Studies on the Constituents of *Cimicifuga* Species. XVII.[1] Four New Glycosides from the Aerial Parts of *Cimicifuga simplex* WORMSK.

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Four new glycosides (1—4) were isolated from the aerial parts of *Cimicifuga simplex* (Ranunculaceae), and their structures were determined to be 12β-hydroxycimigenol-3-*O*-β-D-xylopyranoside (1), 12β-hydroxycimigenol-3-*O*-α-L-arabinopyranoside (2), 7β-hydroxycimigenol-3-*O*-β-D-xylopyranoside (3) and 25-*O*-acetyl-7β-hydroxycimigenol-3-*O*-β-D-xylopyranoside (4).

Key words *Cimicifuga simplex*; 12β-hydroxycimigenol; β-D-xyloside; α-L-arabinoside; cycloartane; 12β-hydroxycimigenol

We recently reported on the isolation of three new triterpenic glycosides from the aerial parts of *Cimicifuga simplex*.[1] In our continuing work, we isolated four new glycosides (**1**—**4**) from the same herb. This paper deals with the isolation and the structural elucidation of these glycosides.

Compounds **1**—**4** were obtained as described in the experimental section by repeated chromatographies on Diaion HP-20, octadecylsilanized silicic acid (ODS) and silica gel columns, and HPLC of the aqueous fraction after removal of the *n*-BuOH fraction from MeOH extracts of the aerial parts.

Compound **1** was obtained as colorless needles, mp 286—287 °C, $[\alpha]_D$ +6.4° (c=0.44%, MeOH), and the molecular formula was determined to be $C_{35}H_{56}O_{10}$ by positive high resolution secondary ion mass spectroscopy

Table 1. ^{1}H-NMR Data of **1**—**4** and Their Aglycones (**1a**, **3a**, **4a**) in Pyridine-d_5

