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NEW STEROIDAL GLYCOSIDES FROM *PAREPIGYNUM FUNINGENSE*

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Abstract -Six new steroidal glycosides with an unusual framework, funingenosides E (**1**), F (**2**), G (**3**), H (**4**), I (**5**) and J (**6**) were isolated from the roots of *Parepigynum funingense*. Their structures were elucidated by a combination of 1D and 2D NMR spectral analysis.

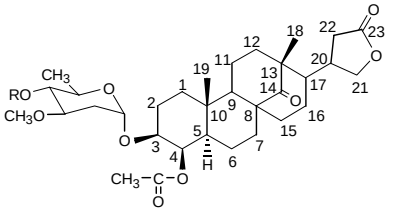
Parepigynum funingense Tsiang *et* P. T. Li (Apocynaceae), a member of a monotypic genus, is distributed widely in Yunnan Province, People′s Republic of China.[1] In the previous paper, we reported structural elucidation of four steroidal glycosides.[2] Our continuing phytochemical investigation into the constituent of this plant has resulted in the isolation of six new 5α-steroidal glycosides, namely, funingenosides E (**1**), F (**2**), G (**3**), H (**4**), I (**5**) and J (**6**).

Funingenoside E (**1**) was obtained as a white powder, and analyzed for $C_{44}H_{68}O_{19}$ by negative-ion HRFABMS spectrum. Its IR spectrum exhibited absorption bands for hydroxyl (3435 cm^{-1}), carbonyl (1778, 1734 and 1699 cm^{-1}). The UV spectrum appears no significant absorptions. The ^{1}H and ^{13}C NMR spectra showed signals due to one acetyl group [δ_C 20.9 (q), 170.8 (s)], two carbonyl groups [δ_C 220.8 (s), 177.3 (s)], and two angular methyl groups [δ_C 16.1 (q), 23.9 (q)]. Also observed were signals of three anomeric carbons and their corresponding anomeric protons [δ_C 94.9 (d), 104.7 (d), 105.5 (d); δ_H 5.30 (1H, br s), 5.25 (1H, d, J = 8.0 Hz), 5.15 (1H, d, J = 7.5 Hz)]. In the negative FABMS spectrum,

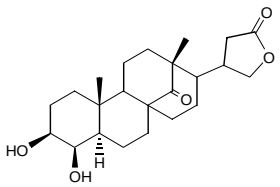
significant peaks occurred at *m/z* 900 $[M]^-$, 737 $[M - H - 162]^-$, 575 $[M - H - 162 - 162]^-$, and 431 $[M - H - 162 - 162 - 144]^-$, and indicated the elimination of three hexosyl moieties.

Acid hydrolysis of **1** with 1 N HCl furnished two monosaccharides and an aglycon (**1a**). The EIMS spectrum of **1a** exhibited a $[M]^+$ ion at *m/z* 390, compatible with the molecular formula $C_{23}H_{34}O_5$. A careful comparison of the ^1H and ^{13}C NMR spectral data of **1a** with those of (8*R*)-3β,4β-dihydroxyl-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-enolide[2] 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 177.1, suggesting the carbonyl group of the five-membered lactone was not conjugated with a double bond in **1a.** The stereochemistry of H-17 was determined to be α-oriented by the ROESY correlation between H-12α (δ_H 2.01) and H-17 (δ_H 1.93) which indicated their *cis* relationship. In addition, other correlations can be observed in the ROESY spectrum between Me-18 (δ_H 1.05) and H-22ß(δ_H 2.25), H-16ß(δ_H 1.24) and H-21α (δ_H 3.82), H-21β (δ_H 4.24), indicating α-configuration of H-20. Thus, **1a** was concluded to be the new compound (8*R*, 17*R,* 20*S*)-3β,4β-dihydroxyl-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-dihydroenolide.

