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Three new cycloartane glycosides from *Thalictrum thunbergii* D.C.☆

Hitoshi Yoshimitsu,[a,*] Makiko Nishida[a] and Toshihiro Nohara[b]

[a]*Faculty of Engineering, Kyushu Kyoritsu University, 1-8 Jiyugaoka Yahata-nishi-ku, Kitakyushu 807-8585, Japan*
[b]*Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi, Kumamoto 862-0973, Japan*

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Abstract—Three new cycloartane glycosides possessing a five-membered ring, which is constructed by a C–C bond, at the side chain have been isolated from the aerial parts of *Thalictrum thunbergii* D.C. Their structures were determined by the use of 2D NMR techniques and chemical evidence.

The genus *Thalictrum* plants grow widely in Japan. Thalictri Herba (dried whole plant of *Thalictrum* sp.) called Takatogusa has been used as a folk medicine for treating stomach disorders in Nagano Prefecture. We have reported the structural characterization of 10 cycloartane glycosides, thalictosides A and C,[2] from the fresh aerial parts of *Thalictrum thunbergii* D.C., which was cultivated in the Botanical Garden of Tokushima University, and thalictosides I, II, III, IV, V, IX, XII and XIII[3] from Thalictri Herba. In our extended search for cycloartane-type glycosides, we have isolated three cycloartane glycosides, named thalictosides D (**1**), E (**2**), and F (**3**), from the aerial parts of *T. thunbergii* D.C., which was collected in Nagano Prefecture. This paper describes their structural elucidation.

The methanolic extract of the air-dried aerial parts of *T. thunbergii* D.C. was partitioned into a benzene–water solvent system. The water-soluble portion was subjected to MCI gel CHP20P, octadecyl silica gel (ODS) and silica gel column chromatographies and finally HPLC to give three glycosides (**1–3**).

Thalictoside D (**1**) was obtained as a white powder, $[\alpha]_D = -28.9°$ (MeOH). In the negative-ion FAB-MS of **1**, a quasi-molecular ion peak was observed at *m/z* 1267 $[M-H]^-$, while its positive-ion FAB-MS showed a quasi-molecular ion peak at *m/z* 1291 $[M+Na]^+$. The positive high-resolution (HR) FAB-MS showed a clustered molecular ion at *m/z* 1291.6300 $[C_{60}H_{100}O_{28}Na]^+$. The ^{1}H NMR spectrum displayed a couple of doublet signals at δ 0.32 and 0.85, which was characteristic of a cyclopropane methylene, five quaternary methyls at δ 1.24, 1.40, 1.43, 1.60 and 1.61, two secondary methyls at δ 1.65 (*J*=6.1 Hz) and 1.73 (*J*=6.1 Hz), five anomeric protons at δ 4.85 (1H, d, *J*=7.3 Hz), 5.01 (1H, d, *J*=7.3 Hz), 5.47 (1H, d, *J*=7.3 Hz), 5.49 (1H, br s), and 6.70 (1H, br s). The above ^{1}H NMR data of **1** was similar to those of cycloartane glycosides from Thalictri Herba. A comparative study of the ^{13}C NMR data of **1** with those of thalictosides III and IV indicated the presence of a diverse side chain. A sequence of connectivities through a methine proton at δ 2.89 (H-17), a methine proton at δ 2.27 (1H, dt, *J*=5.1, 7.2 Hz, H-20), a hydroxymethine proton at δ 4.22 (1H, dd, *J*=3.2, 7.2 Hz, H-22), methylene protons at δ 2.22 (1H, ddd, *J*=3.2, 9.2, 13.8 Hz, H-23β) and 2.68 (1H, br d, *J*=14.0 Hz, H-23α), a methine proton at δ 2.35 (1H, br d, *J*=11.6 Hz, H-24), a hydroxymethine proton at δ 4.82 (1H, br s, H-21) and a methine proton at δ 2.27 (H-20), in turn, was observed in the ^{1}H–^{1}H correlation spectroscopy (COSY) (Fig. 1(A)). The heteronuclear multiple bond correlation spectroscopy (HMBC) was observed between two singlet methyls (δ_H 1.40 and 1.61) and C-24 (δ_C 60.7) (Fig. 1(A)). In addition, the nuclear Overhauser effect spectroscopy (NOESY) was observed between the following protons: H_3-18 and H-20; H-20 and H-22, H-23β, H-24; H-21 and H_3-26, H_3-27; H-23β and H-23α, H-24; H_3-28 and H-17. Consequently, this NOESY experiment suggested the stereo configuration for the structure of **1** to be as shown in Fig. 1(B). On acid hydrolysis, **1** afforded D-glucose and L-rhamnose, together with several unidentified artificial sapogenols.[4] The ^{1}H and ^{13}C NMR spectrum of **1**, which could be assigned with the aid of ^{1}H–^{1}H COSY, heteronuclear multiple quantum coherence (HMQC), total correlation spectroscopy (TOCSY) and HMBC techniques, showed signals due to the pentasaccharide moiety consisted of three glucopyrano-

☆ See Ref. 1.