	1a[a]	**1**	**2**	**3a**	**3**	**4a**	**4**
1	1.25, 1.57	1.20, 1.55	1.20, 1.55	1.20, 1.60	1.25, 1.58	1.20, 1.60	1.25, 1.58
2	1.85, 1.97	1.80, 2.12	1.80, 2.14	1.92, 2.35	1.92, 2.35	1.95, 2.35	1.94, 2.37
3	3.53 dd (11.5, 4.0)	3.45 dd (11.5, 4.2)	3.46 dd (11.5, 4.2)	3.57 dd (11.6, 4.5)	3.52 dd (11.6, 4.3)	3.57 dd (11.5, 4.3)	3.53 dd (11.6, 4.2)
5	1.30 dd (12.0, 3.8)	1.31	1.31	1.55	1.60	1.55	1.58
6	0.82 ddd (12.0, 12.0, 12.0) 1.60	0.72 ddd (12.5, 12.5, 12.5) 1.58	0.72 ddd (12.5, 12.5, 12.5) 1.60	1.20, 2.05	1.20, 2.04	1.20, 2.05	1.20, 2.04
7	1.25, 2.17	1.25, 2.26	1.25, 2.28	3.66 ddd (11.5, 10.5, 3.0)	3.67 ddd (12.0, 10.0, 3.0)	3.68 ddd (12.0, 10.0, 3.0)	3.68 ddd (12.0, 10.0, 3.0)
8	1.85	1.80	1.79	1.82 d (10.0)	1.80 d (10.0)	1.83 d (10.0)	1.82 d (10.0)
11	1.50	1.50	1.50	1.10	1.08	1.10	1.10
	2.83 dd (16.0, 7.7)	2.78 dd (15.5, 9.0)	2.80 dd (15.5, 9.0)	2.08	2.08	2.08	2.06
12	4.23 dd (7.7, 2.5)	4.20 bd (9.0)	4.20 bd (9.0)	1.50, 1.65	1.55, 1.65	1.55, 1.65	1.55, 1.65
15	4.44 s	4.42 s	4.40 s	4.46 s	4.43 s	4.46 s	4.44 s
17	1.84 d (9.2)	1.81 d (9.3)	1.82 d (9.3)	1.51 d (10.8)	1.52 d (10.8)	1.52 d (11.0)	1.51 d (11.0)
18	1.45 s	1.41 s	1.43 s	1.19 s	1.18 s	1.21 s	1.19 s
19	0.46 d (4.0)	0.40 d (4.0)	0.42 d (4.0)	0.37 d (4.0)	0.35 d (4.2)	0.39 d (4.2)	0.36 d (4.2)
	0.67 d (4.0)	0.58 d (4.0)	0.58 d (4.0)	0.67 d (4.0)	0.66 d (4.2)	0.69 d (4.2)	0.67 d (4.2)
20	1.85	1.85	1.86	1.58	1.60	1.60	1.60
21	1.39 d (6.0)	1.35 d (5.7)	1.37 d (5.8)	0.88 d (6.5)	0.87 d (6.4)	0.89 d (6.4)	0.88 d (6.5)
22	1.15, 2.41	1.12, 2.38	1.13, 2.39	1.10, 2.30	1.10, 2.28	1.04, 2.30	1.10, 2.28
23	4.77 d (9.2)	4.74 d (8.8)	4.76 d (8.8)	4.73 d (9.0)	4.72 d (8.8)	4.65 d (9.0)	4.63 d (8.8)
24	3.85 s	3.84 s	3.86 s	3.86 s	3.81 s	4.19 s	4.17 s
26	1.53 s	1.52 s	1.55 s	1.56 s	1.52 s	1.78 s	1.75 s
27	1.50 s	1.49 s	1.51 s	1.52 s	1.49 s	1.74 s	1.73 s
28	1.24 s	1,28 s	1.26 s	1.33 s	1.34 s	1.32 s	1.35 s
29	1.20 s	1.21 s	1.23 s	1.23 s	1.30 s	1.23 s	1.30 s
30	1.07 s	1.01 s	0.99 s	1.10 s	1.07 s	1.11 s	1.08 s
1′		4.82 d (7.6)	4.81 d (7.2)		4.84 d (7.5)		4.86 d (7.5)
2′		4.00 dd (8.5, 7.6)	4.40 dd (8.5, 7.2)		4.02 dd (8.5, 7.5)		4.05 dd (8.0, 7.5)
3′		4.16 dd (8.6, 8.5)	4.20 dd (8.5, 3.0)		4.17 dd (8.8, 8.5)		4.19 dd (8.8, 8.0)
4′		4.24 ddd (10.5, 8.6, 5.0)	4.35 br s		4.23 ddd (11.0, 8.8, 5.0)		4.26 ddd (10.0, 8.8, 5.0)
5′		3.71 dd (10.5, 10.5)	3.80 d (11.0)		3.73 dd (11.0, 11.0)		3.75 dd (11.0, 10.0)
		4.35 dd (10.5, 5.0)	4.30 dd (11.0, 3.0)		4.36 dd (11.0,5.0)		4.38 dd (11.0, 5.0)
$COCH_3$						1.98 s	1.98 s

a) Obtained on a General Electric GN-400. The other data were obtained on a Varian XL-300.

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(pos. HR-SIMS) [(M+H)$^+$, m/z 637.3957], pos. FAB-MS [(M+H)$^+$, m/z 637, (M+Na)$^+$, m/z 659] and the data of the ^{13}C-NMR spectrum. The IR spectrum showed strong hydroxyl bands at 3550—3250 cm^{-1}. The ^{1}H-NMR (Table 1) and the ^{13}C-NMR (Table 2) spectra were similar to those of cimigenol and its related triterpene glycosides previously isolated from the *Cimicifuga* species.[1-5)]

Compound **1** was hydrolyzed with Cellulase T [Amano] 4 to afford **1a**, mp 216—217 °C, $[\alpha]_D$ +10.1° (c=0.71%, MeOH), $C_{30}H_{48}O_6$. The positive high resolution electron impact mass spectroscopy (pos. HR-EI-MS) showed a M$^+$ ion at m/z 504.3447, clarifying the molecular formula. Signals due to 45 Hs and 30 Cs were assigned by the ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY) spectrum coupled with the ^{13}C–^{1}H COSY and heteronuclear multiple bond correlation (HMBC) spectra as summarized in Tables 1 and 2 (3 Hs of 48 Hs were exchanged by D_2O). A long-range correlation, especially among the quaternary carbons (C-4, 9, 10, 13, 14, 16, 25) and hydrogens, was found in the HMBC spectrum in assigning the H signals of the tertiary methyl groups (18-H_3: δ 1.45 ppm, 26-H_3: 1.53, 27-H_3: 1.50, 28-H_3: 1.24, 29-H_3: 1.20, 30-H_3: 1.07) as shown in Fig. 1 and Table 1.

