Studies on the Constituents of *Cimicifuga* Species. XXVIII.[1] Four New Cycloart-7-enol Glycosides from the Underground Parts of *Cimicifuga simplex* WORMSK

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Received October 27, 2000; accepted December 18, 2000

Four new cycloart-7-ene triterpenol arabinosides, bugbanosides C–F, were isolated from the underground parts of *Cimicifuga simplex* WORMSK. (Ranunculaceae). The structures were elucidated as 12β-acetoxy-3β,15α,-24*R*,25-tetrahydroxy-16,23-dione-cycloart-7-ene 3-*O*-α-L-arabinopyranoside, 12β-acetoxy-24*R*,25-epoxy-3β,15α-dihydroxy-16,23-dione-cycloart-7-ene 3-*O*-α-L-arabinopyranoside, 12β-acetoxy-24*R*,25-epoxy-3β-hydroxy-16,23-dione-cycloart-7-ene 3-*O*-α-L-arabinopyranoside, and 16,23*R*:16,24*S*-diepoxy-3β,12β,15α,25-tetrahydroxy-cycloart-7-ene 3-*O*-α-L-arabinopyranoside on the basis of spectral and chemical evidence. The circular dichroism (CD) of bugbanosides C—F showed strong negative maxima at 214—217 nm due to a cycloart-7-ene system, as well as other cycloart-7-ene triterpenes. The CD data showed to be useful in determining basic skeletons, including absolute stereostructures of cycloart-7-ene triterpenes.

Key words *Cimicifuga simplex*; Ranunculaceae; cycloart-7-ene; arabinoside; circular dichroism

Many kinds of cycloartane triterpene glycosides from *Cimicifuga* (*C.*) species (Ranunculaceae) were reported by us[1] and by other groups.[2,3] In our continuing work, we have now isolated four new cycloart-7-ene triterpene arabinosides, named bugbanosides C—F (**1**—**4**), in low yields from the underground parts of *C. simple.* Their circular dichroism (CD) showed strong negative maxima at 214—217 nm (Fig 1). These CD maxima were also found to be characteristic to cycloart-7-ene triterpenic glycosides such as cimicifugoside,[4] bugbanoside A,[5] cimiaceroside A,[6] shengm-7-enol glycosides,[7] and cimig-7-enol glycoside[8] (Fig. 2), and indicated basic skeletons, including absolute stereostructures of cycloart-7-ene triterpene glycosides. Therefore, structural elucidation of new compounds was undertaken on the bases of the CD data, along with the other spectral and chemical data. This paper deals with the isolation and structural elucidation of these minor glycosides.

Compounds **1**—**4** were obtained as described in the experimental section by repeated chromatography on octadecylsilanized silicic acid (ODS) and silica-gel (SiO_2) columns, and preparative (p) HPLC of the methanol extract of the underground parts of *C. Simplex.* The ^{1}H- and ^{13}C-NMR signals were attributed by using ^{1}H–^{1}H correlated spectroscopy (^{1}H–^{1}H COSY), heteronuclear signal quantum coherence (HSQC), heteronuclear multiple bond connectivity (HMBC), and nuclear Overhauser enhancement and exchange spectroscopy (NOESY).

Compound **1** was obtained as a colorless powder, mp 157—158 °C, $[\alpha]_D$ −57.5°, and named bugbanoside C. The molecular formula was determined to be $C_{37}H_{56}O_{12}$ on the basis of positive high resolution secondary ion mass spectrometry (pos. HR-SI-MS) and the data of ^{13}C-NMR. The IR spectrum showed strong hydroxyl bands at 3200—3600 cm^{-1}, an ester carbonyl and a five membered ketone band at 1738 cm^{-1}, and a ketone band at 1717 cm^{-1}. The CD of **1** showed two negative maxima ($\Delta\varepsilon_{312}$: −3.43, $\Delta\varepsilon_{217}$: −9.25). The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) showed the presence of a 3β-hydroxypropyl group (H-1, C-1, H-2, C-2, H-3, C-3), a tetrasubstituted cyclopropane group (H-19, C-19, C-9, C-10), a secondary and six tertiary methyl groups (H-21,