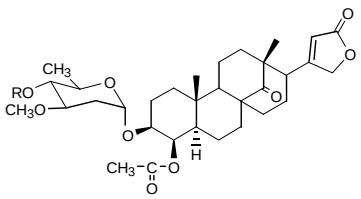
Sugar proton and carbon signals in the NMR spectra of compound (**1**) were assigned by ^1H-^1H COSY, HMQC, and HMQC-TOCSY spectra. One of the two monosaccharides were determined to be D-glucose



1 R=β-D-glucopyranosyl-(1➞6)-*O*-β-D-glucopyranosyl
2 R=β-D-glucopyranosyl-(1➞6)-*O*-β-D-glucopyranosyl -(1➞6)-*O*-β-D-glucopyranosyl
3 R=β-D-glucopyranosyl



1a



4 R=β-D-glucopyranosyl-(1➞6)-*O*-β-D-glucopyranosyl
5 R=β-D-glucopyranosyl

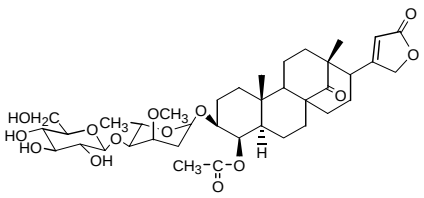


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Figure 1 The structures of compounds (**1, 1a,** and **2-6**)

by measuring its optical rotation value and TLC comparison with the authentic sample. The other monosaccharide was determined to be the 2,6-dideoxysugar, D-oleandrose, by TLC comparison with the authentic sample with three solvent systems; solvent A, $CHCl_3$-MeOH (9:1); solvent B, CH_2Cl_2-EtOH (9:1); solvent C, acetone-petroleum ether (2:3). The *Rf* value of D-oleandrose was 0.4 with solvent A, 0.34 with solvent B, and 0.44 with solvent C. The optical rotation value of this sugar was determined to be $[\alpha]_D^{25}$ −11.9°. Its ^{13}C NMR spectral data and optical rotation value were consistent with those reported.[3,4] In the HMBC spectrum, long-range couplings were observed between H-1′ of the oleandrosyl unit (δ_H 5.30) and C-3 of the aglycon [δ_C 73.7 (d)], H-1″ of the glucosyl unit (δ_H 5.25) and C-4′ of the oleandrosyl unit [δ_C 81.9 (d)], and H-1‴ of the terminal glucosyl unit (δ_H 5.15) and C-6″ of the glucosyl unit [δ_C 70.7 (t)]. The anomeric configurations of D-glucose and D-oleandrose were determined to be β and α, respectively, from the coupling constants of the anomeric proton signals. On the basis of the above evidence, the structure of **1** was elucidated as (8*R*, 17*R*, 20*S*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→4)-α-D-oleandropyranosyl)oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-dihydroenolide, and was named funingenoside E. It is an uncommon 5α-oleagenin-type steroidal glycoside.

Funingenoside F (**2**) was assigned a molecular formula of $C_{50}H_{78}O_{24}$ by negative-ion HRFABMS spectrum, which was confirmed from the ^{13}C and DEPT NMR spectra. A careful comparison of the ^1H and ^{13}C NMR spectra of **2** with those of **1** showed that the two structures were very similar except that there was one additional sugar unit in **2**. The $[M]^-$ ion at 1062, 162 mass units more than that of **1**, coupling with the sugar proton and carbon signals in the NMR spectra indicated that **2** had one additional glucose. In the HMBC spectrum, long-range couplings were observed for H-1⁗ of the terminal glucosyl unit (δ_H 5.17) to C-6‴ of the glucosyl unit [δ_C 70.7 (t)], H-1‴ of the glucosyl unit (δ_H 5.12) to C-6″ of the glucosyl unit [δ_C 70.2 (t)], and H-1″ of the glucosyl unit (δ_H 5.23) to C-4′ of the oleandrosyl unit [δ_C 82.1(d)]. The stereochemistry at the chiral centers in **2** was identical to that of **1**, as supported by its ^1H, ^{13}C NMR and ROESY spectra. Based on the above results, the structure of **2** could be deduced as (8*R*, 17*R*, 20*S*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→4)-α-D-oleandropyranosyl)oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-dihydroenolide, and was named funingenoside F.