The nuclear Overhauser effect (NOE) difference spectra afforded the definitive formulation of **1a** as 12β-hydroxycimigenol, as shown in Fig. 2. Irradiation of the 28-H_3 signal line increased the 12α-H signal at δ 4.23 by 2.8%. This irradiation increased 11α-H (δ 2.83) by 1.4%, 7α-H (δ 2.17) by 1.0% and 17-H (δ 1.84) by 3.4% at the same time. These data clarified the presence of a 12β-hydroxy group in **1a**.

Compound **1** was hydrolyzed with 0.5 N HCl to afford 12β-hydroxycimigenol as an aglycone (**1a**), along with D-xylose, which was detected by HPLC (Shodex RS-Pak DC-6143, 80% CH_3CN, 1 ml/min., 70 °C) equipped with a chiral detection Shodex OR-1.[6)]

The ^{1}H-NMR spectrum of **1** showed 1′-H (δ 4.82, d, J=7.6 Hz), 2′-H (δ 4.00, dd, J=8.5, 7.6 Hz), 3′-H (δ 4.16, dd, J=8.6, 8.5 Hz), 4′-H (δ 4.24, ddd, J=10.5, 8.6, 5.0 Hz), 5′-H (δ 3.71, dd, J=10.5, 10.5 Hz) and 5′-H (δ 4.35, dd, J=10.5, 5.0 Hz), suggesting the presence of a β-D-xylopyranosyl group. On the other hand, the ^{13}C-NMR spectrum showed that C-3 appeared at δ 88.71 by the glycosylation shift of 10.94 ppm from **1a**. Thus, the structure of **1** should be 12β-hydroxycimigenol-3-O-β-D-xylopyranoside, as shown in Fig. 3.

Compound **2** was obtained as colorless needles, mp

Table 2. ^{13}C-NMR Chemical Shifts of **1**—**4** and Their Aglycones (**1a**, **3a**, **4a**) in Pyridine-d_5

	1a[a)]	**1**	**2**	**3a**	**3**	**4a**	**4**
1	32.54	32.42	32.06	30.72	30.18	30.08	30.50
2	30.86	29.99	29.53	30.31	29.98	30.08	29.88
3	77.77	88.71	88.18	77.68	88.28	77.28	88.13
4	40.84	41.23	40.84	40.81	41.03	40.39	40.19
5	47.04	47.35	46.92	46.08	46.28	45.71	46.14
6	21.01	20.80	20.47	32.46	32.29	32.13	32.19
7	26.09	26.08	25.71	69.42	69.29	69.02	69.15
8	47.30	47.35	46.92	56.16	56.28	55.83	56.18
9	20.47	20.53	20.25	18.90	18.94	18.50	18.85
10	26.47	26.49	26.14	27.20	27.17	27.04	27.09
11	40.65	40.63	40.24	26.58	26.57	26.26	26.47
12	72.66	72.89	72.39	33.92	33.96	33.59	33.85
13	47.84	47.85	47.44	42.25	42.37	41.99	42.23
14	48.14	48.27	47.86	47.80	47.76	47.44	47.71
15	79.68	79.93	79.40	79.12	79.15	78.67	78.93
16	112.15	112.53	111.90	111.86	111.72	111.92	112.14
17	59.63	59.81	59.36	59.82	59.85	59.38	59.60
18	11.96	12.04	11.70	19.61	19.63	19.23	19.47
19	30.83	30.75	30.38	30.79	30.64	30.53	30.50
20	23.89	24.00	23.64	23.96	24.00	23.51	23.75
21	20.94	21.03	20.69	19.61	19.63	19.23	19.47
22	38.64	38.78	38.39	38.08	38.10	37.51	37.75
23	71.61	71.89	71.40	71.75	71.70	71.12	71.36
24	89.88	90.22	89.65	90.29	90.30	86.38	86.63
25	70.97	71.33	70.81	71.22	71.18	83.29	83.42
26	25.37	25.43	25.10	25.49	25.54	20.92	21.15
27	26.67	26.49	26.14	26.03	26.37	23.08	23.34
28	11.74	11.81	11.48	11.95	11.94	11.68	11.88
29	26.00	25.71	25.34	26.03	25.65	25.71	25.54
30	14.68	15.32	14.96	14.72	15.29	14.37	15.17
1′		107.60	106.79		107.45		107.78
2′		75.41	72.22		75.31		75.27
3′		78.33	73.95		78.28		78.27
4′		71.11	68.84		71.01		70.96
5′		67.00	66.08		66.96		66.90
CO						170.21	170.23
CH_3						22.04	22.22

a) Measured at 100.5 MHz. The others: at 75.4 MHz.

