Four New Cycloartane Glycosides from *Thalictrum fortunei*

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Four new cycloartane glycosides were isolated from the aerial parts of *Thalictrum fortunei* (Ranunculaceae). The chemical structures of these new glycosides were elucidated as 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-fucopyranosyl (22*S*,24*Z*)-cycloart-24-en-3*β*,22,26-triol 26-*O*-*β*-D-glucopyranoside, 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-fucopyranosyl (22*S*,24*Z*)-cycloart-24-en-3*β*,22,26-triol 26-*O*-*β*-D-quinovopyranosyl-(1→6)-*β*-D-glucopyranoside, 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-fucopyranosyl (22*S*,24*Z*)-cycloart-24-en-3*β*,22,26-triol 26-*O*-*β*-D-xylopyranosyl-(1→6)-*β*-D-glucopyranoside, and 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-fucopyranosyl (22*S*,24*Z*)-cycloart-24-en-3*β*,22,26-triol 26-*O*-*α*-L-arabinopyranosyl-(1→6)-*β*-D-glucopyranoside by extensive NMR methods, HR-ESI-MS, and hydrolysis. This is the first report of (22*S*,24*Z*)-3*β*,22,26-trihydroxycycloartan-24-ene (thelictogenin A, 5) being glycosylated at C-26.

Key words *Thalictrum fortunei*; Ranunculaceae; cycloartane glycoside

Thalictrum fortunei S. MOORE is a perennial plant distributed in the southeastern part of China. The aerial part of this plant is used as an anticancer, antibacterial and anti-inflammatory agent in traditional Chinese medicines.[1)] We previously reported on new cycloartane glycosides from several Cimicifuga species.[2,3)] As part of the continuing investigation on the triterpene glycosides of Ranunculaceous plants,[4—6)] this paper deals with the isolation and structural elucidation of four new cycloartane glycosides (**1**—**4**).

The dried aerial parts of *T. fortunei* were extracted with 95% ethanol. The *n*-BuOH-soluble fraction was subjected to repeated silica gel column chromatography followed by reversed-phase column chromatography to afford four cycloartane glycosides **1**—**4**.

Compound **1** was obtained as a white powder. The molecular formula of **1** was determined to be $C_{48}H_{80}O_{17}$ by high resolution ESI-MS (Found *m/z*: 927.5291 $[M-H]^-$; Calcd for $C_{48}H_{79}O_{17}$: 927.5317). Acid hydrolysis of **1** afforded D-glucose and D-fucose (confirmed by gas chromatography), together with thelictogenin A (**5**), $[\alpha]_D$ 30.2° (c=0.50, pyridine); which was identified by comparison of the NMR data and physical properties with literature values.[7)] The ^{1}H-NMR spectrum of **1** showed two doublet signals at δ 0.25 and 0.50, which is characteristic of a cyclopropane methylene, four tertiary methyls at δ 0.88, 1.05, 1.06 and 1.33, an olefinic methyl at δ 1.95, two secondary methyls at δ 1.18 (d, J=6.6 Hz) and 1.62 (d, J=6.4 Hz), an olefinic proton at δ 5.80 (1H, t, J=7.2 Hz) and three anomeric protons at δ 4.72 (1H, d, J=7.5 Hz), 4.89 (1H, d, J=7.8 Hz) and 5.17 (1H, d, J=7.8 Hz). Similarly, the ^{13}C-NMR spectrum of **1** (Table 1) showed the corresponding signals due to cyclopropane methylene at δ 29.7, methylene carbon bearing oxygen at δ 67.4 (C-26), methine carbons bearing oxygen at δ 73.0 (C-22) and δ 88.7 (C-3), and three anomeric carbons at δ 103.0, 106.9 and 107.0. Further comparison of the ^{13}C-NMR data of **1** with those of thelictogenin A (**5**) indicated that the triterpene was glycosylated at C-3 and C-26. The interglycosidic linkages of the sugar chains could be deduced from an HMBC experiment. Thus, in the HMBC spectrum of **1** (Fig. 1), correlation signals were observed between H-1″ (δ 4.89) of glucose and C-26 (δ 67.4) of aglycone. Moreover, the HMBC spectrum revealed correlations between H-1′ (δ 5.17) of glucose and C-4 (δ 83.4) of fucose, as well as between H-1 (δ 4.72) of fucose and C-3 (δ 88.7) of aglycone. From the above evidence, the structure of **1** was concluded to be 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-fucopyranosyl (22*S*,24*Z*)-cycloart-24-en-3*β*,22,26-triol 26-*O*-*β*-D-glucopyranoside.