Keywords: glycosides; quasi-molecular; glucopyranosyl.

* Corresponding author. Tel.: +93-693-3203; fax: +93-603-8186; e-mail: yoshimit@kyukyo-u.ac.jp

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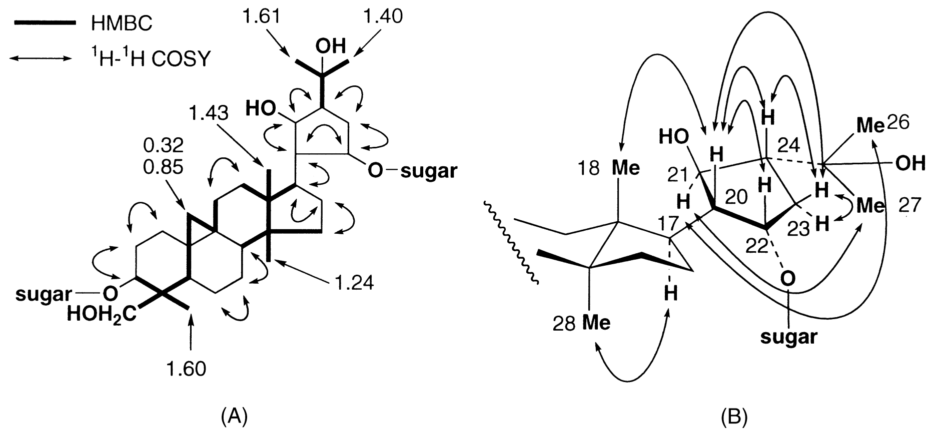


Figure 1. (A) ^{1}H–^{1}H-COSY and HMBC spectrum of **1**; (B) NOESY spectrum of **1**.

syl moieties δ 4.85 (d, *J*=7.3 Hz, H-1′′′′), δ 5.01 (d, *J*=7.3 Hz, H-1′), and δ 5.47 (d, *J*=7.3 Hz, H-1′′′′′)) and two rhamnopyranosyl moieties (δ 5.49 (br s, H-1′′′), and δ 6.70 (br s, H-1′′)). The HMBC experiment showed that the trisaccharide and the disaccharide moieties were linked to the C-3 and C-22 hydroxyl groups of the aglycone, respectively. Moreover, long-range correlations were observed between the H-1′ of the glucopyranosyl moiety and the C-3 of the aglycone, between the H-1′′ of the rhamnopyranosyl moiety and the C-2′ of the glucopyranosyl moiety, between the H-1′′′ of the rhamnopyranosyl moiety and the C-6′ of the glucopyranosyl moiety, between the H-1′′′′ of the glucopyranosyl moiety and the C-22 of the aglycone and between the H-1′′′′′ of the glucopyranosyl moiety and the C-2′′′′ of the glucopyranosyl moiety (Fig. 2). From the above evidence, the structure of **1** was concluded to be 22-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 20*R*,21*R*,22*S*,24*R*-cycloartane-3β,21,22,25,30-pentaol 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Thalictoside E (**2**) was obtained as a white powder, $[\alpha]_D=-29.6°$ (MeOH). In the negative-ion FAB-MS of **1**, a quasi-molecular ion peak was observed at *m/z* 1399 $[M-H]^-$, while its positive-ion FAB-MS showed a quasi-molecular ion peak at *m/z* 1423 $[M+Na]^+$. The positive HR-FAB-MS showed a clustered molecular ion at *m/z* 1423.6727 $[C_{65}H_{108}O_{32}Na]^+$. The ^{1}H and ^{13}C NMR spectrum (Tables 1 and 2) were also similar to those of **1** except for the signals due to the sugar moiety. Meanwhile, the molecular formula $C_{65}H_{108}O_{32}$ was higher by $C_5H_8O_4$ than that of **1**. On acid hydrolysis, **2** afforded D-glucose, D-xylose and L-rhamnose, together with several unidentified artificial sapogenols.[4] Furthermore, a comparative study of the ^{13}C NMR spectrum of **2** with that of **1** indicated the presence of an additional xylosyl unit in **2**, which was linked to the C-6 hydroxyl group of the glucopyranosyl moiety attached to the C-22 hydroxyl group of the aglycone. The ^{1}H and ^{13}C NMR spectrum of **2**, which could be assigned with the aid of ^{1}H–^{1}H COSY, HMQC, TOCSY and HMBC techniques, showed signals due to the hexasaccharide moiety consisted of three glucopyranosyl moieties (δ 4.76 (d, *J*=7.9 Hz, H-1′′′′), δ 5.00 (d, *J*=7.9 Hz, H-1′), and δ 5.41 (d, *J*=7.3 Hz, H-1′′′′′)), one xylopyranosyl moiety (δ 5.01 (d, *J*=7.9 Hz, H-1′′′′′′)) and two rhamnopyranosyl moieties (δ 5.48 (br s, H-1′′′), and δ 6.68 (br s, H-1′′)). The HMBC experiment of **2** showed the same result as that of **1**, except long-range correlations between H-1′′′′′′ of the xylopyranosyl moiety and the C-6′′′′ of the glucopyranosyl moiety attached to the C-22 hydroxyl group of the aglycone. Consequently, the structure of **2** was determined to be 22-*O*-β-D-glucopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→6)]-β-D-glucopyranosyl 20*R*,21*R*,22*S*,24*R*-cycloartane-3β,21,22,25,30-pentaol 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Thalictoside F (**3**) was obtained as a white powder, $[\alpha]_D=-29.1°$ (MeOH). In the negative-ion FAB-MS of **3**, a quasi-molecular ion peak was observed at *m/z* 1399 $[M-H]^-$, while its positive-ion FAB-MS showed a