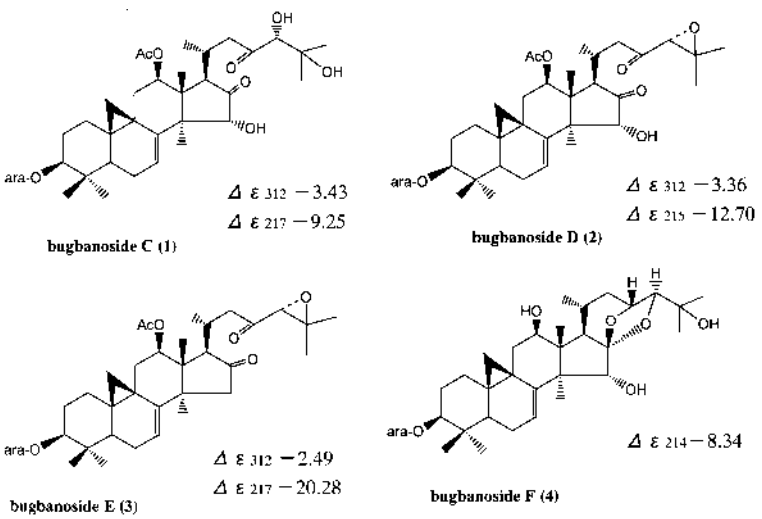

Fig. 1. Structures and CD Data of Compounds **1**—**4**

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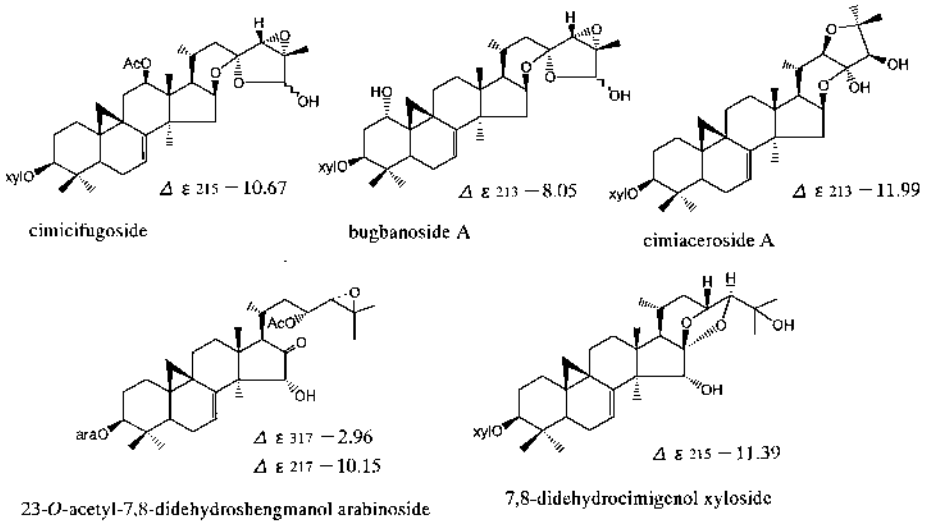

Fig. 2. CD Data of Cycloart-7-enol Glycosides from the Underground Parts of *Cimicifuga Simplex*

Table 1. ^{1}H-NMR Data of Compounds **1**—**4**

	1	**2**	**3**	**4**
1	1.24, 1.64	1.22, 1.62	1.20, 1.62	1.32, 1.63
2	1.90, 2.31	1.92, 2.32	1.90, 2.30	1.85, 2.25
3	3.46 dd (4.1, 11.7)	3.47 dd (4.1, 11.4)	3.46 dd (4.2, 11.6)	3.44 dd (4.0, 11.5)
5	1.23	1.24 bd (5.3)	1.20	1.22
6	1.60, 1.92	1.64, 1.92	1.55, 1.86	1.58, 1.85
7	6.09 dd (1.8, 7.8)	6.15 dd (1.5, 7.5)	5.10 dd (1.7, 7.5)	6.13 dd (2.0, 7.5)
11	1.30, 2.93	1.32	1.30	1.52
		2.96 dd (9.6, 15.8)	2.89 dd (9.3, 16.0)	2.91 dd (9.0, 15.5)
12	5.64 dd (1.6, 9.4)	5.63 dd (1.6, 9.4)	5.62 dd (1.5, 9.3)	4.34
15	4.67 s	4.78 s	2.35 d (17.6)	4.72 s
			2.63 d (17.6)	
17	2.66 d (2.0)	2.64 d (3.0)	2.74 d (2.5)	1.82
18	1.60 s	1.55 s	1.38 s	1.47 s
19	0.61 d (4.0)	0.63 d (4.0)	0.61 d (4.0)	0.76 d (4.0)
	1.14 d (4.0)	1.17 d (4.0)	1.09 d (4.0)	1.11 d (4.0)
20	2.92	2.85	2.83	1.82
21	1.37 d (6.8)	1.27 d (6.9)	1.24 d (7.1)	1.37 d (5.5)
22	3.11 dd (2.0, 19.0)	2.92 dd (8.7, 18.0)	2.97 dd (3.2, 18.3)	1.15, 2.40
	3.70 dd (9.5, 19.0)	3.05 dd (3.2, 18.0)	3.03 dd (8.0, 18.3)	
23	—	—	—	4.76 bd (9.0)
24	4.40 s	3.72 s	3.75 s	3.89 s
26	1.52 s	1.35 s	1.36 s	1.51 s
27	1.54 s	1.30 s	1.30 s	1.55 s
28	1.32 s	1.37 s	1.21 s	1.45 s
29	1.30 s	1.31 s	1.30 s	1.25 s
30	1.02 s	1.02 s	1.01 s	0.98 s
$COCH_3$	2.27 s	2.27 s	2.28 s	
1′	4.77 d (7.0)	4.80 d (7.4)	4.79 d (7.0)	4.78 d (7.0)
2′	4.45 dd (7.0, 8.8)	4.47 dd (7.4, 8.7)	4.46 dd (7.0, 8.7)	4.43 dd (7.0, 8.5)
3′	4.17 dd (3.5, 8.8)	4.18 dd (3.5, 8.7)	4.18 dd (3.5, 8.7)	4.17 dd (3.5, 8.5)
4′	4.32	4.33	4.33	4.34
5′	3.80 dd (2.3, 12.5)	3.81 dd (2.5, 12.5)	3.81 dd (2.5, 12.5)	3.79 dd (2.5, 12.0)
	4.31	4.32	4.30 dd (2.5, 12.5)	4.29 dd (2.5, 12.0)