Compound **2** was obtained as a white powder. The molecular formula of **2** was determined to be $C_{54}H_{90}O_{21}$ by HR-ESI-MS (Found *m/z*: 1073.5875 $[M-H]^-$; Calcd for $C_{54}H_{89}O_{21}$: 1073.5896). Upon acid hydrolysis, **2** afforded D-glucose, D-quinovose, D-fucose, and thelictogenin A (**5**).[7)] The ^{1}H-NMR spectrum of **2** showed two doublet signals at δ 0.25 and 0.50, four tertiary methyls at δ 0.89, 1.04, 1.06 and 1.32, an olefinic methyl at δ 1.95, three secondary methyls at δ 1.18 (d, J=6.6 Hz), 1.59 (d, J=5.7 Hz) and 1.74 (d, J=6.4 Hz), an olefinic proton at δ 5.80 (1H, t, J=7.2 Hz) and four anomeric protons at δ 4.70 (1H, d, J=7.5 Hz), 4.90 (1H, d, J=7.9 Hz), 5.02 (1H, d, J=7.5 Hz) and 5.15 (1H, d, J=7.9 Hz). The above ^{1}H-NMR data of **2** were similar to those of **1** except the additional secondary methyl at δ 1.59 and an anomeric proton at δ 5.02. In the ^{13}C-NMR spectrum of **2** (Table 1), the signals due to the aglycone moiety were in good agreement with those of **1**. Furthermore, a comparative assignment of the ^{13}C-NMR spectrum of **2** with that of **1** also indicated presence of an additional quinovopyranosyl unit in **2**. The interglycosidic linkages of the sugar chains could be deduced from an HMBC experiment. Thus, in the HMBC spectrum of **2** (Fig. 1), correlation signals were observed between H-1 (δ 5.02) of quinovose and C-6″ (δ 70.0) of glucose, between H-1″ (δ 4.90) of glucose and C-26 (δ 67.4) of aglycone. Moreover, the HMBC spectrum revealed correlations between H-1′ (δ 5.15) of glucose and C-4 (δ 83.0) of fucose, as well as between H-1 (δ 4.70) of fucose and C-3 (δ 88.7) of aglycone. Thus, the structure of **2** was identified as 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-fucopyranosyl (22*S*,24*Z*)-cycloart-24-en-3*β*,22,26-triol 26-*O*-*β*-D-quinovopyranosyl-(1→6)-*β*-D-glucopyranoside.

Compound **3** was obtained as a white powder. The molecular formula of **3** was determined to be $C_{53}H_{88}O_{21}$ by HR-

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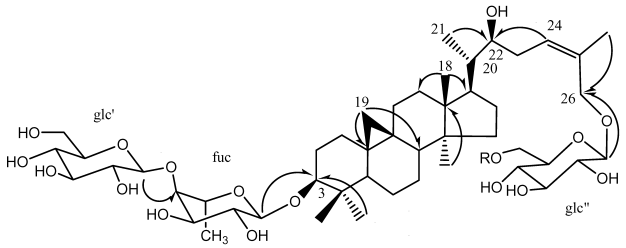
Table 1. ^{13}C-NMR Data for **1**—**5**[a)]