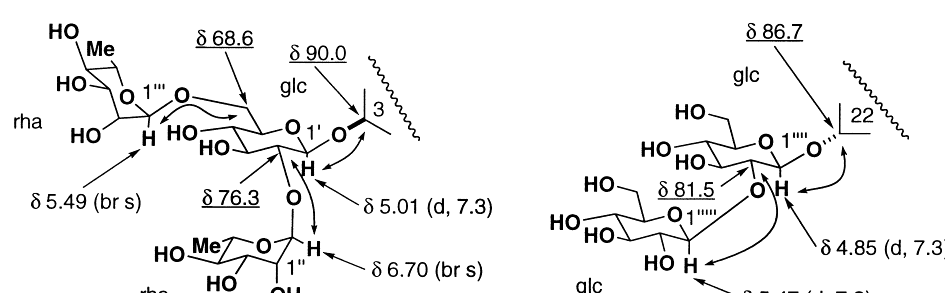


Figure 2. ^{1}H–^{13}C long-range correlation of the saccharide moieties of **1**. *J* values (Hz) in the ^{1}H NMR spectrum are given in parentheses. Underlined values indicate ^{13}C NMR chemical shifts.

Table 1. ^{1}H NMR chemical shifts for oligosaccharide moieties of **1**–**3** (pyridine-d_5)

