Triterpene Glycosides from Thalictri Herba. II[1)]

Hitoshi YOSHIMITSU,[a] Kazuhiro HAYASHI, Miki KUMABE, and Toshihiro NOHARA*,[b]

Faculty of Engineering, Kyushu Kyoritsu University,[a] 1–8 Jiyugaoka Yahata-nishi-ku, Kitakyushu 807, Japan and Faculty of Pharmaceutical Sciences, Kumamoto University,[b] 5–1 Oe-honmachi, Kumamoto 862, Japan.
Received May 24, 1993

Five new triterpene glycosides were isolated from the methanolic extract of Thalictri Herba (Takatogusa), the dried aerial parts of *Thalictrum* sp. plants (Ranunculaceae). They were designated as thalictosides III (1) and IV (2), being cycloartane-type glycosides, and thalictosides VI (3), VII (4) and VIII (5), being oleanene-type glycosides. By chemical and spectroscopic evidence, their structures were elucidated as 22*R*-21*S*,23*R*-epoxy- and 22*R*-21*R*,23*R*-epoxy-21-methoxycycloart-24-en-3β,22,30-triol 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosides (1 and 2, respectively), 3-*O*-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→4)-β-D-xylopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl ester (3) and 3-*O*-α-L-rhamnopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→4)-β-D-xylopyranosyl oleanolic acid and hederagenin 28-*O*-β-D-glucopyranosyl esters (4 and 5, respectively).

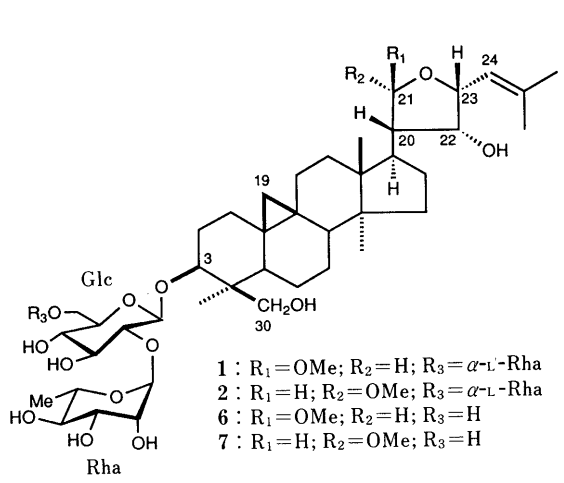
Keywords Thalictri Herba; Ranunculaceae; cycloartane glycoside; oleanene glycoside; thalictoside

In the preceding paper,[1)] we reported the isolation and structural determination of two new cycloartane glycosides, named thalictosides I (**6**) and II (**7**), from Thalictri Herba (Takatogusa), the dried aerial parts of *Thalictrum* sp. plants (Ranunculaceae).

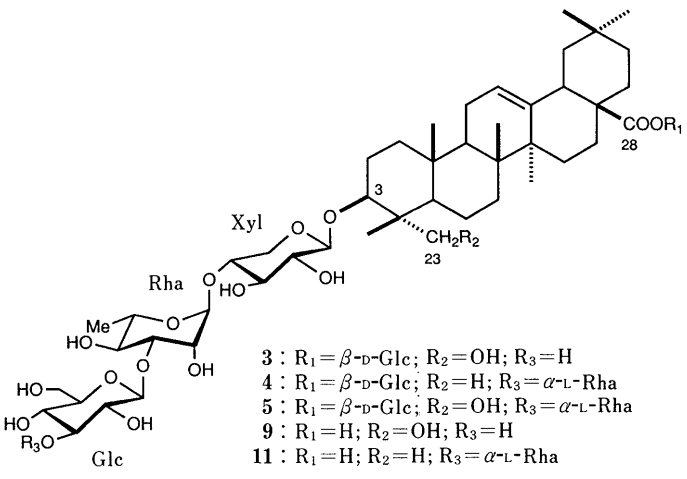
In a continuing study on glycosidic constituents, we obtained five additional new triterpene glycosides, named thalictosides III (**1**), IV (**2**), VI (**3**), VII (**4**) and VIII (**5**). This paper describes the structural characterization of each.

