2] showed that the two structures were very similar except that **1a** had one additional hydroxyl group. The downfield resonance of H-4 [δ_H 4.03 (1H, br s)] suggested that an additional hydroxyl group was attached at C-4. This observation was confirmed by the $^1H-^1H$ COSY spectrum of **1a**, in which H-4 correlated with H-3 [δ_H 3.78 (1H, m) and H-5 [δ_H 0.98 (1H, m)]. Comparison of the ^{13}C NMR data for **1a** with those for oleagenin also showed that the C-19 methyl of **1a** was shifted downfield to δ_C 16.7, suggesting a 5α-structure.[3] The stereochemistry of H-3 was determined to be α-oriented by the ROESY correlation between H-5α and H-3, which indicated their *cis* relationship. The configuration of OH-4 could be determined by the signal of H-4. For a chairlike conformation of the A-ring, when the substituent at C-4 is β-oriented, H-4α appears as a broad singlet. The signal of H-4 (1H, br s) thus confirmed the β-orientation of OH-4. This was further supported by the evidence that there was no correlation between H-4 and Me-19 in the ROESY spectrum. Thus, **1a** was concluded to be the new compound (8*R*)-3β,4β-dihydrox-yl-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-enolide.

Sugar proton and carbon signals in the NMR spectra of compound **1** were assigned by $^1H-^1H$ COSY, HMQC, and HMQC-TOCSY spectra. The HMBC spectrum was used to determine the binding sites of each sugar. In the HMBC spectrum, long-range couplings were observed for H-1′ of the cymarosyl unit (δ_H 5.12) to C-3 of the aglycon [δ_C 75.2 (d)], H-1″ of the glucosyl unit (δ_H 4.96) to C-4′ of the cymarosyl unit [δ_C 78.5 (d)], and H-1‴ of the terminal glucosyl unit (δ_H 5.15) to C-6″ of the glucosyl unit [δ_C 70.5 (t)]. The anomeric configurations of D-glucose and L-

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10.1021/np020411o CCC: $25.00
Published on Web 06/07/2003

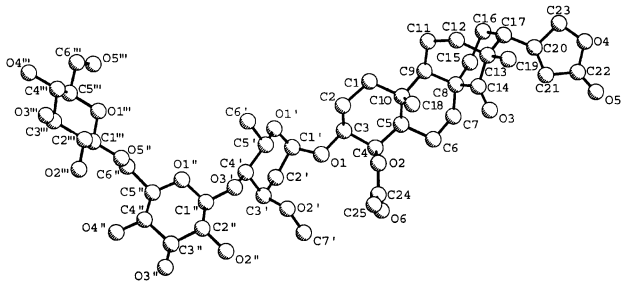

Figure 1. Crystal structure of compound **1**.

cymarose were determined to be β and α, respectively, from the coupling constants of the anomeric proton signals.

The only remaining problem in the structure determination of **1** was the placement of the acetyl group which was not conjugated with a double bond. In the HMBC spectrum of **1**, long-range couplings were observed between the deshielded H-4 [δ_H 5.37 (1H, br s)] and the acetyl carbonyl carbon [δ_C 170.8 (s)], suggesting the location of the acetyl group at C-4.

On the basis of the above evidence, the structure of **1** was elucidated as (8*R*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl)oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-enolide and was named funingenoside A. Finally, the structure and relative stereochemistry of **1** were demonstrated unambiguously by X-ray crystallographic analysis, which confirmed its proposed configuration, the results of which are shown in Figure 1. This is the first report of the isolation of a 5α-oleagenin-type cardenolide.

Funingenoside B (**2**) was assigned a molecular formula of $C_{44}H_{68}O_{19}$ by negative-ion HRFABMS, which was confirmed from the ^{13}C and DEPT NMR spectra. Comparison of the ^1H and ^{13}C NMR spectra with those of **1** showed that the two structures were very similar except for the absence of the olefinic group and the downfield resonance of C-23 to δ_C 177.4, suggesting the carbonyl group of the five-membered lactone was not conjugated with a double bond in **2**. This observation was confirmed by the absorption of the carbonyl group at 1777 cm^{-1} in the IR spectrum and the absence of any significant UV absorption. The stereochemistry at the other chiral centers in **2** was identical to that of **1**, as supported by its ^1H, $^1H-^1H$ COSY, and ^{13}C NMR spectra. Hence, the structure of funingenoside B was deduced as (8*R*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl)-oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-dihydroenolide and was named funingenoside B.