C	1	2	3	4	5
1	32.2	32.2	32.2	32.2	32.4
2	30.0	30.0	30.0	30.0	31.0
3	88.7	88.7	88.6	88.6	80.1
4	41.3	41.3	41.3	41.3	41.1
5	47.7	47.7	47.7	47.7	47.8
6	21.2	21.2	21.2	21.2	21.3
7	26.2	26.2	26.2	26.2	26.3
8	48.0	48.1	48.0	48.0	48.1
9	20.1	20.1	20.1	20.1	20.2
10	26.7	26.7	26.7	26.7	26.7
11	26.4	26.4	26.4	26.4	26.4
12	35.8	35.8	35.8	35.8	36.0
13	45.5	45.5	45.5	45.5	45.6
14	49.1	49.1	49.1	49.1	49.2
15	33.4	33.4	33.4	33.4	33.5
16	28.0	28.0	28.0	28.0	28.1
17	49.1	49.1	49.1	49.1	49.2
18	18.3	18.3	18.3	18.3	18.4
19	29.7	29.7	29.7	29.7	29.9
20	41.7	41.7	41.7	41.7	41.7
21	12.1	12.1	12.1	12.1	12.1
22	73.0	73.0	73.0	73.0	73.1
23	35.0	35.0	35.0	35.0	35.1
24	128.5	128.5	128.5	128.5	125.9
25	133.2	133.2	133.2	133.2	137.3
26	67.4	67.4	67.4	67.4	61.1
27	22.2	22.2	22.2	22.2	22.3
28	19.6	19.6	19.6	19.6	19.6
29	25.8	25.8	25.8	25.8	25.9
30	15.4	15.4	15.4	15.4	15.5
Fuc 1	106.9	106.9	106.9	106.9	
2	73.5	73.5	73.5	73.5	
3	75.7	75.7	75.7	75.7	
4	83.4	83.0	83.0	83.0	
5	70.4	70.4	70.4	70.4	
6	17.7	18.0	17.9	17.9	
Glc′ 1	107.0	106.6	106.6	106.6	
2	76.2	75.8	75.8	75.8	
3	78.6	78.6	78.6	78.6	
4	71.8	71.7	71.7	71.7	
5	78.6	78.4	78.4	78.4	
6	62.8	62.8	62.8	62.8	
Glc″ 1	103.0	103.0	103.0	103.0	
2	75.2	75.2	75.2	75.2	
3	78.7	78.7	78.7	78.7	
4	71.7	71.7	71.5	71.7	
5	78.4	77.5	77.4	77.2	
6	62.9	70.0	70.0	69.9	
Quin 1		105.3			
2		75.5			
3		78.0			
4		76.9			
5		73.0			
6		18.6			
Xyl 1			106.0		
2			74.9		
3			78.1		
4			71.2		
5			67.0		
Ara 1				105.6	
2				72.4	
3				74.3	
4				69.0	
5				66.4	

a) Spectra were measured in pyridine-d_5. Assignments were established by interpretation of the ^{13}C-DEPT, HMQC, HMBC and ^{1}H–^{1}H COSY spectra. Ara: α-L-arabinopyranosyl; Fuc: β-D-fucopyranosyl; Glc: β-D-glucopyranosyl; Quin: β-D-quinovopyranosyl; Xyl: β-D-xylopyranosyl.