The methanol extract of Thalictri Herba was partitioned into a benzene–water solvent system. Diaion HP-20 column chromatography of the water soluble portion provided the glycosidic constituents, which were purified by using a combination of Sephadex LH-20, silica gel and octadecyl silica (ODS) column chromatography to furnish five thalictosides (**1**—**5**).

Thalictoside III (**1**) obtained as a white powder, $[\alpha]_D$ +4.5° (MeOH), showed a clustered molecular ion at *m/z* 979.5248 $[C_{49}H_{80}NaO_{18}]^+$ in the positive high resolution (HR) FAB-MS, and an AB quartet signal at δ 0.28 and 0.87, which is characteristic of cyclopropane methylene, five singlet methyl signals at δ 0.99, 1.26, 1.56, 1.67 and 1.70, and a methoxy signal at δ 3.55 in the ^{1}H-NMR spectrum. In addition, signals at δ 5.15, 4.27, 4.96 and 5.97 could be assigned to H-21, H-22, H-23 and H-24, respectively, on the five-membered ring at the side chain of cycloartane skeletone, similarly to thalictosides I and II (**6** and **7**) as reported previously.[1)] Furthermore, the ^{1}H-NMR spectrum of **1** suggested the occurrence of three anomeric proton signals at δ 4.99 (1H, d, *J*=7.7 Hz), 5.50 (1H, br s) and 6.71 (1H, br s). In the ^{13}C-NMR spectral data of **1**, the signals due to the aglycone moiety were also in good agreement with those of **6**, although the signals due to the sugar moiety were not identical. Meanwhile, the negative FAB-MS of **1** gave a peak at *m/z* 955 due to $[M-H]^-$, which was higher by 146 mass units than that of **6**. Furthermore, a comparative study of the ^{13}C-NMR spectrum of **1** with that of **6** indicated the presence of one additional mole of the rhamnosyl group in **1**, which was linked to the C-6 hydroxy group of a glucopyranosyl moiety according to the glycosylation shifts[2)] [δ: C-5, 76.6 (−1.6); C-6, 68.2 (+5.4) in the inner glucosyl moiety]. From the above evidence, the structure of **1** was concluded to be 22*R*-21*S*,23*R*-epoxy-21-methoxycycloart-24-en-3β,22,30-triol 3-*O*-α-L-rhamno-



1 : R_1=OMe; R_2=H; R_3=α-L-Rha
2 : R_1=H; R_2=OMe; R_3=α-L-Rha
6 : R_1=OMe; R_2=H; R_3=H
7 : R_1=H; R_2=OMe; R_3=H



3 : R_1=β-D-Glc; R_2=OH; R_3=H
4 : R_1=β-D-Glc; R_2=H; R_3=α-L-Rha
5 : R_1=β-D-Glc; R_2=OH; R_3=α-L-Rha
9 : R_1=H; R_2=OH; R_3=H
11 : R_1=H; R_2=H; R_3=α-L-Rha

© 1994 Pharmaceutical Society of Japan

NII-Electronic Library Service

TABLE I. ^{13}C-NMR Data for **1**, **2**, **6** and **7** (Pyridine-d_5)