A molecular formula of $C_{38}H_{58}O_{14}$ was deduced for funingenoside C (**3**) by negative-ion HRFABMS. Its molecular weight was 738, 162 mass units less than that of **2**. The spectral data of ^1H and ^{13}C NMR of compound **3** were almost identical with those of **2** except that there were only two sugar units in compound **3**. This was also confirmed by the C-6″ of the glucosyl unit, which was shifted downfield to δ_C 63.0. On the basis of the above results, the structure of **3** was elucidated as (8*R*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl)oxy]-14-oxo-5α-15 (14→8)-*abeo*-card-20(22)-dihydroenolide, and was named funingenoside C.

Funingenoside D (**4**) was assigned a molecular formula of $C_{50}H_{78}O_{24}$ by negative-ion HRFABMS. A careful comparison of the ^1H and ^{13}C NMR spectra of **4** with those of **2** showed that the two structures were very similar except that there was one additional sugar unit in **4**. The $[M]^-$ ion at 1062, 162 mass units more than that of **2**, coupled with the sugar proton and carbon signals in the NMR spectra indicated that **4** had one additional glucose. In the HMBC spectrum, long-range couplings were observed between H-1‴″ of the terminal cymarosyl unit (δ_H 5.09) and C-6‴ of the glucosyl unit [δ_C 70.3 (t)], H-1‴ of the glucosyl unit (δ_H 5.04) and C-6″ of the glucosyl unit [δ_C 70.2 (t)], and H-1″ of the glucosyl unit (δ_H 4.96) and C-4′ of the cymarosyl unit [δ_C 78.5 (d)]. On the basis of the above results, the structure of **4** could be deduced as (8*R*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaopyranosyl)oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-dihydroenolide and was named funingenoside D.

Experimental Section

General Experimental Procedures. Melting points were obtained on an XRC-1 apparatus and are uncorrected. Optical rotations were measured with a Horiba SEAP-300 spectropolarimeter. UV spectra were taken on a Shimadzu double-beam 210A spectrophotometer. IR spectra were obtained on a Bio-Rad FTS-135 infrared spectrophotometer with KBr pellets. ^1H NMR, ^{13}C NMR, and 2D NMR spectra were recorded on Bruker AM-400 MHz and DRX-500 spectrometers with TMS as internal standard. MS data were recorded on a VG Autospec-3000 spectrometer. X-ray analysis was performed with a MAC DIP-2030K diffractometer.

Plant Material. The roots of *Parepigynum funingense* were collected from Jinchang, Malipo County, Yunnan Province, People's Republic of China, in April 2000. The plant was identified by Prof. X. Gong, Kunming Insitiute of Botany, Chinese Academy of Sciences, Kunming, Yunnan, People's Republic of China, where a voucher specimen (No. 0774313) is deposited.

Extraction and Isolation. The dried roots (15 kg) of *P. funingense* were extracted with 75% EtOH three times under reflux. After removal of the solvent in vacuo, the aqueous solution was passed through a HPD-100 column and the absorbed materials were eluted with 65% aqueous methanol and methanol, successively. The 65% methanol eluate was concentrated in vacuo to give a residue (138 g), which was chromatographed on a silica gel (200−300 mesh) column and eluted with gradient mixtures of $CHCl_3$−MeOH (9:1 → 2:1) to afford eight fractions. Each fraction was further subjected to repeated silica gel (200−300 mesh) column chromatography using mixtures of EtOEt−MeOH−H_2O of increasing polarity (8:1:0.1 → 4:1:0.1) as eluents and passage over RP-18 eluted with MeOH−H_2O (4:6). Fraction 4 (14.78 g) afforded **1** (385 mg). Fraction 5 (12.1 g) yielded **2** (1.1 g). Fraction 2 (9.0 g) gave **3** (205 mg), and fraction 8 (8.2 g) afforded **4** (52 mg).