Obtained on a Varian Unity-INOVA-500 in pyridine-d_5.

C-21, H-18, C-18, H-26, C-26, H-27, C-27, H-28, C-28, H-29, C-29, H-30, C-30), a methine group bearing an acetyl group (H-12, C-12, AcO), two oxymethine groups (H-15, C-15, H-24, C-24), two methine groups (H-5, C-5, H-17, C-17), a trisubstituted double bond (H-7, C-7, C-8), an isolated methylene group (H-11, C-11), an arabinopyranosyl group, two carbonyl groups (C-16, C-23), a quaternary oxycarbon (C-25), and three quarternary carbons (C-4, C-13, C-14). The connectivities of these partial structures were determined on the basis of the HMBC spectrum, and the relative stereochemistry of **1** was disclosed by the nuclear Overhauser effects (NOEs) in the NOESY spectrum. NOEs were observed between H-3 and H-29, H-12 and H-28, H-12 and H-17, H-28 and H-17, H-15 and H-18, H-18 and H-20, to es-

tablish 12β-acetoxy, 3β-hydroxy, and 15α-hydroxy groups (Fig. 3). The coupling constant (J=7.0 Hz) of H-1′, NOEs between H-1′ and H-3, H-1′ and H-3′, and HMBC correlations between H-1′ and C-3, H-3 and C-1′, showed the presence of a 3-*O*-α-arabinopyranosyl group. On acid hydrolysis, L-arabinose was detected as the sugar of **1** by TLC and HPLC with a chiral detector (Shodex OR-1). The configuration of C-24 was determined by a new modified Mosher's method.[9] The ^{1}H-NMR signals of the penta (*S*)- and (*R*)-2-methoxy-2-(trifluorometyhl)-2-phenyl acetic acid (MTPA) esters (**1*S***, **1*R***), prepared from **1**, were assigned by analyzing the ^{1}H–^{1}H COSY, HSQC spectra (500 MHz), and the $\Delta\delta$ ($=\delta_S-\delta_R$) values (Hz) were obtained respectively. The values of H-26, H-27 were +5.0 (Hz), +61.5 (Hz), respectively, to establish the (*R*) configuration at C-24 (Fig. 4). The absolute stereostructure was determined by CD: two negative maxima ($\Delta\varepsilon_{312}$: −3.43, $\Delta\varepsilon_{217}$: −9.25), clarifying the presence of a 16-keto group[10] and 7-ene on a cycloartane skeleton. Thus, compound **1** was formulated as 12β-acetoxy, 3β,15α,24*R*,25-tetrahydroxy-16,23-dione-cycloart-7-ene 3-*O*-α-L-arabinopyranoside.