1 R=H **2** R= β-D-quinovopyranosyl
3 R= β-D-xylopyranosyl **4** R= α-L-arabinopyranosyl

Fig. 1. The Structures of Compounds **1**—**4** and Their Key HMBC Correlations

ESI-MS (Found *m/z*: 1059.5709 $[M-H]^-$; Calcd for $C_{53}H_{87}O_{21}$: 1059.5740). On acid hydrolysis, **3** afforded D-glucose, D-xylose, D-fucose, and thelictogenin A (**5**).[7)] The ^{1}H- and ^{13}C-NMR spectra of **3** (Tables 1, 2) revealed the presence of four sugar residues and the aglycone thelictogenin A. A comparison of the NMR spectral data between **1** and **3** suggested that the latter contained one additional xylose residue on the sugar moiety located at the C-26 position. The results of HMBC (Fig. 1) also supported this assumption. Thus, the HMBC spectrum of **3** displayed correlation signals between H-1 (δ 4.99) of xylose and C-6″ (δ 70.0) of glucose, as well as between H-1″ (δ 4.90) of glucose and C-26 (δ 67.4) of aglycone. Moreover, the correlations were also demonstrated between H-1′ (δ 5.14) of glucose and C-4 (δ 83.0) of fucose, and between H-1 (δ 4.70) of fucose and C-3 (δ 88.6) of aglycone. All available evidence led to the conclusion that **3** was a new triterpene glycoside with the structure of 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-fucopyranosyl (22*S*,24*Z*)-cycloart-24-en-3β,22,26-triol 26-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside.

Compound **4** was obtained as a white powder, and the molecular formula was determined to be $C_{53}H_{88}O_{21}$ by HR-ESI-MS (Found *m/z*: 1059.5811 $[M-H]^-$; Calcd for $C_{53}H_{87}O_{21}$: 1059.5740). Acid hydrolysis of **4** afforded thelictogenin A (**5**),[7)] D-glucose, L-arabinose, and D-fucose. Analysis of the NMR data of **4** (Tables 1, 2), and a comparison with those of **1**—**3**, showed that the former compound possessed an arabinose residue besides a glucose and a fucose. The oligosaccharide structure was subsequently determined by 2D-NMR studies. Thus, in the HMBC spectrum of **4** (Fig. 1), correlation peaks between H-1 (δ 4.93) of arabinose and C-6″ (δ 69.9) of glucose, between H-1″ (δ 4.90) of glucose and C-26 (δ 67.4) of aglycone, between H-1′ (δ 5.14) of glucose and C-4 (δ 83.0) of fucose, as well as between H-1 (δ 4.71) of fucose and C-3 (δ 88.6) of aglycone were displayed. Hence, the structure of **4** was established as 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-fucopyranosyl (22*S*,24*Z*)-cycloart-24-en-3β,22,26-triol 26-*O*-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranoside.

Cycloartane glycosides had been found to widely distribute in the plants of the genus Cimicifuga.[2,3)] Based on the literature information[7—10)] and the results of this paper, these cycloartane glycosides have also been isolated from plants of the genus Thalictrum of the same family (Ranunculaceae). This could imply a close relationship between the two genera.

Table 2. ^{1}H-NMR Data of the Saccharide Moieties of Compounds **1**—**4**[a,b]