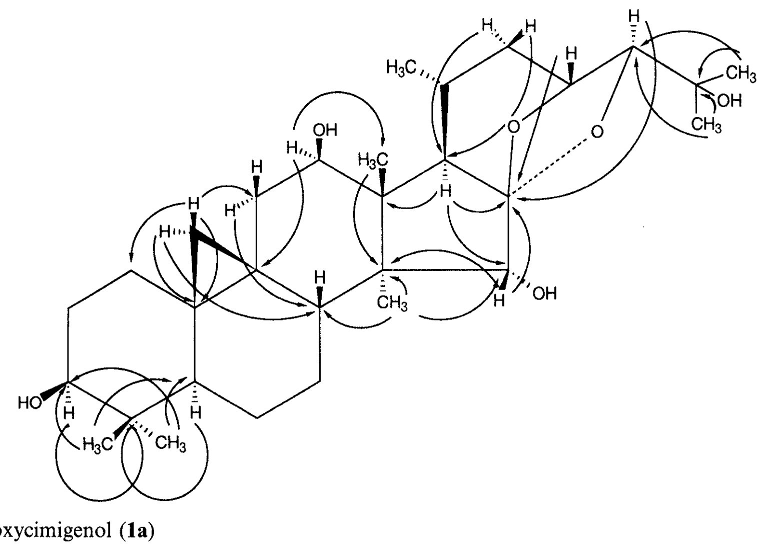


Fig. 1. HMBC of 12β-Hydroxycimigenol (**1a**)

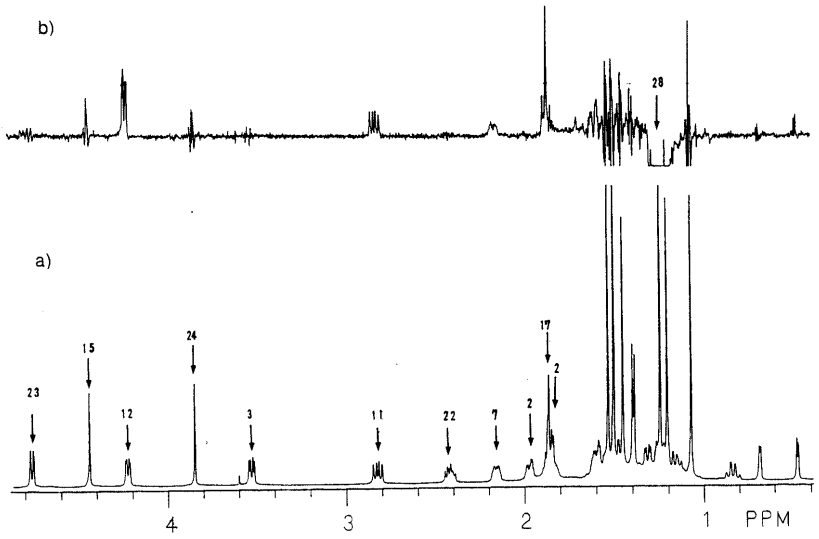
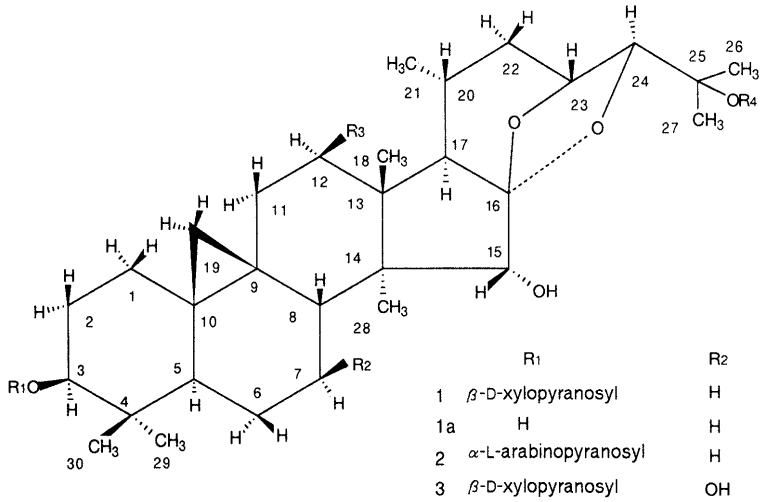