Table 2. ^{13}C-NMR Data of Compounds **1**—**4**

	1	**2**	**3**	**4**
1	30.06	30.08	30.09	30.42
2	29.21	29.28	29.29	29.33
3	87.80	87.81	87.82	88.25
4	40.25	40.29	40.35	40.29
5	42.30	42.30	42.34	42.51
6	21.64	21.68	21.81	21.75
7	115.18	115.34	114.94	114.16
8	145.08	145.11	145.87	147.41
9	21.57	21.55	21.37	21.82
10	28.86	28.83	28.97	27.90
11	35.84	35.94	35.85	39.89
12	76.99	76.90	75.91	72.41
13	44.01	44.11	47.65	46.96
14	49.10	49.27	46.42	51.04
15	80.40	80.31	49.51	77.92
16	218.96	219.10	217.38	112.39
17	59.46	59.26	62.06	59.67
18	14.88	14.79	14.69	13.15
19	29.21	29.12	29.20	28.54
20	26.52	26.66	26.07	23.68
21	23.21	23.00	23.00	21.25
22	46.12	46.36	46.50	38.39
23	213.65	205.27	205.48	72.00
24	83.68	65.55	65.67	90.02
25	72.27	60.90	60.97	71.15
26	25.90	24.37	24.45	25.40
27	27.63	18.08	18.16	26.38
28	18.34	18.35	26.46	18.21
29	25.62	25.65	25.69	25.70
30	14.12	14.15	14.18	14.18
$\underline{C}OCH_3$	170.76	170.73	170.87	
$CO\underline{C}H_3$	21.32	21.31	21.11	
1′	107.21	107.25	107.24	107.06
2′	72.64	72.72	72.73	72.56
3′	74.34	74.41	74.42	74.26
4′	69.29	69.36	69.37	69.19
5′	66.66	66.71	66.72	66.46

Measured at 125.7 MHz, in pyridine-d_5.

Compound **2** was obtained as a colorless powder, mp 171—172 °C, $[\alpha]_D$ −58.1°, and named bugbanoside D. The molecular formula was determined to be $C_{37}H_{54}O_{11}$ on the basis of pos. HR-SI-MS and the data of ^{13}C-NMR. The IR spectrum and the CD of **2** were very similar to those of **1**; the IR of **2** showed hydroxyl bands at 3250—3630 cm^{-1}, an ester carbonyl and a five membered ketone band at 1738 cm^{-1}, and a ketone band at 1716 cm^{-1}, and the CD of **2** showed two negative maxima ($\Delta\varepsilon_{312}$: −3.36, $\Delta\varepsilon_{215}$: −12.70). The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) were also similar to those of **1** except for signals of a side chain (H-22, H-24, H-26, H-27, C-23, C-24, C-25, C-26, C-27), and suggested the presence of 24,25-epoxy ring: H-24 (3.72, s), C-24 (65.55), C-25

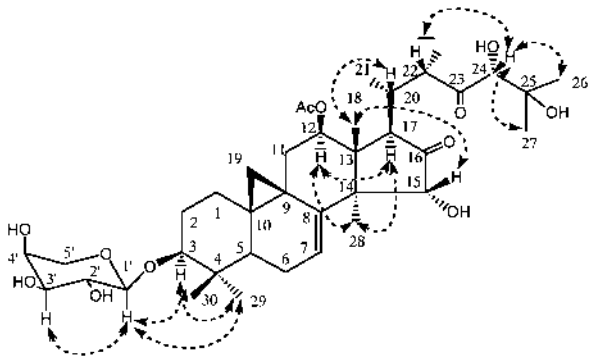

Fig. 3. NOEs of **1**

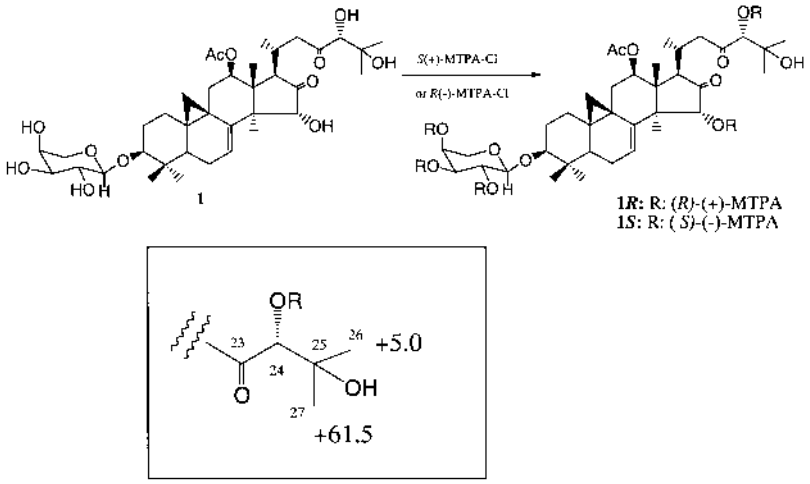

Fig. 4. Preparation of **1*R*** and **1*S***, and $\Delta\delta$ Values (Hz) of H-26, 27

(60.90). Treatment of **2** with 0.03% *p*-TsOH acid[11] gave a 24,25-dihydroxy derivative of **2**, which was identified with direct comparison with **1**. Thus, compound **2** was formulated as 12β-acetoxy-24*R*,25-epoxy-3β,15α-dihydroxy-16,23-dione-cycloart-7-ene 3-*O*-α-L-arabino pyranoside. The 16,23-dione-cycloart-7-ene derivatives, such as the desacetoxy-11β-hydroxy-xyloside-**1** and -**2**, have been reported from C. foetida[3] and Shoma[2,10], respectively.