Funingenoside A (1): colorless needles (MeOH); mp 261−265 °C; $[\alpha]^{26}_D$ −53.7° (*c* 0.87, MeOH); UV (MeOH) λ_{max} (log ϵ) 211 (3.98) nm; IR (KBr) ν_{max} 3431, 2931, 1742, 1701, 1627, 1455, 1371, 1245, 1164, 1049 cm^{-1}; ^1H NMR (C_5D_5N, 500 MHz) δ 5.88 (1H, s, H-22), 5.37 (1H, br s, H-4), 5.15 (1H, d, J = 7.8 Hz, H-1‴$_{glc}$), 5.12 (1H, br s, H-1′$_{cym}$), 4.96 (1H, d, J = 7.6 Hz, H-1″$_{glc}$), 4.81 (1H, d, J = 11.5 Hz, H-21β), 3.95 (1H, d, J = 11.5 Hz, H-21α), 3.74 (1H, m, H-3), 3.38 (3H, s, OMe-3′), 2.99 (1H, dd, J = 6.1, 1.5 Hz, H-17), 1.99 (3H, s, Ac), 1.53 (3H, d, J = 6.3 Hz, H-6′), 1.00 (1H, m, H-5α), 0.93 (3H, s, Me-18), 0.91 (3H, s, Me-19); ^{13}C NMR, see Table 1; negative-ion FABMS *m*/*z* 898 $[M]^-$ (100), 736 (3), 573 (6), 429 (3), 245 (7), 123 (30); HRFABMS *m*/*z* 897.4146 $[M - H]^-$ (calcd for $C_{44}H_{65}O_{19}$, 897.4091).

X-ray crystal structure analysis of funingenoside A (1): space group $P2_12_12_1$, a = 8.584(1) Å, b = 12.426(1) Å, c = 49.504(2) Å, V = 5280.3(8) Å^3, D_x = 1.274 g/cm^3, Z = 4. X-ray diffraction data of an approximate 0.30 × 0.50 × 0.50 mm crystal were collected at 296 K on a MAC DIP-2030k area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were collected and reduced using DENZO and SCALE.[4] A total of 14 733 reflections were measured, of which 4777 (R_{int} = 0.034) reflections were unique. The

Table 1. ^{13}C NMR Data for Compounds **1**, **1a**, and **2**−**4** (in pyridine-d_5 at 100 MHz)

