Two New 15-Deoxycimigenol-Type and Three New 24-*epi*-Cimigenol-Type Glycosides from Cimicifuga Rhizome

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Two new 15-deoxycimigenol-type (1, 2) and three new 24-*epi*-cimigenol-type glycosides (3—5) were isolated from Cimicifuga Rhizome, and the structures were elucidated on the basis of spectroscopic data including 2D NMR spectra and chemical evidence. The two new 15-deoxycimigenol-type glycosides were the first cimigenol-type glycosides lacking a hydroxyl group at C-15.

Key words Cimicifuga Rhizome; cycloartane glycoside; *Cimicifuga* sp.; Ranunculaceae

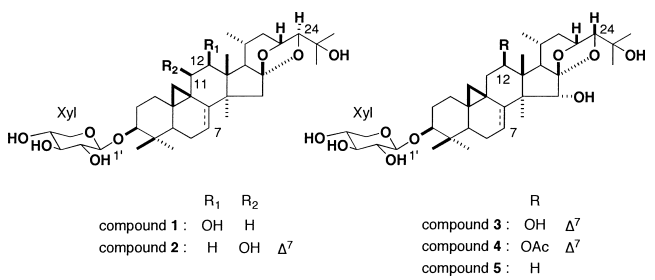
In our search for cycloartane glycosides with unique structures, cycloartane glycosides such as two tetranor-type[1)] and two 15,16-*seco*-type[2)] glycosides have been isolated from Cimicifuga Rhizome. Further investigation of the extracts of Cimicifuga Rhizome resulted in the isolation of two new 15-deoxycimigenol-type (**1**, **2**) and three new 24-*epi*-cimigenol-type glycosides (**3**—**5**). The two new 15-deoxycimigenols were the first cimigenol-type glycosides lacking a hydroxyl group at C-15. In this paper we describe the isolation and structural elucidation of **1**—**5**.

Results and Discussion

A commercial Cimicifuga Rhizome was extracted with MeOH, and the MeOH extract was partitioned between chloroform-soluble, water-soluble, and insoluble portions. The water-soluble portion was separated by MCI gel CHP20P, octadecyl silica gel (ODS) and silica gel column chromatographies, and finally HPLC to give five new cycloartane glycosides (**1**—**5**).

The molecular formula of compound (**1**) was determined as $C_{35}H_{56}O_9$ by high-resolution (HR)-FAB-MS showing a $[C_{35}H_{56}O_9Na]^+$ ion at *m/z* 643.3813. The ^{1}H-NMR spectrum revealed signals due to one cyclopropane methylene at δ 0.31 (d, J=3.7 Hz) and 0.63 (d, J=3.7 Hz), six quaternary methyls at δ 1.05, 1.24, 1.36, 1.41, 1.47 and 1.54, a secondary methyl at δ 1.39 (d, J=6.8 Hz), an anomeric proton at δ 4.88 (d, J=7.8 Hz), and four oxygen-bearing methines at δ 3.51 (dd, J=3.9, 11.2 Hz), 3.78 (br s), 4.22 (br d, J=9.0 Hz) and 4.80 (br d, J=8.8 Hz). In the ^{1}H-NMR spectrum, characteristic signals of four oxygen-bearing methines and an anomeric proton indicated that **1** was a cycloartane glycoside related to 12β-hydroxycimigenol 3-*O*-β-xyloside.[3)] The chemical shifts of the aglycon moiety, except for signals owing to the D-ring, and the sugar moiety in the ^{13}C-NMR spectrum of **1** showed coincidence with those of 12β-hydroxycimigenol 3-*O*-β-xyloside. In addition, the ^{1}H–^{1}H correlation spectroscopy (COSY) and heteronuclear multiple bond connection (HMBC) led us to the plane structure of **1** as a 12-hydroxy-15-deoxycimigenol 3-*O*-xyloside (Fig. 1). The stereochemistry at C-12 was determined on the basis of the proton coupling constants and nuclear Overhauser effect (NOE) experiments. An NOE was observed between H-12 and H_3-28 in the NOE difference spectrum (NOEDS). Furthermore, the coupling constant values of the signal due to H-12 [δ 4.22 (br d, J=9.0 Hz)] and H-11 [δ 2.67 (dd, J=8.6, 15.4 Hz)] were superimposable on those of 12β-hydroxycimigenol 3-*O*-β-xyloside. Hydrolysis of **1** afforded D-xylose, the structure of which was confirmed by the ^{1}H-NMR coupling pattern and optical rotation using chiral detection in the HPLC analysis, together with several unidentified artificial sapogenols. The structural assignment was achieved by ^{1}H–^{1}H COSY, ^{1}H-detected heteronuclear multiple quantum coherence (HMQC) and HMBC experiments. The anomeric center of the xylose moiety was determined to be β-configuration from the large $^3J_{H1-H2}$ value. The $^4C_1$-conformation of xylose was shown by comparison of the carbon resonances for monosaccharide. From the above evidence, the structure of **1** was concluded to be (23*R*,24*S*)-16β,23;16α,24-diepoxycycloartane-3β,12β,25-triol 3-*O*-β-D-xylopyranoside.