H	1	2	3	4
Fuc 1	4.72 d (7.5)	4.70 d (7.5)	4.70 d (7.5)	4.71 d (7.5)
2	4.35 dd (7.5, 8.2)	4.32 dd (7.5, 8.2)	4.31 dd (7.5, 8.0)	4.32 dd (7.5, 8.1)
3	4.10[c]	4.02[c]	4.02[c]	4.02[c]
4	4.11[c]	4.04[c]	4.05	4.03[c]
5	3.79 dd (13.2, 6.4)	3.75 dd (13.2, 6.4)	3.75 dd (13.3, 6.5)	3.77 dd (13.2, 6.4)
6	1.62 d (6.4)	1.74 d (6.4)	1.74 d (6.5)	1.74 d (6.4)
Glc′ 1	5.17 d (7.8)	5.15 d (7.9)	5.14 d (7.9)	5.14 d (7.9)
2	4.03 dd (7.8, 9.2)	3.94 dd (7.8, 9.0)	3.95 dd (7.8, 9.0)	3.95 dd (7.8, 9.2)
3	4.20[c]	4.11[c]	4.11[c]	4.12[c]
4	4.29[c]	4.24[c]	4.25[c]	4.25[c]
5	3.91[c]	3.94[c]	3.94[c]	3.95[c]
6a	4.48 br d (11.0)	4.55 br d (12.0)	4.55 br d (11.9)	4.56 br d (11.6)
6b	4.38 dd (11.0, 4.4)	4.41 dd (12.0, 4.7)	4.40 dd (11.9, 4.3)	4.42 d (11.6, 4.6)
Glc″ 1	4.89 d (7.8)	4.90 d (7.9)	4.90 d (7.5)	4.90 d (7.6)
2	4.05 dd (7.8, 9.0)	4.04[c]	4.05 dd (7.5, 8.8)	4.03[c]
3	4.23[c]	4.24[c]	4.23[c]	4.25[c]
4	4.20[c]	4.13[c]	4.18[c]	4.10[c]
5	3.95[c]	4.00[c]	3.98[c]	3.99
6a	4.54 br d (11.5)	4.78 br d (11.0)	4.76 br d (11.4)	4.76 br d (11.5)
6b	4.41 dd (11.5, 4, 7)	4.33 dd (11.0, 4.6)	4.30 dd (11.4, 4.7)	4.25 dd (11.5, 4.5)
Quin1		5.02 d (7.5)		
2		4.10[c]		
3		3.70[c]		
4		4.03[c]		
5		3.71[c]		
6		1.59 d (5.7)		
Xyl 1			4.99 d (7.4)	
2			4.02 dd (7.4)	
3			3.94[c]	
4			4.12[c]	
5a			4.30 br d (11.3)	
5b			3.65 dd (11.3, 9.5)	
Ara 1				4.93 d (6.7)
2				4.45 dd (6.7, 6.8)
3				4.16 dd (6.8, 3.2)
4				4.29[c]
5a				4.27 dd (10.7, 2.5)
5b				3.73 br d (10.7)

a) Recorded in pyridine-d_5. Assignments were established by HMQC, HMBC, and ^{1}H–^{1}H COSY spectra. *b*) *J* values (in Hz) in parentheses. *c*) Overlapped signals. Ara: α-L-arabinopyranosyl; Fuc: β-D-fucopyranosyl; Glc: β-D-glucopyranosyl; Quin: β-D-quinovopyranosyl; Xyl: β-D-xylopyranosyl.

Experimental

Optical rotations were obtained using a Perkin-Elmer 241 polarimeter. IR spectra were measured on a Nicolet Impact 410 FT-IR instrument. UV spectra were recorded on a Shimadzu UV-2501 spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker AV500 Avance spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz) and chemical shifts were given in δ (ppm) with TMS as a reference. HR-ESI-MS spectra were obtained on an Applied Biosystems Mariner 5140 spectrometer. HPLC was carried out using a Zobax XDB-18 column (10 mm i.d.×15 cm). Column chromatography was performed on silica gel (230—400 mesh, Merck), Sephadex LH-20 (Pharmacia Fine Chem. Co., Ltd.) and ODS (Merck). TLC was conducted on precoated silica gel 60 F_{254} and RP-18 F_{254}S plates (Merck). GC experiments were carried out on an HP-1 TCD instrument (Hewlett-Packard) using an HP-Chiral column (30×0.25×1.0, 20% permethylated β-cyclodextrin). The conditions selected for GC analysis were: front inlet 250 °C, column 80 °C→230 °C, 5 °C/min. All chemical reagents (AR grade) were purchased from Nanjing Reagent Co., Ltd.

Plant Material The aerial parts of *T. fortunei* were collected in Anhui province of the People's Republic of China in April 2004, and authenticated by Dr. Ming-Jian Qin of China Pharmaceutical University. A voucher specimen (no. 040192) was deposited in the herbarium of China Pharmaceutical University, Nanjing.