Compound **3** was obtained as a colorless powder, mp 125—126 °C, $[\alpha]_D$ −54.2°, and named bugbanoside E. The molecular formula was determined to be $C_{37}H_{54}O_{10}$ on the basis of pos. HR-SI-MS and the data of ^{13}C-NMR. The IR spectrum and the CD of **3** were very similar to those of **1** and **2**; the IR of **3** showed hydroxyl bands at 3200—3600 cm^{-1}, an ester carbonyl and a five membered ketone band at 1735 cm^{-1}, and a ketone band at 1716 cm^{-1}, and the CD of **3** showed two negative maxima ($\Delta\varepsilon_{312}$: −2.49, $\Delta\varepsilon_{217}$: −20.28). The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) were also similar to those of **2**, except for the absence of 15-OH. Two C_{15}-H were observed as an AB-type doublet (2.35, 2.63, each d, J=17.6 Hz), and C-15 was observed as a methylene carbon (49.51). H-7 (5.10, dd, J=1.7, 7.5 Hz) and H-28 (1.21, s) were shifted by Δ1.05 and Δ0.16 ppm, respectively, from H-7 (6.15, dd, J=1.5, 7.5 Hz) and H-28 (1.37, s) of **2**. The connectivities of these partial structures were determined on the basis of the HMBC spectrum, and the relative stereochemistry of **3** was disclosed by NOEs. NOEs were observed between H-3 and H-29, H-12 and H-28, H-12 and H-17, H-28 and H-17, H-18 and H-20, to establish 12β-acetoxy and 3β-hydroxy groups. The (*R*)-configuration at C-24 was determined by comparison with the NMR data of the side chain of **2** as follows. The chemical shifts of ^{1}H- and ^{13}C-NMR were very similar to those of **2**, and NOE was observed between H-24 (3.75, s) and H-26 (1.36, s), which was similarly observed between H-24 (3.72, s) and H-26 (1.35, s) of **2**. The coupling constant (J=7.0 Hz) of H-1′, NOEs between H-1′ and H-3, H-1′ and H-3′, and HMBC correlations between H-1′ and C-3, H-3 and C-1′, showed the presence of a 3-*O*-α-arabinopyranosyl group. On acid hydrolysis, L-arabinose was detected as the sugar of **3** by TLC and HPLC with a chiral detector. The absolute stereostructure was determined by CD, showing negative maximum at 217 nm. Therefore, the structure of **3** was concluded to be 12β-acetoxy-24*R*,25-epoxy-3β-hydroxy-16,23-dione-cycloart-7-ene 3-*O*-α-L-arabinopyranoside, which appears to correspond to an arabinoside of cimicifol (xyloside, from *C. foetida*), whose 24-configuration and absolute stereochemistry have not been determined.[3]

Compound **4** was obtained as a colorless powder, mp 255—256 °C, $[\alpha]_D$ −18.5°, and named bugbanoside F. The molecular formula was determined to be $C_{35}H_{54}O_{10}$ on the basis of pos. HR-SI-MS and the data of ^{13}C-NMR. The IR spectrum of **4** showed hydroxyl bands at 3250—3600 cm^{-1}, and the CD of **4** showed a negative maximum ($\Delta\varepsilon_{214}$: −8.34). The ^{1}H- and ^{13}C-NMR spectra (Tables 1, 2) were similar to those of 12β-hydoxy cimigenol arabinoside,[12] except for signals of B ring, and suggested the presence of 7(8) double bond; H-7 (6.13, dd , J=2.0, 7.5 Hz), C-7 (114.16), C-8 (147.41). The data of the side chain of **4** suggested 16,23*R*:16,24*S*-diepoxy groups (cimigenol type): H-23 (4.76, bd, J=9.0 Hz), C-23 (72.00), H-24 (3.89, s), C-24 (90.02).[13] NOEs were observed between H-3 and H-29, H-12 and H-28, H-12 and H-17, H-28 and H-17, H-15 and H-18, H-18 and H-20, to establish 3β-hydroxy, 12β-hydroxy and 15α-hydroxy groups. The coupling constant (J=7.0 Hz) of H-1′, NOEs between H-1′ and H-3, and H-1′ and H-3′, and HMBC correlations between H-1′ and C-3, and H-3 and C-1′, showed the presence of a 3-*O*-α-arabinopyranosyl group. On acid hydrolysis, L-arabinose was detected as the sugar of **4** by TLC and HPLC with a chiral detector. The absolute stereostructure was determined by CD, having a negative maximum at 214 nm. Therefore, the structure of **4** was concluded to be 16,23*R*:16,24*S*-diepoxy-3β,12β,15α,25-tetrahydroxy-cycloart-7-ene 3-*O*-α-L-arabinopyranoside.