Fig. 2. ^{1}H-NMR (Normal and NOE) Spectra of 12β-Hydroxycimigenol (**1a**)
a) Normal spectrum. b) NOE difference spectrum on irradiation at δ 1.24 (C-28).



	R_1	R_2	R_3	R_4
1	β-D-xylopyranosyl	H	OH	H
1a	H	H	OH	H
2	α-L-arabinopyranosyl	H	OH	H
3	β-D-xylopyranosyl	OH	H	H
3a	H	OH	H	H
4	β-D-xylopyranosyl	OH	H	Ac
4a	H	OH	H	Ac

Fig. 3. The Structures of **1**—**4** and Their Aglycones (**1a**, **3a**, **4a**)

267—268 °C, $[\alpha]_D$ +15.3° (c=0.38%, MeOH), and the molecular formula was determined to be $C_{35}H_{56}O_{10}$ by the pos. HR-SIMS [(M+H)$^+$, m/z 637.3954]. The IR-spectrum showed strong hydroxyl bands at 3550—3200 cm^{-1}.

Compound **2** was hydrolyzed with 0.5 N HCl to afford 12β-hydroxycimigenol (**1a**) as an aglycone and L-arabinose as a sugar detected by HPLC equipped with Shodex OR-1, as in **1**. The ^{1}H-NMR spectrum showed the presence of an α-L-arabinopyranosyl moiety (1′-H: δ 4.81, d, J=7.2; 2′-H: δ 4.40, dd, J=8.5, 7.2 Hz; 3′-H: δ 4.20, dd, J=8.5, 3.0 Hz; 4′-H: δ 4.35, br s; 5′-H: δ 3.80, d, J=11.0 Hz; 5′-H: δ 4.30, dd, J=11.0, 3.0 Hz). The glycosylation position of 3-*O* was clarified by the ^{13}C-NMR data (δ 88.18 ppm for 3-C) . Thus, the structure of **2** should be 12β-hydroxycimigenol-3-*O*-α-L-arabinopyranoside, as shown in Fig. 3.

Compound **2** seems to be the same compound isolated from the roots of *Cimicifuga dahurica* by Kondo *et al.*[7] They reported it as a 12-hydroxycimigenol arabinoside at the 96th Annual Meeting of the Japan Pharmaceutical Society (1976). We looked for a direct comparison , but neither the authentic sample nor the spectral data were available. Therefore, in this report we treated **2** as a new compound.

Compound **3** was obtained as colorless needles, mp 310 °C, $[\alpha]_D$ +14.7° (c=1.17%, MeOH), and the molecular formula was determined to be $C_{35}H_{56}O_{10}$ by the pos. HR-SIMS [(M+H)$^+$, m/z 637.3947]. The IR-spectrum showed strong hydroxyl bands at 3450—3200 cm^{-1}.

Compound **3** was hydrolyzed with 0.5 N methanolic HCl to afford 7β-hydroxycimigenol (**3a**), mp 255—256 °C as an aglycone and D-xylose ($[\alpha]_D$ +17.4°) as a sugar. The structure of **3a** was reported previously and the primary ^{1}H-NMR data in $CDCl_3$ were described.[2] In this report, the detailed data of ^{1}H- and ^{13}C-NMR spectra(pyridine-d_5) of this aglycone are described (Tables 1, 2). The glycosylation position of 3-*O* was clarified by the ^{13}C-NMR data (δ 88.28 ppm for 3-*C*). Thus, the structure of

3 should be 7β-hydroxycimigenol-3-*O*-β-D-xylopyranoside, as shown in Fig. 3.