H	**1**	**2**	**3**
1	1.25, 1.74	1.27, 1.74	1.22, 1.69
2	1.87, 2.48	1.86, 2.49	1.88, 2.48
3	3.68 dd(4.3, 11.6)	3.68 dd(4.9, 11.6)	3.65 dd(4.3, 11.6)
5	1.38	1.38	1.37
6	1.39, 1.78	1.38, 1.78	1.39, 1.78
7	0.90, 1.23	0.90, 1.23	0.91, 1.24
8	1.62	1.61	1.54
11	1.08, 2.08	1.08, 2.06	0.99, 1.99
12	2.08, 2.44	2.06, 2.43	1.68, 2.28
15	1.25, 1.41	1.26, 1.36	1.31, 1.42
16	1.41, 2.39	1.29, 2.33	1.44, 2.12
17	2.89	2.86	3.07
18	1.43 s	1.45 s	1.01 s
19	0.32 d(3.7)	0.32 d(3.6)	0.32 d(3.6)
	0.85 d(3.7)	0.85 d(3.6)	0.82 d(3.6)
20	2.27 dt(5.1, 7.2)	2.22 dt(5.2, 7.0)	1.75
21	4.82 br s	4.78 br s	4.55 br d(4.4)
22	4.22 dd(3.2, 7.2)	4.21 dd(3.0, 7.0)	4.35 br s
23	2.22 ddd(3.2, 9.2, 13.8)	2.37 ddd(3.0, 9.3, 13.2)	1.95 ddd(3.1, 9.3, 13.2)
	2.68 br d(14.0)	2.77 br d(13.4)	2.65 dd(9.2, 13.2)
24	2.35 br d(11.6)	2.34 br d(11.3)	2.75 dd(9.2, 9.2)
26	1.61 s	1.60 s	1.52 s
27	1.40 s	1.40 s	1.30 s
28	1.24 s	1.23 s	1.07 s
29	1.60 s	1.59 s	1.58 s
30	4.33, 4.41	4.32, 4.40	4.33, 4.40
glc-1′	5.01 d(7.3)	5.00 d(7.9)	5.00 d(7.9)
2′	4.36 dd(7.3, 9.2)	4.35 dd(7.9, 9.2)	4.34 dd(7.9, 9.2)
3′	4.29 dd(9.2, 9.2)	4.28 dd(9.2, 9.2)	4.28
4′	3.93 dd(9.2, 9.2)	3.93 dd(9.2, 9.2)	3.94 dd(9.2, 9.2)
5′	4.03 m	4.04 m	4.04 m
6′	4.15 dd (5.5,11.0)	4.14 dd (4.3,11.6)	4.15 dd (4.8,11.5)
	4.64 br d(11.0)	4.64 br d(10.4)	4.63 br d(10.4)
rha-1″	6.70 br s	6.68 br s	6.69 br s
2″	4.78 br s	4.77 br s	4.77 br s
3″	4.77 dd (3.0,9.1)	4.76 dd (3.0,9.2)	4.76 br d(9.2)
4″	4.29 dd (9.1,9.2)	4.30 dd (9.2,9.2)	4.31
5″	4.93 m	4.94 m	4.93 m
6″	1.73 d (6.1)	1.72 d (6.1)	1.74 d (6.1)
rha-1‴	5.49 br s	5.48 br s	5.50 br s
2‴	4.56 d (3.0)	4.55 br s	4.57 br s
3‴	4.51 dd (3.0,9.2)	4.50 dd (3.1,9.2)	4.50 dd (3.1,9.2)
4‴	4.27 dd (9.2,9.2)	4.28 dd (9.2,9.2)	4.27 dd (9.2,9.2)
5‴	4.35 m	4.32 m	4.33 m
6‴	1.65 d (6.1)	1.64 d (6.1)	1.65 d (6.1)
glc-1⁗	4.85 d (7.3)	4.76 d (7.9)	4.90 d (7.9)
2⁗	4.07 dd (7.3,8.5)	3.98 dd (7.9,9.2)	3.84 dd (7.9,8.5)
3⁗	4.18 dd (8.5,9.2)	4.11 dd (9.2,9.2)	4.19 dd (8.5,8.5)
4⁗	4.01 dd (9.2,9.2)	3.93 dd (9.2,9.2)	4.13 dd (8.5,8.5)
5⁗	3.89 m	3.89 m	4.05 m
6⁗	4.32 dd (5.0,11.8)	4.19 dd (4.9,11.5)	4.39 dd (4.8,11.6)
	4.56	4.79 br d (10.4)	4.80 br d (10.4)
glc-1″‴′	5.47 d (7.3)	5.41 d (7.3)	5.30 d (7.3)
2″‴′	4.18 dd (7.3,8.5)	4.14 dd (7.3,8.5)	4.13 dd (7.3,8.5)
3″‴′	4.19	4.17 dd (8.5,9.2)	4.18 dd (8.5,8.5)
4″‴′	3.96 dd (9.2,9.2)	3.93 dd (9.2,9.2)	4.23
5″‴′	3.95 m	3.96 m	3.73 m
6″‴′	4.32 dd (5.0,11.0)	4.29	4.33
	4.40 br d (11.0)	4.63 br d (10.4)	4.40
xyl-1″‴″		5.00 d (7.9)	5.10 d (7.3)
2″‴″		4.04 dd (7.9,8.5)	4.07 dd (7.3,7.9)
3″‴″		4.17 dd (8.5,8.5)	4.16 dd (7.9,8.5)
4″‴″		4.26 m	4.25 m
5″‴″		3.72 br t (10.4)	3.73 dd (9.8,11.6)
		4.37 dd (4.5,11.0)	4.40 dd (4.9,11.6)

Coupling constants (*J* in Hz) are given in parentheses.