The HR-FAB-MS of compound (**2**) showed a peak at *m/z* 641.3660 corresponding to the molecular formula $[C_{35}H_{54}O_9+Na]^+$ (Calcd for 641.3666). The ^{1}H-NMR data showed a remarkable difference between **2** and **1**, except for characteristic signals due to three oxygen-bearing methyl-



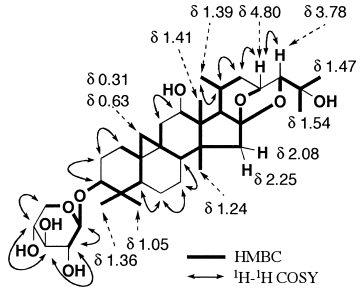


Fig. 1. ^{1}H–^{1}H COSY and HMBC Correlations of **1**

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enes [δ 3.61 (dd, J=3.7, 11.5 Hz), 3.71 (br s) and 4.78 (br d, J=8.8 Hz)] and an anomeric proton [δ 4.90 (d, J=7.8 Hz)]. In the ^{13}C-NMR spectrum of **2**, signals due to the side chain in the aglycon moiety and the sugar moiety were also in good agreement with those of **1**, although the signals due to the tetracarbocyclic ring in the aglycon moiety were not identical. Meanwhile, signals due to one cyclopropane methylene [δ 1.01 (d, J=3.4 Hz) and 2.00 (d, J=3.4 Hz)] at lower field and an olefinic proton [δ 5.23 (br d, J=6.8 Hz)] indicated a partial structure of 11β-hydroxy-cycloart-7-en in the aglycon moiety.[4] In the ^{13}C-NMR spectrum, chemical shifts of the aglycon moiety, except for signals owing to the side chain and the D-ring, and the sugar moiety showed coincidence with those of foetidinol 3-*O*-β-xyloside.[4] The long-range correlations between H_3-18 (δ 1.27) and C-12 (δ 48.4, CH_2), C-13 (δ 45.6, C), C-14 (δ 48.2, C) and C-17 (δ 61.1, CH); H_3-28 (δ 1.43) and C-8 (δ 148.8, C), C-13 (δ 45.6, C), C-14 (δ 48.2, C) and C-15 (δ 45.4, CH_2), and the sequence of correlation in H-11 (δ 4.57) and H-12 (δ 2.01, 2.74) resulted in the methylene at C-15 and the oxygen-bearing methine at C-11. In the NOEDS, an NOE was observed between H-11 and H_3-28, indicating that the hydroxyl group at C-11 has a β configuration. Furthermore, the coupling constant values of the signal due to H-11 [δ 4.57 (dd, J=3.5, 9.0 Hz)] between the H-11 and the H-12 also suggested a β configuration.[4] Hydrolysis of **2** afforded D-xylose together with several unidentified artificial sapogenols. Therefore, the structure of **2** was formulated as (23*R*,24*S*)-16β,23;16α,24-diepoxy-cycloart-7-en-3β,11β,25-triol 3-*O*-β-D-xylopyranoside.