We isolated four new cycloart-7-ene triterpene arabinosides, named bugbanosides C—F (**1**—**4**), in low yields from the underground parts of *C. simple* and determined their structures on the bases of the CD data, along with the other spectral and chemical data. The absolute stereostructures of cycloart-7-ene triterpenic glycosides, such as cimicifugoside, bugbanoside A, cimiaceroside A, shengm-7-enol glycosides, and cimig-7-enol glycosides, have been determined without the data of CD due to a cycloart-7-ene system. At this time, they showed strong negative maxima at 213—217 nm as well as bugbanoside C—F. Therefore, the CD data showed to be useful in determining basic skeletons, including absolute stereostructures of cycloart-7-ene triterpenes.

Experimental

General The instruments used in this investigation were as follows: a Yanagimoto micromelting apparatus (for melting points, uncorrected); a JASCO DIP-1000 digital polarimeter (for specific rotation, measured at 25 °C); a Perkin–Elmer 1720X-FT IR spectrometer (for IR spectra); a Hitachi M-80 spectrometer (for MS spectra); a JASCO J-500 spectrometer and JASCO J-820 (for CD, measured at 24 °C) and a Varian Mercury-300, JEOL α-400 and a Varian Unity-INOVA-500 instrument (for NMR spectra, measured in pyridine-d_5 solution containing a few drops of D_2O, on the δ scale using tetramethylsilane as an internal standard). Column chromatography was carried out on SiO_2 (Wakogel C-200, 75—150 μm) and ODS-A (YMC, 60—400/230 mesh) columns. HPLC was carried out using a Gilson 305 pump equipped with a JASCO 830-RI detector. SiO_2 60 F_{254} (Merck) precoated TLC plates were used and detection was carried out by spraying with 40% H_2SO_4 followed by heating.

Isolation of 1—4 *Cimicifuga simplex* was collected at Miyagi prefecture in Japan. The underground parts were dried at 60 °C in the drying room for several days. The powder material (200 g) was extracted four times with MeOH (300 ml) on a boiling water bath. The extract was partitioned between EtOAc–*n*-BuOH and water (1 : 1 : 1). After evaporation of the former phase, the residue was chromatographed on an ODS column by using MeOH–H_2O (2 : 1—5 : 0) to afford fractions (fr.) 1 to 13. Frs. 1 and 2 [eluted with MeOH–H_2O (2 : 1)] were subjected to SiO_2 chromatography, and the fraction, eluted with $CHCl_3$–MeOH (19 : 1), was subjected to p-HPLC [column: Cosmosil 10 Ph, i.d. 10×250 mm; mobile phase MeCN–H_2O (36 : 64/30 : 70); flow rate: 2.0 ml/min; column temperature: 40 °C] to give **1** (13.2 mg) and **4** (4.1 mg). Similarly, fr. 3 [eluted with MeOH–H_2O (2 : 1)] was subjected to SiO_2 chromatography, and the eluate, with $CHCl_3$–MeOH (19 : 1), was subjected to p-HPLC [column: Develosil PhA-T-5, i.d. 10×250 mm; mobile phase MeOH–H_2O–MeCN (10 : 7 : 3); flow rate: 2.0 ml/min; column temperature: 40 °C] to give **2** (15.0 mg). Similarly, fr. 4 [eluted with MeOH–H_2O (3 : 1)] was subjected to SiO_2 chromatography, and the eluate, with $CHCl_3$–MeOH (19 : 1), was subjected to p-HPLC [column: Develosil PhA-T-5, i.d. 10×250 mm; mobile phase MeOH–H_2O–MeCN (10 : 10 : 3); flow rate: 2.0 ml/min; column temperature: 40 °C] to give **3** (11.6 mg).