Table 2. ^{13}C NMR data for **1**–**3** (pyridine-d_5)

C	**1**	**2**	**3**
1	32.4	32.5	32.4
2	30.0	30.0	29.9
3	90.0	90.0	89.8
4	45.4	45.4	45.3
5	48.7	48.7	48.2
6	22.9	22.9	22.7
7	27.4	27.4	27.0
8	48.8	48.8	48.5
9	19.9	19.9	19.8
10	26.5	26.5	26.5
11	26.7	26.7	26.8
12	30.8	30.8	31.5
13	45.7	45.7	45.5
14	48.8	48.8	48.8
15	36.1	36.1	36.2
16	28.1	28.1	28.4
17	45.7	45.7	40.1
18	18.9	18.9	19.2
19	31.2	31.2	30.7
20	57.3	57.2	52.6
21	77.4	77.5	75.6
22	86.7	86.8	87.2
23	34.5	34.7	35.9
24	60.7	60.4	61.1
25	71.1	71.2	70.6
26	29.2	29.2	29.6
27	29.8	29.8	27.4
28	21.2	21.2	20.4
29	20.1	20.1	20.0
30	60.8	60.9	60.8
glc-1′	105.4	105.4	105.3
2′	76.3	76.4	76.4
3′	80.2	80.2	80.2
4′	72.1	72.1	72.1
5′	76.6	76.6	76.6
6′	68.6	68.6	68.5
rha-1″	101.0	101.0	101.0
2″	72.3	72.3	72.3
3″	72.4	72.4	72.4
4″	74.5	74.5	74.5
5″	69.2	69.2	69.2
6″	18.5	18.5	18.5
rha-1‴	102.7	102.7	102.7
2‴	72.2	72.2	72.3
3‴	72.9	72.9	72.8
4‴	73.9	73.9	73.9
5‴	69.8	69.8	69.8
6‴	18.7	18.7	18.7
glc-1⁗	103.2	103.1	102.6
2⁗	81.5	81.3	83.5
3⁗	78.6	78.6	78.6
4⁗	71.6	71.2	70.8
5⁗	78.6	77.3	77.4
6⁗	63.0	68.9	69.5
glc-1″″′	105.4	105.4	106.2
2″″′	75.5	75.5	75.6
3″″′	78.7	78.2	78.4
4″″′	71.9	71.9	70.8
5″″′	77.8	79.8	78.9
6″″′	63.9	63.9	62.1
xyl-1″″″		105.9	106.0
2″″″		75.0	75.0
3″″″		78.2	78.3
4″″″		71.2	71.2
5″″″		67.2	67.2

quasi-molecular ion peak at m/z 1423 $[M+Na]^+$. The positive HR-FAB-MS showed a clustered molecular ion at m/z 1423.6724 $[C_{65}H_{108}O_{32}Na]^+$. The ^{1}H NMR spectrum displayed signals due to a cyclopropane methylene (δ 0.32 and 0.82 (each 1H, d, J=3.6 Hz)), five quaternary methyls (δ 1.01, 1.07, 1.30, 1.52, and 1.58), two secondary methyls (δ 1.65 (J=6.1 Hz), and 1.74 (J=6.1 Hz)), six anomeric protons (δ 4.90 (1H, d, J=7.9 Hz), 5.00 (1H, d, J=7.9 Hz), 5.10 (1H, d, J=7.3 Hz), 5.30 (1H, d, J=7.3 Hz), 5.50 (1H, br s), and 6.69 (1H, br s). The above ^{1}H NMR data of **3** was similar to that of thalictoside E (**2**). A sequence of connectivities through a methine proton at δ 3.04 (H-17), a methine proton at δ 1.75 (1H, overlapped, H-20), a hydroxymethine proton at δ 4.53 (1H, br s, H-22), methylene protons at δ 1.95 (1H, ddd, J=3.1, 9.3, 13.2 Hz, H-23β) and 2.65 (1H, dd, J=9.2, 13.2 Hz, H-23α), a methine proton at δ 2.75 (1H, dd, J=9.2, 9.2 Hz, H-24), a hydroxymethine proton at δ 4.55 (1H, br d, J=4.4 Hz, H-21) and a methine proton at δ 1.75 (H-20), in turn, was observed in the ^{1}H–^{1}H COSY (Fig. 3(A)). The HMBC was observed between two singlet methyls (δ_H 1.30 and 1.52) and C-24 (δ_C 61.1) (Fig. 3(A)). The above data indicated the presence of a different configuration five-membered ring, which was constructed by a C–C bond. In addition, the NOESY was observed between the following protons: H_3-18 and H-21, H-20; H-20 and H-21, H-22; H-21 and H_3-26, H_3-27; H-22 and H-23β; H-23β and H-23α; H-23α and H-24; H_3-28 and H-17. Consequently, this NOESY experiment suggested the stereo configuration for the structure of **3** to be as shown in Fig. 3(B). On acid hydrolysis, **3** afforded D-glucose, D-xylose and L-rhamnose, together with several unidentified artificial sapogenols.[5] The ^{1}H and ^{13}C NMR spectrum of **3**, which could be assigned with the aid of ^{1}H–^{1}H COSY, HMQC, TOCSY and HMBC techniques, showed signals due to the hexasaccharide moiety consisted of three glucopyranosyl moieties (δ 5.00 (d, J=7.9 Hz, H-1′), and δ 4.90 (d, J=7.9 Hz, H-1⁗), δ 5.30 (d, J=7.3 Hz, H-1″″′)), two rhamnopyranosyl moieties (δ 6.69 (br s, H-1″), and δ 5.50 (br s, H-1‴)) and one xylopyranosyl moiety (δ 5.10 (d, J=7.3 Hz, H-1⁗)). The HMBC experiment showed that two trisaccharide moieties were linked to the C-3 and C-22 hydroxyl groups of the aglycone, respectively. Moreover, long-range correlations were observed between the H-1′ of the glucopyranosyl moiety and the C-3 of the aglycone, between the H-1″ of the rhamnopyranosyl moiety and the C-2′ of the glucopyranosyl moiety, between the H-1‴ of the rhamnopyranosyl moiety and the C-6′ of the glucopyranosyl moiety, between the H-1⁗ of the glucopyranosyl moiety and the C-22 of the aglycone, between the H-1″″′ of the glucopyranosyl moiety and the C-2⁗ of the glucopyranosyl moiety and between the H-1⁗ of the xylopyranosyl moiety and the C-6⁗ of the glucopyranosyl moiety (Fig. 4). From the above evidence, the structure of **3** was concluded to be 22-*O*-β-D-glucopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→6)]-β-D-glucopyranosyl 20*R*,21*S*,22*S*,24*S*-cycloartane-3β,21,22,25,30-pentaol 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside. They are novel cycloartane glycosides having structural peculiarities, namely, a C–C bond between 21 and 24 and bisdesmoside at C-3 and C-22. The coexistent analogous[3] having a carbonyl group at C-21 and a double bond at Δ^{24} would cause a new C–C bond formation between C-21 and C-24.