Compound (**3**) showed a clustered molecular ion at *m*/*z* 657.3614 $[C_{35}H_{54}O_{10}Na]^+$ in the HR-FAB-MS. The ^{1}H-NMR spectrum of **3** and 24-*epi*-7,8-didehydrocimigenol 3-*O*-β-xyloside[5] were almost identical, except for the appearance of an oxygen-bearing methine [δ 4.25 (dd, J=2.4, 8.9 Hz)]. The chemical shifts of the aglycon moiety, except for signals owing to the C-ring, and the sugar moiety in the ^{13}C-NMR spectrum of **2** showed coincidence with those of 24-*epi*-7,8-didehydrocimigenol 3-*O*-β-xyloside. Meanwhile, the molecular formula $C_{35}H_{54}O_{10}$ was higher by O_1 than that of 24-*epi*-7,8-didehydrocimigenol 3-*O*-β-xyloside. This evidence indicated that **3** has an additional hydroxyl group in the C-ring. Meanwhile, HMBC correlations of H_3-18 (δ 1.51) to C-12 (δ 72.4, CH), C-13 (δ 47.0, C), C-14 (δ 51.5, C) and C-17 (δ 61.1, CH) determined the presence of an additional hydroxyl group at C-12. In the NOEDS, irradiation at H_3-18 and H_3-28 enhanced the signal intensity of H-15 [δ 4.71 (s)] and H-12 [δ 4.25 (dd, J=2.4, 8.9 Hz)], respectively. Two hydroxyl groups at C-12 and C-15 were concluded to be β and α configurations, respectively. Hydrolysis of **3** afforded D-xylose together with several unidentified artificial sapogenols. Thus, the structure of **3** was elucidated as (23*R*,24*R*)-16β,23;16α,24-diepoxy-cycloart-7-en-3β,12β,15α,25-tetraol 3-*O*-β-D-xylopyranoside.

The molecular formula of compound (**4**) was higher by C_2H_2O than that of **3**. A comparative study of the ^{1}H-NMR spectrum of **4** with that of **3** showed them to be identical except for the appearance of the acetyl methyl [δ 2.16 (s)] and an oxygen-bearing methine [δ 5.25 (br d, J=8.2 Hz)] at lower field. In the ^{13}C-NMR spectrum, signals due to the aglycon moiety, except for signals of the C-ring, and the sugar moiety were in good agreement with those of **3**. The above data indicated the presence of an additional acetoxyl group, linked to the C-ring, in **4**. The long-range correlations between H-12 (δ 5.25) and the acetyl carbon (δ 170.5, C); H_3-18 (δ 1.40) and C-12 (δ 76.8, CH), C-13 (δ 47.0, C), C-14 (δ 51.4, C) and C-17 (δ 60.7, CH); the acetyl methyl (δ 2.16) and the acetyl carbon (δ 170.5) determined the presence of an acetoxyl group at C-12. In the NOEDS, irradiation at H_3-18 and H_3-28 enhanced the signal intensity of H-15 [δ 4.64 (s)] and H-12 (δ 5.25), respectively. Hydrolysis of **4** afforded D-xylose together with several unidentified artificial sapogenols. Consequently, **4** was characterized as (23*R*,24*R*)-16β,23;16α,24-diepoxy-12β-acetoxy-cycloart-7-en-3β,15α,25-triol 3-*O*-β-D-xylopyranoside.