1: A colorless powder (from MeOH+isopropyl ether), mp 157—158 °C. $[\alpha]_D$ −57.5° (c=0.98, MeOH). Pos. SI-MS m/z: 715 $[M+Na]^+$. Pos. HR-SI-MS m/z: 715.3661 $[C_{37}H_{56}O_{12}+Na]^+$, error: −0.5 m.m.u. IR (KBr) cm^{-1}: 3200—3600 (OH), 1738 (AcO, CO), 1717 (CO). CD: $\Delta\varepsilon_{312}$: −3.43 (c=1.27×10^{-4} g/ml), $\Delta\varepsilon_{217}$: −9.25 (c=0.64×10^{-4} g/ml). ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables 1 and 2.

2: A colorless powder (from MeOH+isopropyl ether), mp 171—172 °C. $[\alpha]_D$ −58.1° (c=0.33, MeOH). Pos. SI-MS m/z: 697 $[M+Na]^+$. Pos. HR-SI-MS m/z: 697.3560 $[C_{37}H_{54}O_{11}+Na]^+$, error: −0.1 m.m.u. IR (KBr) cm^{-1}: 3250—3630 (OH), 1738 (AcO, CO), 1716 (CO). CD: $\Delta\varepsilon_{312}$: −3.36 ($c=1.48\times10^{-4}$ g/ml), $\Delta\varepsilon_{215}$: −12.70 ($c=0.30\times10^{-4}$ g/ml). ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables 1 and 2.

3: A colorless powder (from MeOH+isopropyl ether), mp 125—126 °C. $[\alpha]_D$ −54.2° (c=0.52, MeOH). Pos. SI-MS m/z: 659 $[M+H]^+$, 681 $[M+Na]^+$. Pos. HR-SI-MS m/z: 659.3773 $[C_{37}H_{54}O_{10}+H]^+$, error: −1.9 m.m.u. IR (KBr) cm^{-1}: 3200—3600 (OH), 1735 (AcO, CO) 1716 (CO). CD: $\Delta\varepsilon_{312}$: −2.49 ($c=1.18\times10^{-4}$ g/ml), $\Delta\varepsilon_{217}$: −20.28 ($c=0.59\times10^{-4}$ g/ml). ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables 1 and 2.

4: A colorless powder (from MeOH+isopropyl ether), mp 255—256 °C. $[\alpha]_D$ −18.5° (c=0.36, MeOH). Pos. SI-MS m/z: 635 $[M+H]^+$. 657 $[M+Na]^+$. Pos. HR-SI-MS m/z: 635.3795 $[C_{35}H_{54}O_{10}+H]^+$, error: 0.3 m.m.u. IR (KBr) cm^{-1}: 3250—3600 (OH). CD: $\Delta\varepsilon_{214}$: −8.34 ($c=2.1\times10^{-4}$ g/ml). ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables 1 and 2.

Preparation (*S*)-(−)-MTPA and (*R*)-(+)-MTPA ester of 1 To the solution of **1** (2.7 mg) in pyridine (200 μl) was added (*R*)-(−)-MTPA chloride (20 μl), and the solution was allowed to stand at r.t. over night. *N*,*N*-Dimethyl-1,3-propanediamine (40 μl) was added, and after having been left standing for 10 min, the product was purified with a TLC preparation to afford (*S*)-(−)-MTPA ester (5.0 mg). In a similar manner, **1** (3.1 mg) and (*S*)-(+)-MTPA chloride (20 μl) were reacted to yield (*R*)-(+)-MTPA ester (6.4 mg). ^{1}H-NMR ($CDCl_3$) of both esters were measured successively on a Varian Unity-INOVA-500, and assigned by analyzing the ^{1}H–^{1}H COSY and HSQC.

(*S*)-(−)-MTPA Ester: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.10*, 1.50* (H-1), 1.64*, 1.88* (H-2), 3.31 (dd, J=4.1, 11.7 Hz, H-3), 1.16* (H-5), 1.45, 1.87* (H-6), 5.39 (dd, J=1.8, 7.8 Hz, H-7), 1.32, 2.89* (H-11), 5.67 (dd, J=1.6, 9.4 Hz, H-12), 6.205 (s, H-15), 2.88* (H-17), 1.652 (3H, s, H-18), 0.59, 1.05 (each, d, J=4.0 Hz, H-19), 2.90* (H-20), 1.388 (3H, d, J=6.8 Hz, H-21), 2.97*, 3.19 (dd, J=9.5, 19.0 Hz, H-22), 5.359 (s, H-24), 1.464 (3H, s, H-26), 1.600 (3H, s, H-27), 1.328 (3H, s, H-28), 0.868 (3H, s, H-29), 0.738 (3H, s, H-30), 2.295 (3H, s, AcO), 5.15 (d, J=6.5 Hz, H-1′), 5.93 (dd, J=6.5, 8.8 Hz, H-2′), 6.32 (dd, J=3.5, 8.8 Hz, H-3′), 6.10 (H-4′), 4.10 (dd, J=2.3, 12.5 Hz, H-5′), 4.30 (dd, J=4.5, 12.5 Hz, H-5′), 3.515, 3.644, 3.671, 3.699, 3.728 (each, 3H, s, OCH_3—MTPA). (*: overlapping)