Carbon	6	1	7	2
C-1	30.8	30.8	31.5	31.4
2	29.9	30.3	29.9	30.5
3	89.3	89.7	89.3	89.6
4	45.3	45.4	45.3	45.4
5	47.6	48.2	47.4	48.2
6	22.6	22.9	22.5	22.8
7	27.7	27.7	27.0	27.0
8	48.2	48.5	48.2	48.3
9	20.1	20.1	20.1	20.1
10	26.4	26.4	26.5	26.5
11	26.6	26.5	26.6	26.7
12	35.7	35.8	35.8	36.0
13	45.5	45.5	45.3	45.4
14	48.8	48.8	48.8	48.8
15	32.2	32.3	32.2	32.3
16	26.7	27.0	26.9	26.9
17	44.7	44.8	40.7	40.7
18	18.6	18.7	19.5	19.7
19	29.8	30.1	29.7	30.1
20	54.8	54.8	52.5	52.5
21	108.7	108.7	104.9	104.9
22	76.7	76.7	75.0	75.0
23	79.0	79.0	80.6	80.6
24	122.7	122.6	123.7	123.8
25	136.1	136.1	135.9	135.8
26	26.0	26.0	26.0	26.0
27	19.7	19.8	19.6	19.8
28	18.6	18.8	18.6	18.7
29	19.9	19.9	19.9	19.9
30	60.7	60.7	60.7	60.7
OMe	55.5	55.6	54.6	54.6
Glc-1	105.4	105.4	105.4	105.3
2	80.3	80.1	80.3	80.1
3	76.3	76.3	76.3	76.3
4	72.4	72.8	72.4	72.8
5	78.2	76.6	78.2	76.6
6	62.8	68.2	62.8	68.2
Rha-1	100.2	100.9	100.9	101.0
2	71.9	72.2	72.0	72.1
3	72.1	72.3	72.1	72.3
4	74.5	74.4	74.4	74.5
5	69.1	69.2	69.1	69.2
6	18.5	18.5	18.4	18.5
Rha-1		102.5		102.5
2		72.2		72.1
3		72.3		72.3
4		74.0		74.0
5		69.8		69.8
6		18.5		18.4

TABLE II. ^{13}C-NMR Data for **3**—**5** and **8**—**11** (Pyridine-d_5)

Carbon	8	9	3	10	11	4	5
C-1	38.9	38.9	39.1	39.0	38.9	39.0	39.1
2	27.6	26.3	26.4	28.1	26.7	26.7	26.4
3	73.7	81.2	81.2	78.2	88.7	88.7	81.1
4	42.9	43.5	43.6	39.4	39.6	39.6	43.5
5	48.8	47.5	47.6	55.9	56.0	56.0	47.6
6	18.7	18.0	18.1	18.8	18.5	18.5	18.1
7	33.0	32.8	32.8	33.3	32.2	32.5	32.8
8	39.8	39.7	40.0	39.8	39.7	39.9	39.9
9	48.2	48.1	48.2	48.2	48.1	48.1	48.2
10	37.3	36.8	36.9	37.5	37.1	37.1	36.9
11	23.8	23.8	23.9	23.8	23.8	23.8	23.9
12	122.7	122.5	123.0	122.7	122.5	122.9	122.9
13	145.0	144.8	144.1	145.0	144.0	144.1	144.1
14	42.2	42.1	42.1	42.2	42.2	42.1	42.1
15	28.4	28.2	28.3	28.4	28.3	28.3	28.3
16	23.8	23.6	23.4	23.8	23.7	23.4	23.4
17	46.7	46.6	47.0	46.7	46.7	47.0	47.0
18	42.0	41.9	41.7	42.1	42.0	41.7	41.7
19	46.5	46.3	46.1	46.6	46.5	46.2	46.1
20	31.0	30.9	30.8	31.0	31.0	30.8	30.8
21	34.3	34.1	34.0	34.3	34.3	34.0	34.0
22	33.3	33.2	33.1	33.3	33.2	33.1	33.1
23	68.2	63.9	64.0	28.8	28.2	28.1	63.9
24	13.1	14.0	14.1	16.6	17.1	17.2	14.1
25	16.0	16.0	16.2	15.6	15.5	15.7	16.2
26	17.5	17.4	17.5	17.4	17.4	17.5	17.5
27	26.2	26.1	26.1	26.2	26.2	26.1	26.1
28	180.4	*a)*	176.4	180.3	*a)*	177.4	176.4
29	33.3	33.2	33.1	33.3	33.0	33.1	33.1
30	23.8	23.7	23.6	23.8	23.8	23.7	23.7
Xyl-1		106.7	106.9		106.2	106.3	106.3
2		75.5	75.4		75.8	75.5	75.3
3		75.8	75.9		76.1	76.1	76.0
4		72.9	73.0		73.1	73.1	73.0
5		66.3	66.5		65.7	66.0	66.5
Rha-1		101.5	101.4		101.7	101.5	101.4
2		69.7	69.8		69.6	69.9	70.0
3		82.9	83.0		82.8	82.3	82.5
4		71.6	71.6		71.6	71.6	71.7
5		69.7	69.7		69.9	69.7	69.6
6		18.4	18.5		18.6	18.4	18.6
Glc-1		104.8	104.9		105.3	105.4	104.9
2		74.9	75.2		74.3	74.7	75.2
3		78.4	78.5		83.6	83.7	83.7
4		71.6	71.8		69.3	69.4	69.6
5		78.5	78.5		78.4	78.4	78.4
6		62.5	62.5		62.2	62.1	62.2
Rha-1					102.9	102.9	102.8
2					72.5	72.5	72.5
3					72.7	72.7	72.6
4					74.1	74.1	74.1
5					69.8	69.6	69.6
6					18.4	18.4	18.4
28-*O*-							
Glc-1			95.7			95.8	95.7
2			74.2			74.2	74.2
3			79.3			79.3	79.3
4			71.1			71.3	71.1
5			78.9			78.9	78.9
6			62.2			62.2	62.2