Compound (**5**) showed a molecular formula of $C_{35}H_{56}O_9$ based on the HR-FAB-MS. The ^{1}H-NMR spectrum revealed one cyclopropane methylene at δ 0.30 (d, J=4.3 Hz) and 0.55 (d, J=4.3 Hz), six quaternary methyls at δ 1.08, 1.08, 1.19, 1.27, 1.34 and 1.44, a secondary methyl at δ 0.96 (J=6.1 Hz), an anomeric proton at δ 4.87 (d, J=7.9 Hz), and four oxygen-bearing methine protons at δ 3.52 (dd, J=4.3, 11.6 Hz), 3.69 (br d, J=4.3 Hz), 4.25 (s) and 4.60 (ddd, J=2.0, 4.3, 9.2 Hz). The ^{1}H-NMR data showed the similarity between **5** and 24-*epi*-7,8-didehydrocimigenol 3-*O*-β-xyloside[5] except for the disappearance of an olefinic proton. Meanwhile, the plane structure of **5** was determined as illustrated in Fig. 2. In the ^{13}C-NMR spectrum, signals due to the side chain of the aglycon moiety and sugar moiety were in good agreement with those of 24-*epi*-7,8-didehydrocimigenol 3-*O*-β-xyloside. Furthermore, carbon signals of the aglycon moiety other than the side chain and sugar moiety showed coincidence with those of 25-anhydrocimigenol 3-*O*-β-xyloside.[4] In the nuclear Overhauser and exchange spectroscopy (NOESY) spectrum, the NOE correlations of **5** except for the correlations between H-8 and each proton at C-18 and C-19, showed coincidence with those of 24-*epi*-7,8-didehydrocimigenol[5] (Fig. 3). Hydrolysis of **5** afforded D-xylose together with several unidentified artificial sapogenols. Thus, **5** was determined to be (23*R*,24*R*)-

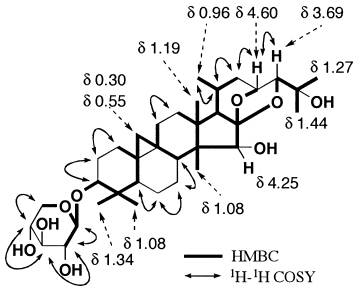

Fig. 2. ^{1}H–^{1}H COSY and HMBC Correlations of **5**

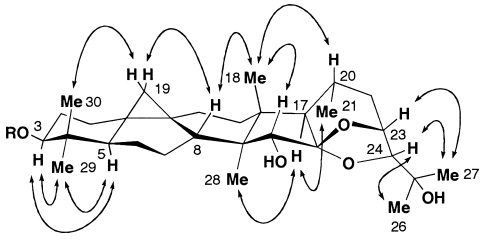

Fig. 3. NOESY Correlations of **5**

Table 1. ^{13}C-NMR Data for **1**—**5** (in Pyridine-d_5, 125 MHz, δ ppm)

	1	2	3	4	5
C-1	32.3	27.5	30.6	30.1	32.5
2	30.2	29.5	29.7	29.6	30.2
3	88.4	88.4	88.3	88.0	88.6
4	41.5	40.8	40.5	40.5	41.4
5	47.4	43.9	42.8	42.5	47.7
6	20.9	22.1	21.9	21.8	21.2
7	26.2	114.2	114.4	114.9	26.4
8	45.8	148.8	147.5	146.1	48.7
9	20.8	27.7	22.0	21.4	20.1
10	27.0	29.2	28.1	28.4	26.7
11	41.0	63.4	40.3	37.2	26.6
12	72.4	48.4	72.4	76.8	34.0
13	45.9	45.6	47.0	47.0	41.8
14	52.3	48.2	51.5	51.4	47.5
15	47.0	45.4	78.6	77.9	80.8
16	115.0	114.6	112.6	112.3	112.3
17	61.5	61.1	61.1	60.7	60.8
18	12.0	19.8	13.2	13.9	19.6
19	30.0	18.8	28.7	28.7	30.2
20	24.0	23.9	23.4	23.3	23.5
21	22.0	20.8	20.8	19.8	19.6
22	38.8	38.1	30.3	30.3	29.7
23	72.0	71.9	73.7	73.5	73.7
24	90.3	90.6	84.1	84.1	84.1
25	71.2	71.0	68.7	68.6	68.6
26	28.1	27.9	30.8	30.9	30.8
27	25.1	24.7	26.1	26.1	26.0
28	19.7	27.6	18.4	18.4	11.7
29	26.0	25.9	25.9	25.3	25.8
30	15.6	14.6	14.4	14.4	15.5
OAc				170.5	
OAc				21.8	
	xyl	xyl	xyl	xyl	xyl
C-1′	107.6	107.5	107.5	107.5	107.6
2′	75.7	75.5	75.6	75.7	75.6
3′	78.7	78.6	78.6	78.7	78.6
4′	71.4	71.2	71.3	71.3	71.3
5′	67.3	67.1	67.2	67.2	67.1