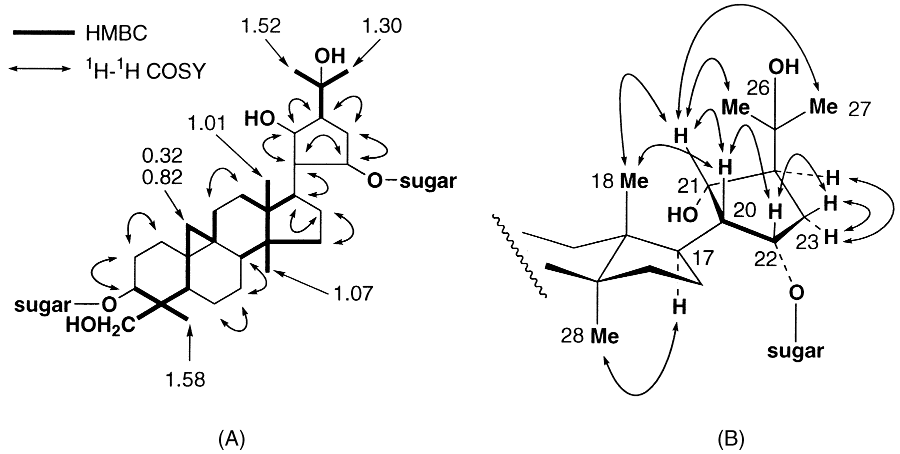


Figure 3. (A) ^{1}H–^{1}H-COSY and HMBC spectrum of **3**; (B) NOESY spectrum of **3**.