a) Undistinguished.

pyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Thalictoside IV (**2**) obtained as a white powder, $[\alpha]_D$ −40.8° (MeOH), showed the same ion peak at *m/z* 955 due to $[M-H]^-$ as that of **1** in the neg. FAB-MS. In the ^{1}H- and ^{13}C-NMR spectral data for **2**, the signals due to an aglycone moiety were in good consistent with those of thalictoside II (**7**),[1] while signals due to a sugar moiety were almost superimposable on those of **1**. From the above evidence, the structure of **2** was concluded to be the epimer at C-21 of **1**.

Thalictoside VI (**3**) obtained as a white powder, $[\alpha]_D$ +0.41° (MeOH), exhibited a $[M-H]^-$ peak at *m/z* 1073 in the neg. FAB-MS. The ^{1}H-NMR spectrum displayed six singlet methyl signals at δ 0.88, 0.89, 0.96, 1.13, 1.15 and 1.20, one olefinic proton signal at δ 5.42, and four anomeric proton signals at δ 5.02 (1H, d, J=7.0 Hz), 5.51 (1H, d, J=8.1 Hz), 6.30 (1H, br s) and 6.34 (1H, d, J=7.7 Hz). The ^{13}C-NMR spectrum revealed the presence of six quaternary carbon signals at δ 30.8, 36.9, 40.0, 42.1,

NII-Electronic Library Service

43.6 and 47.0, a set of olefinic carbon signals at δ 123.0 and 144.1, one ester carbonyl carbon signal at δ 176.4, and four anomeric carbon signals at δ 95.7, 101.4, 104.9 and 106.9. These spectral data indicated that **3** was the 3,28-bisdesmoside of hederagenin (**8**),[3] having four monosaccharide units. On selective cleavage of the ester-glycoside linkage with anhydrous LiI and 2,6-lutidine in anhydrous methanol,[4] **3** provided an anomeric mixture of methyl glucopyranose and a prosapogenin (**9**). The prosapogenin (**9**), on further acid hydrolysis afforded hederagenin, glucose, xylose and rhamnose. Moreover, the neg. FAB-MS of **9** gave a $[M-H]^-$ ion peak at *m/z* 911 along with fragment peaks at *m/z* 749 [*m/z* 911 − 162 (hexose unit)]$^-$, 603 [*m/z* 749 − 146 (deoxyhexose unit)]$^-$ and 471 [*m/z* 603 − 132 (pentose unit), hederagenin − H]$^-$. This evidence suggested that its sugar moiety was composed of a glucosyl-rhamnosyl-xylosyl unit. In the ^{13}C-NMR signals due to the sugar moiety of **9**, glycosylation shifts[2] observed at C-4 (72.9 ppm) of xylose and C-3 (82.9 ppm) of rhamnose. From the above evidence, the structure of **3** was concluded to be 3-*O*-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→4)-β-D-xylopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl ester.