A molecular formula of $C_{38}H_{58}O_{14}$ was deduced for funingenoside G (**3**) by negative-ion HRFABMS spectrum. Its molecular weight was 738, 162 mass units less than that of **1**. The ^1H and ^{13}C NMR

spectral data of compound (**3**) were almost identical with those of **1** 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 upfield to δ_C 62.8. Hence, the structure of **3** was elucidated as (8*R*, 17*R*, 20*S*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→4)-α-D-oleandropyranosyl)oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-dihydroeolide, and was named funingenoside G.

Funingenoside H (**4**) and I (**5**) were assigned molecular formulae of $C_{44}H_{66}O_{19}$ and $C_{38}H_{56}O_{14}$, Respectively, by negative-ion HRFABMS spectra. Comparison of the ^1H and ^{13}C NMR spectra of **4** and **5** with those of **1** showed that the sugar moieties were identical except that there were only two sugar units in compound (**5**). The aglycones of **4** and **5** were also very similar to that of **1** except for the presence of the olefinic group and the upfield resonance of C-23 to δ_C 171.8, 171.7, respectively**,** suggesting the carbonyl group of the five-membered lactone was conjugated with a double bond in **4** and **5**. This was further supported by the presence of an α,β-unsaturated carbonyl group (λ_{max} 211 nm) in the UV spectrum of **4**. On the basis of the above results, the structures of **4** and **5** could be elucidated as (8*R*,17*R*, 20*S*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→4)-α-D-oleandropyranosyl)oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-enolide and (8*R*,17*R*, 20*S*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→4)-α-D-oleandropyranosyl)oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-enolide, respectively.

Funingenoside J (**6**) was analyzed for $C_{38}H_{56}O_{14}$ by negative-ion HRFABMS spectrum. The ^1H and ^{13}C NMR spectral data of compound (**6**) were almost identical with those of funingenoside A[2] except that there were only two sugar units in **6**, indicating that compound (**6**) contained the 2,6-dideoxy sugar, α-L-cymarose, as its inner sugar unit. Thus, the structures of **6** was determined to be (8*R*,17*R*, 20*S*)-4β-acetoxy-3β-[(*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl)oxy]-14-oxo-5α-15(14→8)-*abeo*-card-20(22)-enolide.

EXPERIMENTAL

General Experimental Procedures. Melting points were obtained on an XRC-1 apparatus and are uncorrected. Optical rotations were measured with a Horiba SEAP-300 polarimeter. 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.

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 (3 × 50 L) under reflux for three times (3 h, 2 h, 2 h, respectively). After removal of the solvent *in vacuo*, the aqueous solution of the residue (350 g) 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 passaged over RP-18 eluted with MeOH-H_2O (4:6). Fraction 5 (12.1 g) yielded **1** (486 mg). Fraction 8 (8.2 g) afforded **2** (35 mg). Fraction 2 (9.0 g) gave **3** (25 mg). Fraction 4 (14.78 g) afforded **4** (68 mg), and Fraction 3 (7.5 g) gave **5** (37 mg) and **6** (18 mg).

Funingenoside E (**1**): white powder; $[\alpha]_D^{23}$ −44.6° (*c* 0.70, MeOH); IR (KBr) ν_{max} 3435, 2933, 1778, 1734, 1699, 1456, 1372, 1243, 1047 cm^{-1}; ^1H NMR (C_5D_5N, 500 MHz) δ 5.38 (1H, br s, H-4), 5.30 (1H, br s, H-1′$_{ole}$), 5.25 (1H, d, *J* = 8.0 Hz, H-1″$_{glc}$), 5.15 (1H, d, *J* = 7.5 Hz, H-1‴$_{glc}$), 4.24 (1H, dd, *J* = 15.0, 4.5 Hz, H-21β), 3.82 (1H, dd, *J* = 15.0, 6.8 Hz, H-21α), 3.78 (1H, m, H-3), 3.38 (3H, s, OMe-3′), 1.96 (3H, s, Ac), 1.93 (1H, m, H-17), 1.05 (3H, s, Me-18), 1.02 (1H, m, H-5α), 0.92 (3H, s, Me-19); ^{13}C NMR, see Table 1; negative-ion FABMS *m/z* 900 $[M]^-$ (100), 737 (4), 575 (3), 431, (1), 159 (16), 119 (20); HRFABMS *m/z* 899.4263 $[M - H]^-$ (calcd for $C_{44}H_{67}O_{19}$, 897.4276).