Compound **4** was obtained as colorless needles, mp 252—253 °C, $[\alpha]_D$ +14.0° (c=0.41%, MeOH), and the molecular formula was determined to be $C_{37}H_{58}O_{11}$ by the pos. HR-SIMS [$(M+H)^+$, m/z 679.4053]. The IR-spectrum showed strong hydroxyl bands at 3560—3200 cm^{-1} and an acetyl band at 1720 cm^{-1}. The ^{1}H-NMR (Table 1) and the ^{13}C-NMR (Table 2) spectra were similar to those of 25-*O*-acetylcimigenol.[2,5] An acetyl group (δ_H 1.98, 3H, s, δ_C 170.23, 22.22 ppm), 25-dimethyl groups (δ_H 1.75, 1.73 ppm, 26, 27-3H, s), 24-H (δ_H 4.17 ppm, 1H, s) and 25-C (δ_C 83.42 ppm) are characteristic to **4**.

Compound **4** was hydrolyzed with Cellulase T [Amano] 4 to afford 25-*O*-acetyl-7β-hydroxycimigenol (**4a**), mp 160—161 °C, $[\alpha]_D$ +22.6° (c=0.93, MeOH), and the molecular formula was determined to be $C_{32}H_{50}O_7$ by the pos. HR-SIMS [$(M+H)^+$, m/z 547.3627].

Compound **4** was hydrolyzed with 1% Na_2CO_3 to afford **3**. Thus, the structure of **4** should be 25-*O*-acetyl-7β-hydroxycimigenol-3-*O*-β-D-xylopyranoside, as shown in Fig. 3.

Experimental

General The instruments used in this work were as follows: Yanagimoto micromelting apparatus (melting points), Perkin-Elmer 1720X-FT-IR spectrometer (IR spectra), Varian Gemini-200, Varian XL-300, and General Electric GN-400 (NMR spectra). Hitachi M-80 and JMS-DX-300 spectrometers (MS spectra). Melting points are uncorrected. NMR spectra were measured in pyridine-d_5 solution, and chemical shifts are expressed on the δ scale using tetramethylsilane as an internal standard. Column chromatography was carried out on silica gel (Wakogel C-200) and ODS-A YMC. HPLC was conducted on a Gilson 305 pump equipped with a Shodex refractometer as a detector.

Extraction of 1—4 The residue (185 g) after the isolation of cimigenol diglycosides from the aerial parts of *Cimicifuga simplex*[1] was chromatographed on SiO_2 (1.0 kg, i.d. 6.0 × 40.0 cm). Elution fractions with $CHCl_3$–MeOH (10—9 : 1) were chromatographed on ODS (100 g, i.d. 3.5 × 24 cm). Elution with MeOH–H_2O (2 : 1) afforded the mixtures of **1** and **2**. HPLC [column: Crest Pak C18T-5 (5 μm, i.d. 4.6 mm × 250 mm); solvent, MeOH–H_2O–CH_3CN (10 : 13 : 3); effluent speed: 1 ml/min; column temperature, 40 °C] and recrystallization from MeOH afforded **1** as colorless needles (28 mg), **2** as colorless needles (25 mg). Elution with MeOH : H_2O (3 : 1) afforded **3** and (5 : 1) **4**. HPLC [same condition as in **1**, **2** except the solvent: MeOH–H_2O–CH_3CN (10 : 7 : 3)] and recrystallization from CH_3CN–CH_3OH afforded **3** as colorless needles (60 mg) and **4** as colorless needles (65 mg).

1, mp 286—287 °C, $[\alpha]_D$ +6.4° (c=0.44%, MeOH), $C_{35}H_{56}O_{10}$. Pos. HR-SIMS: m/z 637.3957 [$(M+H)^+$], error: 0.9 (m mass). Pos. FAB-MS: m/z 637 [$(M+H)^+$], m/z 659 [$(M+Na)^+$]. IR (KBr) cm^{-1}: 3550—3250 (OH). ^{1}H- and ^{13}C-NMR (pyridine-d_5) δ: Tables 1 and 2.

2, mp 267—268 °C, $[\alpha]_D$ +15.3° (c=0.38%, MeOH). $C_{35}H_{56}O_{10}$. Pos. HR-SIMS: m/z 637.3954 [$(M+H)^+$], error: 0.6 (m mass), pos. SIMS: m/z 637 [$(M+H)^+$], m/z 659 [$(M+Na)^+$]. IR (KBr) cm^{-1}: 3550—3200 (OH). ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables 1 and 2.