Thalictoside VII (**4**), obtained as a white powder, $[\alpha]_D$ −18.6° (MeOH), exhibited a $[M-H]^-$ peak at *m/z* 1203 in the neg. FAB-MS. The ^{1}H-NMR spectrum showed seven singlet methyl signals at δ 0.88, 0.90, 0.93, 1.11, 1.15, 1.27 and 1.32, one olefinic proton signal at δ 5.43 and five anomeric proton signals at δ 5.00 (1H, d, *J*=6.2 Hz), 5.45 (1H, d, *J*=8.0 Hz), 6.23 (1H, br s), 6.23 (1H, br s) and 6.35 (1H, d, *J*=8.0 Hz). The ^{13}C-NMR spectrum revealed the presence of six quaternary carbon signals at δ 30.8, 37.1, 39.6, 39.9, 42.1 and 47.0, a pair of olefinic carbon signals at δ 122.9 and 144.1, one ester carbonyl carbon signal at δ 177.4, and five anomeric carbon signals at δ 95.8, 101.5, 102.9, 105.4 and 106.3. These spectral data indicated that **4** was the 3,28-bisdesmoside of oleanolic acid (**10**),[3] having five monosaccharide units. On alkaline hydrolysis with 2 N aq. NaOH, **4** afforded 1,6-anhydroglucopyranose and a prosapogenin (**11**). The prosapogenin (**11**), on the acid hydrolysis, gave oleanolic acid, glucose, xylose and rhamnose. Furthermore, the neg. FAB-MS of **11** gave a $[M-H]^-$ ion peak at *m/z* 1041 along with fragment peaks at *m/z* 895 [*m/z* 1041 − 146 (deoxyhexose unit)]$^-$, 733 [*m/z* 895 − 162 (hexose unit)]$^-$, 587 [*m/z* 733 − 146 (deoxyhexose unit)]$^-$ and 455 [*m/z* 587 − 132 (pentose unit), oleanolic acid − H]$^-$. This evidence suggested that its sugar moiety was constituted of a rhamnosyl-glucosyl-rhamnosyl-xylosyl unit. A comparative study of the ^{13}C-NMR signals due to the sugar moiety of **11** with that of **9** suggested the presence of one additional mole of a rhamnosyl unit in **11**, which was linked to the C-3 hydroxy group of the glucopyranosyl moiety according to the glycosylation shifts[2] [δ: C-2, 74.3 (−0.6); C-3, 83.6 (+5.2); C-4, 69.3 (−1.3) in the glucosyl moiety]. From the above evidence, the structure of **4** was concluded to be 3-*O*-α-L-rhamnopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→4)-β-D-xylopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl ester.

Thalictoside VIII (**5**), obtained as a white powder, $[\alpha]_D$ −11.6° (MeOH), exhibited a $[M-H]^-$ peak at *m/z* 1219 in the neg. FAB-MS. In the ^{1}H- and ^{13}C-NMR spectral data of **5**, signals due to an aglycone moiety were in good agreement with those of **3**, while signals due to a sugar moiety were almost identical with those of **4**. From the above evidence, the structure of **5** could be demonstrated to be 3-*O*-α-L-rhamnopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→4)-β-D-xylopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl ester.

Experimental

Optical rotations were taken with a JASCO DIP-360 automatic digital polarimeter. The ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL JNM-GX 400 NMR spectrometer and chemical shifts are given on a δ (ppm) scale with tetramethylsilane (TMS) as an internal standard. The FAB-MS was measured with a JEOL DX-303 HF spectrometer and taken in a 3-nitrobenzylalcohol matrix. The HR FAB-MS were recorded with a JEOL HX-110 spectrometer. TLC was performed on pre-coated Kiesel gel 60 F_{245} (Merck) and detection was achieved by spraying them with 10% H_2SO_4 followed by heating. Column chromatography was carried out on Kiesel gel (230—400 mesh, Merk), Sephadex LH-20 (Pharmacia Find Chem. Co. Ltd.), ODS (PrePak-500/C_{18}, Waters) and Diaion HP-20 (Mitsubishi Chemical Ind.)