16β,23;16α,24-diepoxy-cycloartane-3β,15α,25-triol 3-*O*-β-D-xylopyranoside.

A previous phytochemical investigation resulted in the isolation of two 24-*epi*-cimigenol-type sapogenols (24-*epi*-7,8-didehydrocimigenol[5] and 24-*epi*-acerinol[5]) from the plant kingdom. Compounds **3**—**5** are very rare cycloartane glycosides possessing a 24-*epi*-cimigenol-type sapogenol.

Experimental

General Procedure Optical rotations were taken with a JASCO DIP-1000 automatic digital polarimeter. The NMR spectra were measured with a JEOL alpha 500 NMR spectrometer. The NMR samples of compounds **1**—**5** were prepared by pyridine-d_5. 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. HPLC was carried out using a TSK gel-120A (7.8 mm i.d.×30 cm) column with a Tosoh CCPM pump, Tosoh RI-8010 detector and JASCO OR-2090 detector. TLC was performed on pre-coated Kieselgel 60 F_{254} plates (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.).

Plant Material Cimicifuga Rhizome was purchased from Uchida Wakanyaku Co., Ltd. This dried rhizome originated from Heilungkiang Province in China.

Extraction and Isolation Cimicifuga Rhizome (20 kg) was extracted with MeOH at room temperature for six months. The MeOH extract (2 kg) was partitioned between chloroform-soluble (1046 g), water-soluble (941 g) and insoluble (12 g) portions. The water-soluble portion was subjected to MCI gel CHP20P column chromatography (MeOH/H_2O, 1 : 1→9 : 1) to afford eight fractions (fr. 1—fr. 8). Fraction 5 was further separated by ODS column chromatography (MeOH/H_2O, 1 : 1→9 : 1) to afford five fractions (fr. 9—fr. 13). Fraction 9 was subjected to silica gel column chromatography ($CHCl_3$/MeOH/H_2O, 8 : 2 : 0.2), followed by HPLC (MeOH/H_2O, 13 : 7), to furnish compound **3** (29 mg). Fraction 12 was subjected to silica gel column chromatography ($CHCl_3$/MeOH/H_2O, 8 : 2 : 0.2), followed by HPLC (MeOH/H_2O, 7 : 3), to furnish compound **1** (5 mg) and **2** (4 mg). Fraction 13 was subjected to silica gel column chromatography ($CHCl_3$/MeOH/H_2O, 8 : 2 : 0.2), followed by HPLC (MeOH/H_2O, 3 : 1), to furnish compound **4** (9 mg). Fraction 7 was further separated by ODS column chromatography (MeOH/H_2O, 1 : 1→9 : 1) to afford seven fractions (fr. 14—fr. 20). Fraction 19 was subjected to silica gel column chromatography ($CHCl_3$/MeOH/H_2O, 9 : 1 : 0.1), followed by HPLC (MeOH/H_2O, 4 : 1), to furnish compound **5** (23 mg).