Extraction and Isolation The dried aerial parts (4.8 kg) of *T. fortunei* were extracted with 95% EtOH (3×20 l) under reflux. The EtOH extract was suspended in water and then successively extracted with petroleum ether, EtOAc, and *n*-BuOH. The *n*-BuOH solution was concentrated and given a residue (207 g), which was separated by a silica gel column using $CHCl_3$–MeOH (1 : 0→1 : 1) as eluent, affording five fractions (frs. 1—5). Fraction 4 was further purified by Sephadex LH-20 chromatography with MeOH, followed by ODS column chromatography with MeOH–H_2O (65%) to afford compound **1** (230 mg). Fraction 5 was purified by Sephadex LH-20 chromatography with MeOH, followed by ODS column chromatography with MeOH–H_2O (50%→67%) and HPLC with CH_3CN–H_2O (27%→29%) to afford compounds **2** (120 mg), **3** (80 mg), and **4** (190 mg), respectively.

Compound **1**: White powder, $[\alpha]_D$ 7.40° (*c*=0.14, MeOH); IR (KBr) ν_{max} 3417, 2937, 1604, 1384, 1363, 1107, 1081, 773, 627, 471 cm^{-1}; ESI-MS (negative ion mode) *m/z* 927 $[M-H]^-$, 765 $[M-163]^-$, 603 $[M-325]^-$; HR-ESI-MS *m/z* 927.5291 $[M-H]^-$, Calcd for $C_{48}H_{79}O_{17}$: 927.5317; ^{1}H-NMR (pyridine-d_5) δ: 0.25, 0.50 (each 1H, ABq, *J*=3.8 Hz, H-19a, -19b), 0.88, 1.05, 1.06, 1.33, 1.95 (each 3H, s, Me-28, -30, -18, -29, -27), 1.18 (3H, d, *J*=6.6 Hz, Me-21), 1.62 (3H, d, *J*=6.4 Hz, Me-6 of fucose), 3.47 (1H, dd, *J*=11.7, 4.3 Hz, H-3), 4.51, 4.71 (each 1H, ABq, *J*=12.0 Hz, H-26a, -26b), 5.80 (1H, t, *J*=7.2 Hz, H-24); ^{1}H-NMR data of the saccharide residues, see Table 2; ^{13}C-NMR (125 MHz, pyridine-d_5), see Table 1.

Compound **2**: White powder, $[\alpha]_D$ 3.58° (*c*=0.12, MeOH); IR (KBr) ν_{max} 3413, 2935, 1600, 1400, 1363, 1107, 1070, 775, 625, 471 cm^{-1}; ESI-MS (negative ion mode) *m/z* 1073 $[M-1]^-$, 927 $[M-147]^-$, 765 $[M-309]^-$, 603 $[M-471]^-$; HR-ESI-MS *m/z* 1073.5875 $[M-H]^-$, Calcd for $C_{54}H_{89}O_{21}$: 1073.5896; ^{1}H-NMR (pyridine-d_5) δ: 0.25, 0.50 (each 1H, ABq, *J*=3.8 Hz, H-19a, -19b), 0.89, 1.04, 1.06, 1.32, 1.95 (each 3H, s, Me-28, -30, -18, -29, -27), 1.18 (3H, d, *J*=6.6 Hz, Me-21), 1.74 (3H, d, *J*=6.4 Hz, Me-6 of fucose), 1.59 (3H, d, *J*=5.7 Hz, Me-6 of quinovose), 3.45 (1H, dd, *J*=11.7, 4.3 Hz, H-3), 4.51, 4.73 (each 1H, ABq, *J*=12.0 Hz, H-26a, -26b); ^{1}H-NMR data of the saccharide residues, see Table 2; ^{13}C-NMR (125 MHz, pyridine-

d_5), see Table 1.