Extraction and Separation Thalictri Herba (Takatogusa, 4.9 kg, purchased from Uchida Wakanyaku) was extracted with MeOH, and the extract was partitioned between benzene and water (1 : 1, v/v). The water soluble portion (605.1 g) was subjected to Diaion HP-20 column chromatography with MeOH–H_2O (0→30→50→70→90→100%) to afford seven fractions (fr. 1—7). Fr. 7 (22.1 g) was then chromatographed on Sephadex LH-20 with MeOH to provide four fractions (fr. 8—11). Fr. 9 (14.0 g) was further separated by silica gel column chromatography with $CHCl_3$–MeOH–H_2O (9 : 2 : 0.2→8 : 2 : 0.2→7 : 3 : 0.5, v/v) to give six fractions (fr. 12—17). Fr. 14 (478 mg) was subsequently purified by ODS column chromatography with MeOH–H_2O (50→66%), followed by silica gel column chromatography with $CHCl_3$–MeOH–H_2O (7 : 3 : 0.5, v/v), to furnish thalictosides III (**1**) (83 mg) and IV (**2**) (62 mg). Fr. 15 (654 mg) was also purified by ODS column chromatography with MeOH–H_2O (50→63%), and followed by silica gel column chromatography with $CHCl_3$–MeOH–H_2O (7 : 3 : 0.5, v/v) to give thalictosides VI (**3**) (62 mg) and VII (**4**) (78 mg). Further purification by ODS column chromatography with MeOH–H_2O (50→58%), followed by silica gel column chromatography with $CHCl_3$–MeOH–H_2O (7 : 3 : 0.5, v/v) of the fr. 16 (863 mg) provided thalictoside VIII (**5**) (60 mg).

Thalictoside III (1) A white powder, $[\alpha]_D^{25}$ +4.5° (*c*=0.51, MeOH). Neg. FAB-MS *m/z*: 955 $[M-H]^-$. HR FAB-MS *m/z*: 979.5248 $[M+Na]^+$ (Calcd for $C_{49}H_{80}NaO_{18}$ 979.5198). ^{1}H-NMR (pyridine-d_5) δ: 0.28, 0.87 (each 1H, ABq, *J*=3.7 Hz, CH_2-19), 0.99, 1.26, 1.56, 1.67, 1.70 (each 3H, s, Me-28, Me-18, Me-29, Me-27, Me-26), 1.66 (3H, d, *J*=6.2 Hz, Rha Me-6), 1.73 (3H, d, *J*=6.2 Hz, Rha Me-6), 2.45 (1H, m, H-20), 2.70 (1H, m, H-17), 3.55 (3H, s, OMe), 3.63 (1H, br d, *J*=13.6 Hz, H-3), 4.27 (1H, br s, H-22), 4.96 (1H, dd, *J*=8.4, 4.4 Hz, H-23), 4.99 (1H, d, *J*=7.7 Hz, Glc H-1), 5.15 (1H, d, *J*=4.8 Hz, H-21), 5.50 (1H, br s, Rha H-1), 5.97 (1H, d, *J*=8.4 Hz, H-24), 6.71 (1H, br s, Rha H-1).

Thalictoside IV (2) A white powder, $[\alpha]_D^{25}$ −40.8° (*c*=0.63, MeOH). Neg. FAB-MS *m/z*: 955 $[M-H]^-$. HR FAB-MS *m/z*: 979.5250 $[M+Na]^+$ (Calcd for $C_{49}H_{80}NaO_{18}$ 979.5180). ^{1}H-NMR (pyridine-d_5) δ: 0.37, 0.89 (each 1H, ABq, *J*=3.7 Hz, CH_2-19), 0.94, 1.06, 1.56, 1.72, 1.74 (each 3H, s, Me-28, Me-18, Me-29, Me-27, Me-26), 1.65 (3H, d, *J*=6.2 Hz, Rha Me-6), 1.73 (3H, d, *J*=6.2 Hz, Rha Me-6), 2.11 (1H, m, H-20), 2.75 (1H, m, H-17), 3.42 (3H, s, OMe), 3.62 (1H, dd, *J*=11.8, 4.4 Hz, H-3), 4.15 (1H, br s, H-22), 4.88 (1H, dd, *J*=9.2, 3.8 Hz, H-23), 5.00 (1H, d, *J*=7.7 Hz, Glc H-1), 5.05 (1H, d, *J*=4.4 Hz, H-21), 5.51 (1H, br s, Rha H-1), 5.86 (1H, d, *J*=9.2 Hz, H-24), 6.71 (1H, br s, Rha H-1).