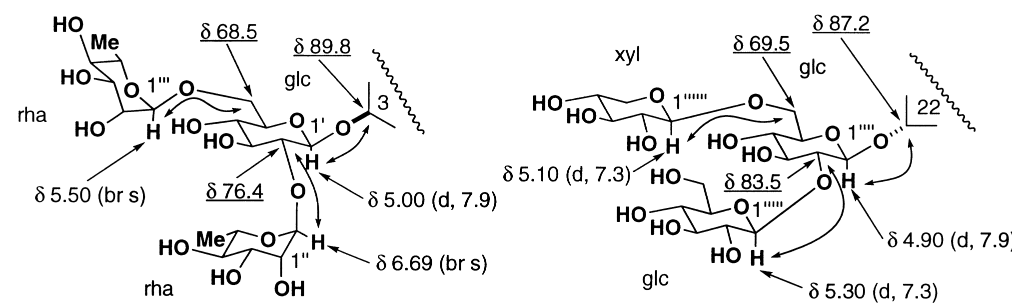
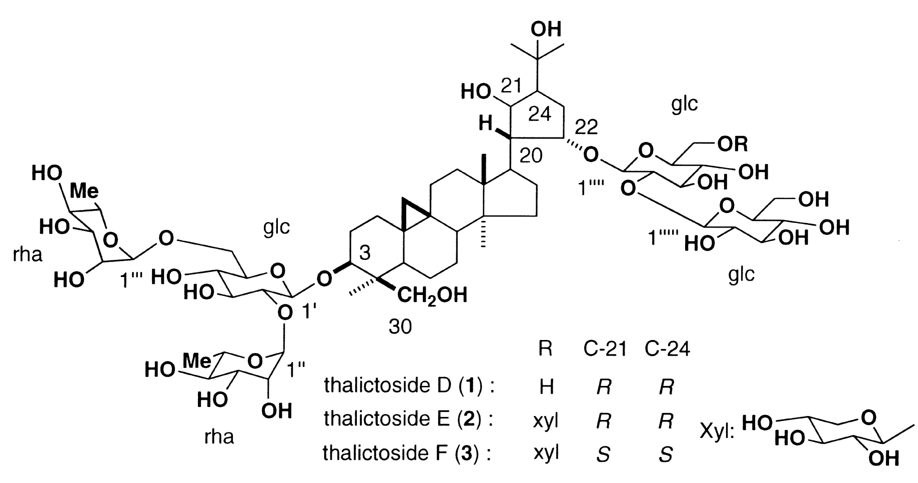


Figure 4. ^{1}H–^{13}C long-range correlation of the saccharide moieties of **3**. *J* values (Hz) in the ^{1}H NMR spectrum are given in parentheses. Underlined values indicate ^{13}C NMR chemical shifts.



1. Experimental

1.1. General procedures

Optical rotations were taken with a JASCO DIP-1000 automatic digital polarimeter. The NMR spectra were measured with a JEOL alpha 500 NMR spectrometer and chemical shifts are given on a δ (ppm) scale with tetramethylsilane (TMS) as an internal standard. The HR-FAB-MS was recorded with a JEOL HX-110 spectrometer. Gas liquid chromatography (GLC) was performed on a HP5890A gas chromatography with a flame ionization detector (FID). HPLC was carried out using a TSK gel-120A (7.8 mm i.d.×30 cm) column with a Tosoh CCPM pump and Tosoh RI-8010 differential refractometer as a detector. TLC was performed on pre-coated Kieselgel 60 F_{254} (Merck), and detection was achieved by spraying with 10% H_2SO_4 followed by heating. Column chromatography was carried out on Kieselgel (230–400 mesh, Merck), ODS (PrePAK-500/C_{18}, Waters) and MCI gel CHP20P (Mitsubishi Chemical Ind.).

1.2. Extraction and isolation

The fresh aerial parts of *T. thunbergii* D.C. were collected in Nagano Prefecture of Japan. The dried aerial parts of

(4.0 kg) were extracted with MeOH at room temperature for 6 months, and the extract (549 g) was partitioned in benzene and water (1:1). The water-soluble portion (466 g) was subjected to MCI gel CHP20P column chromatography with MeOH–H_2O (30→40→50→60→70→80→90%) to afford 10 fractions (fr.1–fr.10). Fraction 2 (15 g) was further separated by ODS column chromatography with MeOH–H_2O (35→40→45→50→55→60%) to afford five fractions (fr.11–fr.15). Fraction 12 (239 mg) was subjected to silica gel column chromatography with $CHCl_3$–MeOH–H_2O (6:4:1), followed by HPLC with MeOH–H_2O (1:1), to furnish thalictosides D (**2**) (9 mg) and E (**3**) (8 mg). Fraction 14 (103 mg) was subjected to silica gel column chromatography with $CHCl_3$–MeOH–H_2O (6:4:1), followed by HPLC with MeOH–H_2O (1:1), to furnish tahlictoside F (**1**) (9 mg).

1.2.1. Thalictoside D (1). A white powder, $[\alpha]_D^{25}$=28.9° (c=0.45, MeOH). Neg. FAB-MS (m/z): 1267 $[M-H]^-$. Pos. FAB-MS (m/z): 1291 $[M+Na]^+$. HR-FAB-MS (m/z): 1291.6300 $[M+Na]^+$ (Calcd for $C_{60}H_{100}O_{28}Na$ 1291.6311). ^1H and ^{13}C NMR (pyridine-d_5): Tables 1 and 2.