carbon	1	1a	2	3	4
1	38.5 t	39.2 t	38.4 t	38.4 t	38.4 t
2	25.3 t	26.4 t	25.4 t	25.3 t	25.3 t
3	75.2 d	72.6 d	75.3 d	75.2 d	75.2 d
4	72.4 d	74.8 d	72.4 d	71.8 d	72.4 d
5	46.5 d	48.2 d	46.6 d	46.5 d	46.6 d
6	35.1 t	35.6 t	35.1 t	35.0 t	35.0 t
7	23.4 t	24.4 t	23.8 t	23.7 t	23.9 t
8	49.6 s	49.4 s	49.4 s	49.3 s	49.3 s
9	60.6 d	60.6 d	60.5 d	60.6 d	60.5 d
10	38.6 s	38.6 s	38.4 s	38.4 s	38.4 s
11	21.4 t	21.0 t	21.0 t	20.9 t	21.1 t
12	42.3 t	42.2 t	42.3 t	42.3 t	42.3 t
13	47.7 s	47.8 s	49.6 s	49.5 s	49.5 s
14	220.8 s	220.8 s	221.1 s	220.7 s	220.9 s
15	43.5 t	43.6 t	43.5 t	43.4 t	43.4 t
16	26.3 t	26.8 t	23.6 t	23.5 t	23.5 t
17	52.8 d	52.7 d	56.0 d	56.0 d	56.0 d
18	23.3 q	23.7 q	23.9 q	23.8 q	23.9 q
19	16.1 q	17.1 q	16.2 q	16.1 q	16.3 q
20	173.5 s	173.6 s	36.5 d	36.5 d	36.5 d
21	73.6 t	73.3 t	71.6 t	71.5 t	71.7 t
22	116.4 d	116.3 d	36.6 t	36.5 t	36.5 t
23	171.9 s	171.5 s	177.4 s	177.1 s	177.2 s
Ac	170.8 s		170.8 s	170.7 s	170.7 s
Ac	21.1 q		21.1 q	21.0 q	21.1 q
cymarosyl					
1′	95.0 d		95.0 d	94.9 d	94.9 d
2′	31.8 t		31.8 t	31.7 t	31.8 t
3′	73.3 d		73.3 d	73.2 d	73.3 d
4′	78.5 d		78.5 d	78.4 d	78.5 d
5′	65.2 d		65.2 d	64.9 d	65.2 d
6′	18.6 q		18.6 q	18.4 q	18.9 q
OMe-3′	56.4 q		56.5 q	56.4 q	56.4 q
glucosyl					
1″	101.7 d		101.8 d	102.0 d	101.8 d
2″	75.3 d		75.3 d	75.5 d	75.3 d
3″	78.3 d		78.4 d	78.7 d	78.4 d
4″	71.8 d		71.8 d	72.3 d	71.6 d
5″	78.3 d		77.8 d	78.6 d	77.1d
6″	70.5 t		70.3 t	63.0 t	70.2 t
glucosyl					
1‴	105.5 d		105.5 d		105.5 d
2‴	75.3 d		75.3 d		75.1 d
3‴	78.5 d		78.4 d		77.7 d
4‴	71.8 d		71.8 d		71.7 d
5‴	78.5 d		78.5 d		78.4 d
6‴	62.8 t		62.9 t		70.3 t
glucosyl					
1⁗					105.5 d
2⁗					75.2 d
3⁗					78.5 d
4⁗					71.6 d
5‴					78.4 d
6‴					62.8 t

structure was solved by direct methods using SHELXS-97.[5] The non-hydrogen atoms were refined by a full-matrix least-squares method with anisotropic displacement parameters. Hydrogen atoms were obtained from geometric calculation and difference Fourier maps and refined with isotropic displacement parameters. There was some disorder for atoms such as O-4, O-5, O-6, C-19, C-22, C-23, C-24, C-25, and the solvent molecule. The final refinement gave $R_1 = 0.079$ and $wR_2 = 0.1988$ [$F^2 > 3\sigma F^2$].[6]

Acidic Hydrohysis of Compound 1. Compound **1** (100 mg) was hydrolyzed with 1:1 2 N HCl−1,4-dioxane (40 mL) for 2 h, and the reaction mixture was extracted with EtOAc (50 mL × 3) to afford **1a** (35 mg). Evaporation of the aqueous layer of the aforementioned hydrolysate gave the residue (56 mg) containing monosaccharides, which was separated by preparative paper chromatography (BuOH−pyridine−H_2O, 6:4:3) to afford D-glucose (21.8 mg, $[\alpha]^{26}_D$ +54° (*c* 0.56, H_2O)) and L-cymarose (9.5 mg, $[\alpha]^{26}_D$ −50° (*c* 0.30, H_2O)) as determined by TLC comparison with authentic samples.

Compound 1a: colorless needles (MeOH); mp 280−286 °C; $[\alpha]^{26}_D$ −53.7° (*c* 0.87, MeOH); ^{1}H NMR (C_5D_5N, 500 MHz) δ 5.85 (1H, s, H-22), 4.78 (1H, d, J = 12.0 Hz, H-21β), 4.03 (1H, br s, H-4), 3.89 (1H, d, J = 12.0 Hz, H-21α), 3.78 (1H, m, H-3), 2.95 (1H, dd, J = 7.0, 1.5 Hz, H-17), 1.02 (3H, s, Me-19), 0.98 (1H, m, H-5α), 0.95 (3H, s, Me-18); ^{13}C NMR, see Table 1; EIMS *m*/*z* 388 $[M]^+$ (100), 370 (58), 352 (20), 337 (25), 311 (10), 262 (28), 233 (31), 206 (33), 180 (25), 143 (46), 137 (25), 119 (35), 93 (38), 79 (42).