Thalictoside VI (3) A white powder, $[\alpha]_D^{25}$ +0.41° (*c*=0.51, MeOH). Neg. FAB-MS *m/z*: 1073 $[M-H]^-$. HR FAB-MS *m/z*: 1097.5508 $[M+Na]^+$ (Calcd for $C_{53}H_{86}NaO_{22}$ 1097.5518). ^{1}H-NMR (pyridine-d_5) δ: 0.88, 0.89, 0.96, 1.13, 1.15, 1.20 (each 3H, s, Me×6), 1.54 (3H, d, *J*=6.2 Hz, Rha Me-6), 3.19 (1H, br d, *J*=10.3 Hz, H-3), 5.02 (1H, d, *J*=7.0 Hz, Xyl H-1), 5.42 (1H, br s, H-12), 5.51 (1H, d, *J*=8.1 Hz, Glc H-1), 6.30 (1H, br s, Rha H-1), 6.34 (1H, d, *J*=7.7 Hz, Glc H-1).

Thalictoside VII (4) A white powder, $[\alpha]_D^{25}$ −18.6° (*c*=0.58, MeOH).

NII-Electronic Library Service

Neg. FAB-MS *m/z*: 1203 $[M-H]^-$. HR FAB-MS *m/z*: 1227.6139 $[M+Na]^+$ (Calcd for $C_{59}H_{96}NaO_{25}$ 1227.6129). ^{1}H-NMR (pyridine-d_5) δ: 0.88, 0.90, 0.93, 1.11, 1.15, 1.27, 1.32 (each 3H, s, Me×7), 1.51 (3H, d, J=5.9 Hz, Rha Me-6), 1.64 (3H, d, J=6.2 Hz, Rha Me-6), 5.00 (1H, d, J=6.2 Hz, Xyl H-1), 5.43 (1H, br s, H-12), 5.45 (1H, d, J=8.0 Hz, Glc H-1), 6.23 (1H, br s, Rha H-1), 6.23 (1H, br s, Rha H-1), 6.35 (1H, d, J=8.0 Hz, Glc H-1).

Thalictoside VIII (5) A white powder, $[\alpha]_D^{25}$ −11.6° (c=0.50, MeOH). Neg. FAB-MS *m/z*: 1219 $[M-H]^-$. HR FAB-MS *m/z*: 1243.6089 $[M+Na]^+$ (Calcd for $C_{59}H_{96}NaO_{26}$ 1243.6079). ^{1}H-NMR (pyridine-d_5) δ: 0.88, 0.89, 0.97, 1.13, 1.13, 1.20 (each 3H, s, Me×6), 1.51 (3H, d, J=6.2 Hz, Rha Me-6), 1.63 (3H, d, J=6.2 Hz, Rha Me-6), 3.18 (1H, br d, J=13.9 Hz, H-3), 5.01 (1H, d, J=7.0 Hz, Xyl H-1), 5.46 (1H, br s, H-12), 5.43 (1H, d, J=6.6 Hz, Glc H-1), 6.21 (1H, br s, Rha H-1), 6.26 (1H, br s, Rha H-1), 6.34 (1H, d, J=8.0 Hz, Glc H-1).