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 at 100°C and the reaction mixture was extracted with EtOAc (50 mL × 3) to afford **1a** (25 mg). Evaporation of the aqueous layer of the aforementioned hydrolysate gave the residue (44 mg) containing monosaccharides, which was chromatographed on a column of silica gel (200-300 mesh) with acetone-petroleum ether (2:3 → 3:1) to afford D-glucose (18.6 mg), $[\alpha]_D^{25}$ +52.3° (*c* 0.36, H_2O) and D-oleandrose (5.3 mg), $[\alpha]_D^{25}$ −11.9° (*c* 0.28, H_2O).

Table 1 ^{13}C NMR Data for Compounds (**1**, **1a** and **2-6**) (in Pyridine-d_5 at 100 MHz)

C	1	1a	2	3	4	5	6
1	38.4 t	39.2 t	38.4 t	38.4 t	38.4 t	38.4 t	38.5 t
2	25.0 t	26.8 t	25.0 t	24.8 t	24.9 t	24.9 t	25.2 t
3	73.7 d	72.6 d	73.8 d	73.7 d	73.9 d	73.8 d	75.2 d
4	72.0 d	74.8 d	71.9 d	72.2 d	71.8 d	71.6 d	72.3 d
5	46.3 d	48.2 d	46.4 d	46.5 d	46.3 d	46.2 d	46.5 d
6	35.0 t	35.6 t	35.0 t	35.0 t	35.0 t	35.1 t	35.1 t
7	23.8 t	24.5 t	23.9 t	23.7 t	23.4 t	23.3 t	23.4 t
8	49.3 s	49.4 s	49.3 s	49.4 s	49.6 s	49.7 s	49.6 s
9	60.4 d	60.6 d	60.4 d	60.4 d	60.6 d	60.5 d	60.6 d
10	38.3 s	38.6 s	38.4 s	38.4 s	38.6 s	38.6 s	38.6 s
11	20.9 t	21.0 t	20.9 t	20.9 t	21.4 t	21.3 t	21.4 t
12	42.3 t	42.3 t	42.3 t	42.3 t	42.2 t	42.2 t	42.3 t
13	49.5 s	49.5 s	49.5 s	49.5 s	47.7 s	47.7 s	47.7 s
14	220.8 s	220.8 s	220.8 s	220.9 s	220.8 s	220.9 s	220.8 s
15	43.4 t	43.6 t	43.4 t	43.4 t	43.4 t	43.4 t	43.5 t
16	23.5 t	23.7 t	23.5 t	23.5 t	26.8 t	26.3 t	26.3 t
17	56.0 d	55.9 d	56.0 d	56.0 d	52.8 d	52.8 d	52.8 d
18	23.9 q	23.8 q	23.9 q	23.8 q	23.4 q	23.3 q	23.3 q
19	16.1 q	17.1 q	16.1 q	16.1 q	16.1 q	16.0 q	16.1 q
20	36.5 d	36.5 d	36.5 d	36.5 d	173.7 s	173.9 s	173.6 s
21	71.5 t	71.5 t	71.7 t	71.6 t	73.5 t	73.5 t	73.5 t
22	36.6 t	36.5 t	36.6 t	36.7 t	116.5 d	116.4 d	116.4 d
23	177.3 s	177.1 s	177.2 s	177.3 s	171.8 s	171.7 s	171.8 s
Ac	170.8 s		170.7 s	170.8 s	170.7 s	170.7 s	170.8 s
Ac	20.9 q		20.9 q	21.0 q	21.1 q	20.9 q	21.1 q
oleandrosyl							cymarosyl
1′	94.9 d		95.0 d	94.9 d	94.9 d	95.0 d	95.0 d
2′	35.0 t		35.0 t	35.1 t	35.0 t	35.0 t	31.8 t
3′	79.2 d		79.2 d	78.8 d	78.8 d	79.0 d	73.2 d
4′	81.9 d		82.1 d	81.9 d	81.7 d	82.3 d	78.4 d
5′	68.0 d		68.0 d	68.1 d	68.0 d	67.9 d	65.2 d
6′	18.9 q		18.9 q	18.9 q	18.7 q	18.8 q	18.6 q
OMe-3′	56.8 q		56.8 q	56.7 q	56.7 q	56.8 q	56.4 q
glucosyl							
1″	104.7 d		104.9 d	104.7 d	104.8 d	105.2 d	101.8 d
2″	75.8 d		75.2 d	75.5 d	75.2 d	76.1 d	75.3 d
3″	78.5 d		78.4 d	78.6 d	78.4 d	78.4 d	78.4 d
4″	71.7 d		71.8 d	71.7 d	71.9 d	72.0 d	71.9 d
5″	77.3 d		78.4 d	78.5 d	78.3 d	78.4 d	78.5 d
6″	70.7 t		70.2 t	62.8 t	70.7 t	63.1 t	62.9 t
glucosyl							
1‴	105.5 d		105.1 d		105.6 d		
2‴	75.3 d		75.1 d		75.2 d		
3‴	78.4 d		78.3 d		78.2 d		
4‴	71.7 d		71.6 d		71.8 d		
5‴	78.5 d		78.4 d		77.9 d		
6‴	62.8 t		70.7 t		62.7 t		
glucosyl							
1⁗			105.6 d				
2⁗			75.8 d				
3⁗			77.2 d				
4⁗			71.6 d				
5‴			77.1 d				
6‴			62.8 t				