Compound **1**: A white powder, $[\alpha]_D^{25}$ −20.4° (c=0.40, pyridine). FAB-MS (m/z): 643 (M+Na^+). HR-FAB-MS (m/z): 643.3813 (M+Na; Calcd for $C_{35}H_{56}O_9Na$: 643.3822). ^{1}H-NMR (pyridine-d_5) δ: 4.88 (1H, d, J=7.8 Hz, xyl H-1), 4.80 (1H, br d, J=8.8 Hz, H-23), 4.37 (1H, dd, J=4.6, 11.0 Hz, xyl H-5), 4.25 (1H, m, xyl H-4), 4.22 (1H, br d, J=9.0 Hz, H-12), 4.17 (1H, t, J=8.7 Hz, xyl H-3), 4.04 (1H, dd, J=7.8, 8.7 Hz, xyl H-2), 3.78 (1H, br s, H-24), 3.75 (1H, dd, J=10.2, 11.0 Hz, xyl H-5), 3.51 (1H, dd, J=3.9, 11.2 Hz, H-3), 2.67 (1H, dd, J=8.6, 15.4 Hz, H-11), 2.40 (1H, m, H-22), 2.34 (1H, m, H-2), 2.25 (1H, d, J=13.7 Hz, H-15), 2.08 (1H, d, J=13.7 Hz, H-15), 1.97 (1H, d, J=9.8 Hz, H-17), 1.92 (1H, m, H-2), 1.88 (1H, m, H-20), 1.66 (1H, m, H-7), 1.60 (1H, m, H-1), 1.56 (overlapping, H-6), 1.54 (3H, s, H_3-26), 1.54 (overlapping, H-11), 1.47 (3H, s, H_3-27), 1.41 (3H, s, H_3-18), 1.39 (3H, d, J=6.8 Hz, H_3-21), 1.37 (overlapping, H-8), 1.36 (3H, s, H_3-29), 1.33 (overlapping, H-5), 1.28 (1H, m, H-1), 1.24 (3H, s, H_3-28), 1.14 (1H, m, H-22), 1.11 (1H, m, H-7), 1.05 (3H, s, H_3-30), 0.79 (1H, m, H-6), 0.31, 0.63 (each 1H, d, J=3.7 Hz, H_2-19). ^{13}C-NMR: Table 1.

Compound **2**: A white powder, $[\alpha]_D^{25}$ −8.1° (c=0.27, pyridine). FAB-MS (m/z): 641 (M+Na^+). HR-FAB-MS (m/z): 641.3660 (M+Na; Calcd for $C_{35}H_{56}O_9Na$: 641.3666). ^{1}H-NMR (pyridine-d_5) δ: 5.23 (1H, br d, J=6.8 Hz, H-7), 4.90 (1H, d, J=7.8 Hz, xyl H-1), 4.78 (1H, br d, J=8.8 Hz, H-23), 4.57 (1H, dd, J=3.5, 9.0 Hz, H-11), 4.35 (1H, dd, J=4.9, 11.2 Hz, xyl H-5), 4.23 (1H, m, xyl H-4), 4.17 (1H, t, J=8.7 Hz, xyl H-3), 4.05 (1H, dd, J=7.8, 8.7 Hz, xyl H-2), 3.75 (1H, dd, J=10.2, 11.2 Hz, xyl H-5), 3.71 (1H, br s, H-24), 3.61 (1H, dd, J=3.7, 11.5 Hz, H-3), 2.79 (1H, m, H-1), 2.74 (1H, m, H-12), 2.49 (1H, d, J=13.4 Hz, H-15), 2.44 (1H, m, H-2), 2.30 (1H, d, J=13.4 Hz, H-15), 2.25 (1H, m, H-22), 2.11 (1H, m, H-2), 2.01 (overlapping, H-12), 1.99 (overlapping, H-6), 1.77 (1H, m, H-6), 1.74 (1H, m, H-1), 1.67 (1H, m, H-20), 1.60 (1H, d, J=10.8 Hz, H-17), 1.52 (3H, s, H_3-26), 1.46 (3H, s, H_3-27), 1.43 (3H, s, H_3-28), 1.40 (3H, s, H_3-29), 1.38 (overlapping, H-5), 1.27 (3H, s, H_3-18), 1.16 (3H, s, H_3-30), 1.01, 2.00 (each 1H, d, J=3.4 Hz, H_2-19), 1.00 (overlapping, H-22), 0.84 (3H, d, J=5.9 Hz, H_3-21). ^{13}C-NMR: Table 1.