Selective Cleavage of Ester–Glycoside Linkage of 3 After a mixture of thalictoside VI (**3**, 20 mg) in 2,6-lutidine (1 ml) containing anhydrous MeOH (1 ml) and LiI (200 mg) was heated at 180 °C for 3 h, the reaction mixture was diluted with 50% MeOH (10 ml) and passed through an Amberlite MB-3 column. The eluate was concentrated *in vacuo* and the resulting product was chromatographed on Diaion HP-20 using 50% MeOH and MeOH as eluents. The 50% MeOH eluate contained an anomeric mixture of methyl glucopyranose on TLC. The MeOH eluate was subjected to silica gel column chromatography with $CHCl_3$–MeOH–H_2O (9:2:0.1, v/v) to furnish the prosapogenin (**9**, 11.0 mg), a white powder, $[\alpha]_D^{25}$ +4.2° (c=0.45, MeOH). Neg. FAB-MS *m/z*: 911 $[M-H]^-$, 749 $[M-H-\text{hexose}]^-$, 603 $[M-H-\text{hexose}-\text{deoxyhexose}]^-$ and 471 $[M-H-\text{hexose}-\text{deoxyhexose}-\text{pentose}, \text{hederagenin}-H]^-$. ^{1}H-NMR (pyridine-$d_5$) δ: 0.92, 0.92, 0.99, 0.99, 1.12, 1.23 (each 3H, s, Me×6), 1.55 (3H, d, J=6.2 Hz, Rha Me-6), 3.29 (1H, br d, J=9.9 Hz, H-3), 5.02 (1H, d, J=7.0 Hz, Xyl H-1), 5.45 (1H, br s, H-12), 5.50 (1H, d, J=6.7 Hz, Glc H-1), 6.26 (1H, br s, Rha H-1). A solution of **9** (5 mg) in 2 N HCl–MeOH (2 ml) was heated at 100 °C for 1.5 h, and then neutralized with 3% KOH–MeOH to detect hederagenin, glucose, xylose and rhamnose on TLC.

Alkaline Hydrolysis of 4 After a solution of thalictoside VII (**4**, 20 mg) in 2 N NaOH–H_2O (10 ml) was heated at 100 °C for 1.5 h, the reaction mixture was subjected to Diaion HP-20 using H_2O and MeOH as eluents. The H_2O eluate contained a 1,6-anhydroglucopyranose, while the MeOH eluate was subjected to silica gel column chromatography with $CHCl_3$–MeOH–H_2O (9:2:0.1, v/v) to provide the prosapogenin (**11**, 11.0 mg), a white powder, $[\alpha]_D^{25}$ −7.4° (c=0.34, MeOH). Neg. FAB-MS *m/z*: 1041 $[M-H]^-$, 895 $[M-H-\text{deoxyhexose}]^-$, 733 $[M-H-\text{deoxyhexose}-\text{hexose}]^-$, 587 $[M-H-\text{deoxyhexose}-\text{hexose}-\text{deoxyhexose}]^-$ and 455 $[M-H-\text{deoxyhexose}-\text{hexose}-\text{deoxyhexose}-\text{pentose}, \text{oleanolic acid}-H]^-$. ^{1}H-NMR (pyridine-$d_5$) δ: 0.85, 0.97, 0.99, 1.02, 1.13, 1.32, 1.32 (each 3H, s, Me×7), 1.53 (3H, d, J=6.2 Hz, Rha Me-6), 1.66 (3H, d, J=6.2 Hz, Rha Me-6), 5.00 (1H, d, J=6.6 Hz, Xyl H-1), 5.42 (1H, d, J=6.7 Hz, Glc H-1), 5.47 (1H, br s, H-12), 6.15 (1H, br s, Rha H-1), 6.20 (1H, br s, Rha H-1). A solution of **11** (5 mg) in 2 N HCl–MeOH (2 ml) was heated at 100 °C for 1.5 h, and then neutralized with 3% KOH–MeOH to detect oleanolic acid, glucose, xylose and rhamnose on TLC.

Acknowledgment We are grateful to Prof. H. Okabe and Mr. H. Hanazono of Fukuoka University for their measurement of HR FAB-MS.

References

1) The preceding paper: H. Yoshimitsu, K. Hayashi, M. Kumabe, T. Nohara, *Chem. Pharm. Bull.*, **41**, 786 (1993).
2) *a*) R. Kasai, M. Suzuo, J. Asakawa, O. Tanaka, *Tetrahedron Lett.*, **1977**, 175; *b*) K. Tori, S. Seo, Y. Yoshimura, H. Arita, Y. Tomita, *ibid.*, **1977**, 179.
3) H. Kizu, S. Kitayama, F. Nakatani, T. Tomimori, T. Namba, *Chem. Pharm. Bull.*, **33**, 3324 (1985).
4) K. Ohtani, K. Mizutani, R. Kasai, O. Tanaka, *Tetrahedron Lett.*, **25**, 4537 (1984).

NII-Electronic Library Service