Compound (**1a):** colorless needles; mp 256-260° (MeOH); ^{1}H NMR (C_5D_5N, 500 MHz) δ 4.24 (1H, dd, *J* = 16.0, 5.8 Hz, H-21β), 4.03 (1H, br s, H-4), 3.85 (1H, dd, *J* = 16.0, 7.5 Hz, H-21α), 3.78 (1H, m, H-3), 1.94 (1H, m, H-17), 1.16 (3H, s, Me-19), 1.02 (3H, s, Me-18), 0.97 (1H, m, H-5α); ^{13}C NMR, see Table 1; EIMS *m/z* 390 $[M]^+$ (100), 372 (56), 354 (20), 264 (35), 145 (42), 105 (15).

Funingenoside F (**2**): white powder; $[\alpha]_D^{23}$ –60.5° (*c* 0.96, MeOH); ^{1}H NMR (C_5D_5N, 500 Hz) δ 5.38 (1H, br s, H-4), 5.30(1H, br s, H-1′$_{ole}$), 5.23 (1H, d, *J* = 7.7 Hz, H-1″$_{glc}$), 5.17 (1H, d, *J* = 8.1 Hz, H-1‴″$_{glc}$), 5.12 (1H, d, *J* = 8.1 Hz, H-1‴$_{glc}$), 4.21 (1H, dd, *J* = 13.8, 4.5 Hz, H-21β), 3.80 (1H, dd, *J* = 13.8, 6.5 Hz, H-21α), 3.86 (1H, m, H-3), 3.37 (3H, s, OMe-3′), 1.96 (3H, s, Ac), 1.92 (1H, m, H-17), 1.05 (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* 1061 $[M - H]^-$ (100), 899 (10), 737 (2), 629 (1), 141 (5); HRFABMS *m/z* 1061.4761 $[M - H]^-$ (calcd for $C_{50}H_{77}O_{24}$, 1061.4804).

Funingenoside G (**3**): white powder; $[\alpha]_D^{23}$ –64.2° (*c* 0.56, MeOH); ^{1}H NMR (C_5D_5N, 500 Hz) δ 5.38 (1H, br s, H-4), 5.32 (1H, br s, H-1′$_{ole}$), 5.22 (1H, d, *J* = 7.5 Hz, H-1″$_{glc}$), 4.28 (1H, dd, *J* = 15.5, 4.8 Hz, H-21β), 3.82 (1H, dd, *J* = 15.5, 6.5 Hz, H-21α), 3.76 (1H, m, H-3), 3.40 (3H, s, OMe-3′), 1.98 (3H, s, Ac), 1.90 (1H, m, H-17), 1.04 (3H, s, Me-18), 1.02 (1H, m, H-5α), 0.93(3H, s, Me-19); ^{13}C NMR, see Table 1; negative-ion FABMS *m/z* 737 $[M - H]^-$ (100), 575 (2); HRFABMS *m/z* 737.4218 $[M - H]^-$ (calcd for $C_{38}H_{57}O_{14}$, 737.4235).