(*R*)-(+)-MTPA Ester: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.30,* 1.55* (H-1), 1.80*, 2.10* (H-2), 3.38 (dd, J=4.1, 11.7 Hz, H-3), 1.02* (H-5), 1.48, 1.70 (H-6), 5.02 (dd, J=1.8, 7.8 Hz, H-7), 1.30* (H-11), 2.84 (dd, J=9.4, 16.0 Hz, H-11), 5.64 (dd, J=1.6, 9.4 Hz, H-12), 6.132 (s, H-15), 2.910 (H-17), 1.605 (3H, s, H-18), 0.59, 1.05 (each, d, J=4.0 Hz, H-19), 3.00 (H-20), 1.439 (3H, d, J=6.8 Hz, H-21), 3.19 (br d, J=19.0 Hz, H-22), 3.66 (dd, J=9.5, 19.0 Hz, H-22), 5.363 (s, H-24), 1.454 (3H, s, H-26), 1.477 (3H, s, H-27), 1.218 (3H, s, H-28), 0.987 (3H, s, H-29), 0.901 (3H, s, H-30), 2.272 (3H, s, AcO), 5.27 (d, J=6.5 Hz, H-1′), 5.98 (H-2′), 6.16 (dd, J=3.5, 8.8 Hz, H-3′), 6.07 (H-4′), 4.22 (dd, J=2.3, 12.5 Hz, H-5′), 4.58 (dd, J=4.5, 12.5 Hz, H-5′), 3.401, 3.448, 3.744, 3.801, 3.882 (each, 3H, s, OCH_3–MTPA). (*: overlapping)

$\Delta\delta$ ($=\delta_S-\delta_R$) values of H-26, H-27 were +5.0, +61.5, respectively (Fig. 5).

Treatment of 2 with *p*-Toluenesulfonic Acid Compound **2** (4.1 mg) in MeOH (1 ml) was treated with 0.03% *p*-TsOH acid solution (20 ml, pH 4.0), stirring at room temperature for 5 d. The mixture was chromatographed on Amberlite IRA-67 (NH_2) [MeOH–H_2O (2 : 1)] followed with p-HPLC [column: Develosil PhA-T-5, i.d. 10×250 mm; mobile phase: MeCN–H_2O (35 : 65); flow rate: 2 ml/min; column temperature: 40 °C] to afford **1** [2.2 mg, SI-MS: m/z 715 $(M+Na)^+$] and unchanged **2** (1.3 mg). The products was identical with **1** by TLC and ^{1}H-NMR.

Sugar Analysis of 1, 3 and 4 **1** (2.6 mg), **3** (2.1 mg) or **4** (1.6 mg) was dissolved in dioxane (1 ml), and after 3% HCl (2 ml) was added, the solution was refluxed for 2 h. The reaction solution was diluted with water and extracted with EtOAc (20 ml×3). The water layer was passed through an Amberlite IR-35 column. The eluate was concentrated *in vacuo* and analyzed by TLC [*n*-PrOH–H_2O (85 : 15), L-arabiose: *Rf* 0.51] and HPLC with a chiral detector, Shodex OR-I; [column: Shodex NH2P-50, i.d. 4.6×250 mm; mobil phase: MeCN–H_2O–H_3PO_4 (950 : 40 : 10); flow rate: 1 ml/min; column temperature: 47 °C, L-(+)-arabinose: t_R 12′10″ (+), comparing with D-(−)-arabinose: t_R 12′10 ″ (−)]. L-(+)-Arabinose was detected from **1**, **3** and **4**, respectively.

Acknowledgements The authors are grateful to Mr. K. Minoura for NMR spectra and Mrs. M. Fujitake for mass spectra at Osaka University of Pharmaceutical Sciences, to Mr. H. Hayasaka and Mr. K. Ohba of the Faculty of Pharmaceutical Sciences, Tohoku University, for culturing *C. simplex*, and to Prof. S. Arihara of Faculty of Pharmaceutical Sciences Tokushima Bunri University, for analysis of sugars.

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