Compound **3**: A white powder, $[\alpha]_D^{25}$ −36.6° (c=1.42, pyridine). FAB-MS (m/z): 657 (M+Na^+). HR-FAB-MS (m/z): 657.3614 (M+Na; Calcd for $C_{35}H_{54}O_{10}Na$: 657.3615). ^{1}H-NMR (pyridine-d_5) δ: 6.18 (1H, br d, J=6.4 Hz, H-7), 4.84 (1H, d, J=7.6 Hz, xyl H-1), 4.71 (1H, s, H-15), 4.65 (1H, ddd, J=1.8, 4.2, 9.3 Hz, H-23), 4.35 (1H, dd, J=5.1, 11.2 Hz, xyl H-5), 4.25 (1H, dd, J=2.4, 8.9 Hz, H-12), 4.24 (1H, m, xyl H-4), 4.16 (1H, t, J=8.7 Hz, xyl H-3), 4.03 (1H, dd, J=7.6, 8.7 Hz, xyl H-2), 3.78 (1H, br d, J=4.2 Hz, H-24), 3.72 (1H, dd, J=10.3, 11.2 Hz, xyl H-5), 3.49 (1H, dd, J=4.2, 11.5 Hz, H-3), 2.90 (1H, dd, J=8.9, 15.3 Hz, H-11), 2.72 (1H, ddd, J=1.8, 11.2, 11.7 Hz, H-22), 2.31 (1H, m, H-2), 2.12 (1H, m, H-22), 2.06 (1H, d, J=10.2 Hz, H-17), 1.95 (overlapping, H-6), 1.94 (overlapping, H-2), 1.89 (1H, m, H-20), 1.71 (1H, m, H-1), 1.66 (1H, m, H-6), 1.53 (overlapping, H-11), 1.52 (3H, d, J=6.1 Hz, H_3-21), 1.51 (3H, s, H_3-18), 1.45 (3H, s, H_3-26), 1.36 (overlapping, H-1), 1.34 (3H, s, H_3-27), 1.33 (3H, s, H_3-29), 1.32 (overlapping, H-5), 1.31 (3H, s, H_3-28), 1.04 (3H, s, H_3-30), 0.71, 1.16 (each 1H, d, J=3.8 Hz, H_2-19). ^{13}C-NMR: Table 1.

Compound **4**: A white powder, $[\alpha]_D^{25}$ −57.5° (c=0.46, pyridine). FAB-MS (m/z): 699 (M+Na^+). HR-FAB-MS (m/z): 699.3720 (M+Na; Calcd for $C_{37}H_{56}O_{11}Na$: 699.3721). ^{1}H-NMR (pyridine-d_5) δ: 6.16 (1H, br d, J=6.8 Hz, H-7), 5.25 (1H, br d, J=8.8 Hz, H-12), 4.84 (1H, d, J=7.8 Hz, xyl H-1), 4.64 (1H, s, H-15), 4.65 (overlapping, H-23), 4.34 (1H, dd, J=5.1, 11.0 Hz, xyl H-5), 4.24 (1H, m, xyl H-4), 4.16 (1H, t, J=8.7 Hz, xyl H-3), 4.04 (1H, dd, J=7.8, 8.7 Hz, xyl H-2), 3.74 (1H, br d, J=4.4 Hz, H-24), 3.72 (1H, dd, J=10.2, 11.0 Hz, xyl H-5), 3.46 (1H, dd, J=3.9, 11.2 Hz, H-3), 2.96 (1H, dd, J=9.0, 15.8 Hz, H-11), 2.74 (1H, dd, J=11.7, 12.7 Hz, H-22), 2.28 (1H, m, H-2), 2.16 (3H, s, O-Ac), 2.04 (1H, m, H-22), 1.97 (1H, d,