Compound **3**: White powder, $[\alpha]_D$ −2.91° (c=0.28, MeOH); mp 118—220 °C; IR (KBr) ν_{max} 3418, 2935, 1600, 1385, 1354, 1105, 1072, 768, 625, 474 cm^{-1}; ESI-MS (negative ion mode) m/z 1059 $[M-1]^-$, 927 $[M-133]^-$, 765 $[M-295]^-$, 603 $[M-457]^-$ and 457 $[M-603]^-$; HR-ESI-MS m/z 1059.5709 $[M-H]^-$, Calcd for $C_{53}H_{87}O_{21}$: 1059.5740; ^{1}H-NMR (pyridine-d_5) δ: 0.25, 0.50 (each 1H, ABq, J=3.8 Hz, H-19a, -19b), 0.90, 1.04, 1.06, 1.32, 1.95 (each 3H, s, Me-28, -30, -18, - 29, -27), 1.18 (3H, d, J=6.6 Hz, Me-21), 1.72 (3H, d, J=6.5 Hz, Me-6 of fucose), 3.45 (1H, dd, J=11.7, 4.3 Hz, H-3), 4.51, 4.73 (each 1H, ABq, J=12.0 Hz, H-26a, -26b); ^{1}H-NMR data of the saccharide residues, see Table 2; ^{13}C-NMR (125 MHz, pyridine-d_5), see Table 1.

Compound **4**: White powder, $[\alpha]_D$ 26.4° (c=0.025, MeOH); IR (KBr) ν_{max} 3427, 2935, 1607, 1385, 1364, 1105, 1082, 773, 627, 471 cm^{-1}; ESI-MS (negative ion mode) m/z 1059 $[M-1]^-$, 927 $[M-133]^-$, 765 $[M-295]^-$, 603 $[M-457]^-$; HR-ESI-MS m/z 1059.5811 $[M-H]^-$, Calcd for $C_{53}H_{87}O_{21}$: 1059.5740; ^{1}H-NMR (pyridine-d_5) δ: 0.25, 0.50 (each 1H, ABq, J=3.8 Hz, H-19a, -19b), 0.89, 1.04, 1.06, 1.32, 1.96 (each 3H, s, Me-28, -30, -18, -29, -27), 1.18 (3H, d, J=6.6 Hz, Me-21), 1.74 (3H, d, J=6.4 Hz, Me-6 of fucose), 3.47 (1H, dd, J=11.7, 4.3 Hz, H-3), 4.53, 4.72 (each 1H, ABq, J=12.0 Hz, H-26a, -26b); ^{1}H-NMR data of the saccharide residues, see Table 2; ^{13}C-NMR (125 MHz, pyridine-d_5), see Table 1.

Acid Hydrolysis and Identification of Sugars in 1—4 A solution of the compound (40 mg) in 50 ml of 1 M HCl (MeOH–H_2O, 1 : 1) was heated under reflux for 3 h. After removal of the solvent, the residue was partitioned between $CHCl_3$ and H_2O. The $CHCl_3$-soluble portion was evaporated and subjected to ODS column using 80% MeOH as an eluent to yield an aglycone, which was identified as thelictogenin A (**5**) by NMR data and physical properties compared with an authentic sample.[7)]

The aqueous layer was neutralized with Dowex (HCO3-), then filtered. The filtrate was concentrated to 2 ml, then treated with $NaBH_4$ (40 mg) at room temperature for 3 h. Excessive $NaBH_4$ was removed with 30% AcOH. After evaporation at 60 °C and washing with 0.1% hydrochloric acid (in MeOH) repeatedly until the BO_3^{3-} was removed, the reaction mixture was heated to dryness at 105 °C for 15 min, followed by the addition of pyridine (0.5 ml) and Ac_2O (0.5 ml). The mixture was incubated in a water bath at 100 °C for 1 h and partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ layer was concentrated for GC analysis. The peaks of each monosaccharide were observed at t_R (min): **1**. D-fucose 27.830, D-glucose 33.052; **2**. D-quinovose 26.907, D-fucose 27.826, D-glucose 33.070; **3**. D-fucose 27.835, D-xylose 28.775, D-glucose 33.073; **4**. D-fucose 27.838, L-arabinose 28.290, D-glucose 33.075 (reference D-quinovose 26.910, D-fucose 27.833, L-arabinose 28.291, D-xylose 28.780, D-glucose 33.077, L-quinovose 28.012, L-fucose 29.363, D-arabinose 29.862, L-xylose 30.695, L-glucose 34.463).

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