Funingenoside H (**4**): coloreless needles (MeOH); mp 238-242°; $[\alpha]_D^{26}$ –41.3° (*c* 0.82, MeOH); UV (MeOH) λ_{max} (log ε) 211 (3.80) nm; IR (KBr) ν_{max} 3432, 2930, 1741, 1702, 1625, 1455, 1371, 1243, 1049 cm^{-1}; ^{1}H NMR (C_5D_5N, 500 Hz) δ 5.92 (1H, s, H-22), 5.38 (1H, br s, H-4), 5.32 (1H, br s, H-1′$_{ole}$), 5.26 (1H, d, *J* = 7.8 Hz, H-1″$_{glc}$), 5.18 (1H, d, *J* = 7.5 Hz, H-1‴$_{glc}$), 4.78 (1H, d, *J* = 12.0 Hz, H-21β), 3.88 (1H, d, *J* = 12.0 Hz, H-21α), 3.72 (1H, m, H-3), 3.38 (3H, s, OMe-3′), 2.95 (1H, dd, *J* = 6.0, 1.5 Hz, H-17), 1.98 (3H, s, Ac), 1.02 (1H, m, H-5α), 0.95 (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 (2), 573 (3), 429 (1), 245 (6), 123 (40); HRFABMS *m/z* 897.3961 $[M - H]^-$ (calcd for $C_{44}H_{65}O_{19}$, 897.3946).

Funingenoside I (**5**): coloreless needles; mp 248-253° (MeOH); $[\alpha]_D^{22}$ –45.7° (*c* 0.23, MeOH); ^{1}H NMR (C_5D_5N, 500 Hz) δ 5.96 (1H, s, H-22), 5.39 (1H, br s, H-4), 5.35 (1H, br s, H-1′$_{ole}$), 5.30 (1H, d, *J* = 7.6 Hz, H-1″$_{glc}$), 4.71 (1H, d, *J* = 11.4 Hz, H-21β), 3.82 (1H, d, *J* = 11.4 Hz, H-21α), 3.78 (1H, m, H-3), 3.40 (3H, s, OMe-3′), 2.96 (1H, dd, *J* = 6.0, 1.2 Hz, H-17), 1.97 (3H, s, Ac), 1.00 (1H, m, H-5α), 0.94 (3H, s,

Me-18), 0.92 (3H, s, Me-19); ^{13}C NMR, see Table 1; negative-ion FABMS *m/z* 735 $[M - H]^-$ (100), 573 (16), 430 (3), 123 (48); HRFABMS *m/z* 735.3580 $[M - H]^-$ (calcd for $C_{38}H_{55}O_{14}$, 735.3591).

Funingenoside J (**6**): coloreless needles; mp 240-247° (MeOH); $[\alpha]_D^{26}$ –61.5° (*c* 0.30, MeOH); ^{1}H NMR (C_5D_5N, 500 Hz) δ 5.90 (1H, s, H-22), 5.37 (1H, br s, H-4), 5.14 (1H, br s, H-1′$_{cym}$), 4.99 (1H, d, *J* = 8.0 Hz, H-1″$_{glc}$), 4.75 (1H, d, *J* = 11.5 Hz, H-21β), 3.86 (1H, d, *J* = 11.5 Hz, H-21α), 3.75 (1H, m, H-3), 3.36 (3H, s, OMe-3′), 2.98 (1H, dd, *J* = 6.5, 1.5 Hz, H-17), 1.98 (3H, s, Ac), 1.00 (1H, m, H-5α), 0.95 (3H, s, Me-18), 0.92 (3H, s, Me-19); ^{13}C NMR, see Table 1; negative-ion FABMS *m/z* 735 $[M - H]^-$ (100), 573 (12), 429 (2), 246 (3), 123 (32); HRFABMS *m/z* 735.4189 $[M - H]^-$ (calcd for $C_{38}H_{55}O_{14}$, 735.4197).

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