J=10.7 Hz, H-17), 1.90 (overlapping, H-6), 1.89 (overlapping, H-2), 1.74 (1H, m, H-20), 1.62 (overlapping, H-1), 1.60 (overlapping, H-6), 1.44 (3H, s, H_3-26), 1.40 (3H, s, H_3-18), 1.32 (3H, s, H_3-27), 1.28 (3H, s, H_3-29), 1.24 (overlapping, H-11), 1.22 (overlapping, H-5), 1.22 (3H, s, H_3-28), 1.17 (overlapping, H-1), 1.07 (3H, d, J=6.4 Hz, H_3-21), 1.04 (3H, s, H_3-30), 0.57, 1.12 (each 1H, d, J=3.7 Hz, H_2-19). ^{13}C-NMR: Table 1.

Compound **5**: A white powder, $[\alpha]_D^{25}$ +35.9° (c=1.13, pyridine). FAB-MS (m/z): 643 (M+Na^+). HR-FAB-MS (m/z): 643.3821 (M+Na; Calcd for $C_{35}H_{56}O_8Na$: 643.3822). ^{1}H-NMR (pyridine-d_5) δ: 4.87 (1H, d, J=7.9 Hz, xyl H-1), 4.60 (1H, ddd, J=2.0, 4.3, 9.2 Hz, H-23), 4.36 (1H, dd, J=5.2, 11.3 Hz, xyl H-5), 4.25 (1H, s, H-15), 4.24 (1H, m, xyl H-4), 4.16 (1H, t, J=8.6 Hz, xyl H-3), 4.04 (1H, dd, J=7.9, 8.6 Hz, xyl H-2), 3.73 (1H, dd, J=10.3, 11.3 Hz, xyl H-5), 3.69 (1H, br d, J=4.3 Hz, H-24), 3.52 (1H, dd, J=4.3, 11.6 Hz, H-3), 2.67 (1H, ddd, J=2.0, 10.8, 11.9 Hz, H-22), 2.37 (1H, m, H-2), 2.10 (1H, m, H-7), 2.04 (1H, m, H-11), 1.97 (overlapping, H-22), 1.96 (overlapping, H-2), 1.77 (1H, d, J=11.0 Hz, H-17), 1.73 (overlapping, H-20), 1.72 (overlapping, H-8), 1.62 (1H, m, H-12), 1.59 (overlapping, H-1), 1.58 (overlapping, H-6), 1.55 (1H, m, H-12), 1.44 (3H, s, H_3-26), 1.36 (1H, m, H-5), 1.34 (3H, s, H_3-29), 1.27 (3H, s, H_3-27), 1.23 (1H, m, H-1), 1.19 (3H, s, H_3-18), 1.19 (overlapping, H-7), 1.08 (6H, s, H_3-28, H_3-30), 1.06 (overlapping, H-11), 0.96 (3H, d, J=6.1 Hz, H_3-21), 0.78 (1H, m, H-6), 0.30, 0.55 (each 1H, d, J=4.3 Hz, H_2-19). ^{13}C-NMR: Table 1.

Sugar Analysis A solution of each compound (**1**, **2**, **3**, **4** or **5**) (1 mg) in 2 N 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. The sugar fraction was concentrated to dryness *in vacuo* to give a residue, which was dissolved in CH_3CN/H_2O (3 : 1, 250 ml). The sugar fraction was analyzed by HPLC under the following conditions: column, Shodex RS-Pac DC-613 (6.0 mm i.d.×150 mm, Showa Denko, Tokyo, Japan); solvent, CH_3CN/H_2O (3 : 1); flow rate, 1.0 ml/min; column temperature, 70 °C; detection, refractive index (RI) and optical rotation (OR). The t_R (min) of the sugars were as follows. **1**: D-xylose 5.5 (+), **2**: D-xylose 5.5 (+), **3**: D-xylose 5.5 (+), **4**: D-xylose 5.5 (+), **5**: D-xylose 5.5 (+). [reference: D-xylose 5.5 (positive optical rotation: +)].

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