Funingenoside B (2): white powder; mp 271−275 °C; $[\alpha]^{26}_D$ −73.9° (*c* 0.43, MeOH); IR (KBr) ν_{max} 3435, 2932, 1777, 1734, 1699, 1456, 1371, 1243, 1166, 1050 cm^{-1}; ^{1}H NMR (C_5D_5N, 500 Hz) δ 5.38 (1H, br s, H-4), 5.16 (1H, d, J = 7 Hz, H-1‴_{glc}), 5.13 (1H, br s, H-1′$_{cym}$), 4.97 (1H, d, J = 7.5 Hz, H-1″$_{glc}$), 4.12 (1H, dd, J = 15.0, 4.5 Hz, H-21β), 3.88 (1H, dd, J = 15.0, 6.5 Hz, H-21α), 3.76 (1H, m, H-3), 3.40 (3H, s, OMe-3′), 2.01 (3H, s, Ac), 1.98 (1H, m, H-17), 1.05 (3H, s, Me-18), 1.03 (1H, m, H-5α), 0.94 (3H, s, Me-19); ^{13}C NMR, see Table 1; negative-ion FABMS *m*/*z* 900 $[M]^-$ (100), 737 (5), 573 (3), 431 (1), 159 (12), 119 (25); HRFABMS *m*/*z* 899.4323 $[M - H]^-$ (calcd for $C_{44}H_{67}O_{19}$, 899.4277).

Funingenoside C (3): white powder; mp 256−259 °C; $[\alpha]^{13}_D$ −75.9° (*c* 0.22, MeOH); ^{1}H NMR (C_5D_5N, 500 Hz) δ 5.38 (1H, br s, H-4), 5.13 (1H, br s, H-1′$_{cym}$), 5.02 (1H, d, J = 7.0 Hz, H-1″$_{glc}$), 4.22 (1H, dd, J = 15.5, 4.8 Hz, H-21β), 3.94 (1H, dd, J = 15.5, 6.8 Hz, H-21α), 3.75 (1H, m, H-3), 3.41 (3H, s, OMe-3′), 2.01 (3H, s, Ac), 1.94 (1H, m, H-17), 1.03 (3H, s, Me-18), 1.00 (1H, m, H-5α), 0.92 (3H, s, Me-19); ^{13}C NMR, see Table 1; negative-ion FABMS *m*/*z* 737 $[M - H]^-$ (100), 573 (3); HRFABMS *m*/*z* 737.3788 $[M - H]^-$ (calcd for $C_{38}H_{57}O_{14}$, 737.3777).

Funingenoside D (4): white powder; mp 248−253 °C; $[\alpha]^{13}_D$ −66.0° (*c* 0.67, MeOH); ^{1}H NMR (C_5D_5N, 500 Hz) δ 5.36 (1H, br s, H-4), 5.11 (1H, br s, H-1′$_{cym}$), 5.09 (1H, d, J = 8.5 Hz, H-1⁗$_{glc}$), 5.04 (1H, d, J = 7.7 Hz, H-1‴$_{glc}$), 4.96 (1H, d, J = 7.7 Hz, H-1″$_{glc}$), 4.20 (1H, dd, J = 16.7, 4.5 Hz, H-21β), 3.83 (1H, dd, J = 16.7, 7.0 Hz, H-21α), 3.74 (1H, m, H-3), 3.38 (3H, s, OMe-3′), 2.00 (3H, s, Ac), 1.95 (1H, m, H-17), 1.03 (3H, s, Me-18), 1.01 (1H, m, H-5α), 0.92 (3H, s, Me-19); ^{13}C NMR, see Table 1; negative-ion FABMS *m*/*z* 1062 $[M]^-$ (100), 899 (11), 737 (3), 159 (12), 111 (2); HRFABMS *m*/*z* 1061.4746 $[M - H]^-$ (calcd for $C_{50}H_{77}O_{24}$, 1061.4733).

Acknowledgment. The authors are grateful to the Analytical Group of the Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Acacemy of Sciences, for the spectral measurements.

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(6) Crystallographic data of compound **1** have been deposited at the Cambridge Crystallographic Data Center, Cambridge, U.K., under the reference number CCDC-201501. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

NP020411O