1.2.2. Thalictoside E (2). A white powder, $[\alpha]_D^{25}$=−29.6° (c=0.40, MeOH). Neg. FAB-MS (m/z): 1399 $[M-H]^-$. Pos. FAB-MS (m/z): 1423 $[M+Na]^+$. HR-FAB-MS (m/z): 1423.6727 $[M+Na]^+$ (Calcd for $C_{65}H_{108}O_{32}Na$ 1423.6721). ^1H and ^{13}C NMR (pyridine-d_5): Tables 1 and 2.

1.2.3. Thalictoside F (3). A white powder, $[\alpha]_D^{25}$=−29.1° (c=0.51, MeOH). Neg. FAB-MS (m/z): 1399 $[M-H]^-$. Pos. FAB-MS (m/z): 1423 $[M+Na]^+$. HR-FAB-MS (m/z): 1423.6724 $[M+Na]^+$ (Calcd for $C_{65}H_{108}O_{32}Na$ 1423.6721). ^1H and ^{13}C NMR (pyridine-d_5): Tables 1 and 2.

1.2.4. Sugar analysis of 1, 2 and 3. A solution each of **1** and **2** (2 mg) in 2N HCl–dioxane (1:1, 2 ml) was heated at 90°C for 2 h. The solution was neutralized with Amberlite IRA-400 and passed through a SEP-PAK C_{18} cartridge to give a sugar fraction. The sugar fraction was concentrated to dryness in vacuo to give a residue, which was dissolved in dry pyridine and added to L-cysteine methyl ester hydrochloride. The reaction mixture was heated at 60°C for 1 h and concentrated to dryness by blowing N_2 gas. To the residue was added trimethylsilylimidazole, and the mixture was heated at 60°C for 1 h. The reaction mixture was concentrated to dryness by blowing N_2 gas. The residue was extracted with n-hexane and H_2O, and the organic layer was analyzed by GLC: column, OV-17 (0.32 mm×30 m); detector, FID; column temperature, 230°C; detector temperature, 270°C; injector temperature, 270°C; carrier gas, He (2.2 kg/cm^2). t_R (min) of trimethylsilyl ether of methyl 2-(polyhydroxyalkyl)-thiazolidine-4(R)-carboxylates were as follows. **1**: D-xylose 9.7, L-rhamnose 11.6, D-glucose 17.1. **2**: D-xylose 9.7, L-rhamnose 11.6, D-glucose 17.1. The standard monosaccharides were subjected to the same reaction and GLC analysis under the same conditions. A solution of **3** (1 mg) in 2N HCl–dioxane (1:1, 2 ml) was heated at 100°C for 1 h. The reaction mixture was diluted with H_2O and evaporated to remove dioxane. The solution was neutralized with Amberlite MB-3 and passed through a SEP-PAK C_{18} cartridge to give a sugar fraction. A solution of the sugar fraction was analyzed by TLC [CH_3CN–MeOH–H_2O (6:4:1), **3**: rhamnose, R_f 0.54; xylose, R_f 0.40; glucose, R_f 0.29]. A solution of the sugar fraction in 1 ml of H_2O was treated with a solution of L-(−)-α-methylbenzylamine (150 μl) and $NaBH_3CN$ (8 mg) in 1 ml of EtOH, and the mixture was kept at 40°C for 3 h. Then, several drops of acetic acid were added and the mixture was concentrated to dryness. The residue dissolved in Ac_2O–C_5H_5N (1:1, 2 ml) was treated with 4-(dimethylamino)-pyridine (DMAP) (20 mg), and the whole mixture was left at room temperature overnight. After removal of excess Ac_2O and C_5H_5N, the residue dissolved in 20% CH_3CN was loaded into a SEP-PAK C_{18} cartridge and eluted with 20% CH_3CN (total 7 ml) and 100% CH_3CN. The fraction eluted with 100% CH_3CN was analyzed by normal-phase HPLC. Conditions of HPLC: column, Develosil 60-3, 3 μm (4.6 mm i.d.×150 mm); solvent, n-hexane–EtOH (19:1); flow rate, 1.20 ml/min; detection, UV (230 nm). t_R (min) of 1-(N-acetyl-L-α-methylbenzylamino)-1-deoxyalditol acetates were as follows. **3**; L-rhamnose 17.1, D-xylose 30.6, D-glucose 30.6. (Reference: L-rhamnose 17.0, D-xylose 30.7, D-glucose 30.8).

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