3, mp 310 °C, $[\alpha]_D$ +14.7° (c=1.17%, MeOH). $C_{35}H_{56}O_{10}$. Pos. HR-SIMS: m/z 637.3947 [$(M+H)^+$], error: −0.1 (m mass). IR (KBr) cm^{-1}: 3450—3200 (OH). ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables 1 and 2.

4, mp 252—253 °C, $[\alpha]_D$ +14.0° (c=0.41%, MeOH), $C_{37}H_{58}O_{11}$. Pos. HR-SIMS: m/z 679.4053 [$(M+H)^+$], error: −0.1 (m mass). IR (KBr) cm^{-1}: 3560—3200 (OH), 1720 (CH_3CO). ^{1}H- and ^{13}C-NMR (pyridine-d_5): Tables 1 and 2.

Hydrolysis of 1 with Cellulase T [Amano] 4 **1** (19 mg) was dissolved in 1% ethanolic AcOH (20 ml), then water (40 ml) was added on stirring and the solution was adjusted to pH 4.5 by the dropwise addition of AcOH. Cellulase T [Amano] 4 (from *Trichoderma viride*, 200 mg) was added. The solution was stirred for 2 d at room temperature. Then, the reaction solution was shaken with EtOAc (30 ml × 3), and after washing the joined EtOAc layer with water and drying it over Na_2SO_4, the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 (12 g) and eluted with *n*-hexane–EtOAc (1 : 1) to afford **1a** as colorless needles (7 mg) by recrystallization from EtOAc. **1a**: mp 216—217 °C, $[\alpha]_D$ +10.1° (c=0.71%, MeOH), $C_{30}H_{48}O_6$ SIMS: m/z 505 [$(M+H)^+$]. Pos. EI-HR-MS: m/z 504.3447 [$(M)^+$], error: −0.2 (m mass). IR (KBr) cm^{-1}: 3500—3100 (OH). ^{1}H- and ^{13}C-NMR (pyridine-d_5) δ: Tables 1 and 2. HMBC: Fig. 1. NOE: Fig. 2.

Acidic Hydrolysis of 1 with 0.5 N HCl **1** (5.8 mg) was treated in the same method as reported previously.[1] The water layer and the water washings after the extraction of the aglycone (**1a**) were joined and passed to an Amberlite IR-35 column. The passed fraction was subjected to HPLC (column: Shodex RS-Pak DC-613, solvent: 80% CH_3CN, effluent speed: 1 ml/min, column temperature: 70 °C) equipped with a chiral detection OR-1: t_R 11 min, +15° (D-xylose).

Acidic Hydrolysis of 2 with 0.5 N HCl **2** (20 mg) was treated as above to afford **1a** (7.2 mg) as an aglycone.The water layer was passed to an Amberlite IR-35 column and the passed fraction was subjected to HPLC equipped with OR-1 as in **1**. L-arabinose: t_R 13.5 min. +10°.

Hydrolysis of 4 with 1% Na_2CO_3 **4** (4.7 mg) was dissolved in MeOH (2 ml) and 1% Na_2CO_3 (2 ml) was added on stirring for 15 h at 25 °C. After neutralization with 5% AcOH, the mixture was shaken with EtOAc (20 ml × 3) and washed with water. The product was chromatographed on SiO_2 (10 g) and recrystallized from CH_3CN–MeOH to afford colorless needles (3.2 mg). The ^{1}H-NMR spectrum (pyridine-d_5) was identical with that of the isolated compound **3**.

Hydrolysis of 3 with 0.5 N HCl **3** (20.5 mg) was treated as above, and the product (10 mg) from the EtOAc layer was identified with 7β-hydroxycimigenol (**3a**) by comparison of the ^{1}H-NMR spectrum. D-Xylose, $[\alpha]_D$ +17.4° (c=0.31%, 50% MeOH) was isolated from the water layer by HPLC [column: LiChrosorb NH_2 (5 μ, i.d 4.6 mm × 250 mm) solvent: CH_3CN–H_2O (4 : 1), effluent speed: 1 ml/min, column temperature: 40 °C, t_R 5:40 min].

Hydrolysis of 4 with Cellulase T [Amano] 4 **4** (27.4 mg) was treated as in **1** with Cellulase T [Amano] 4 (200 mg) to afford **4a** as colorless needles (12 mg), mp 160—161 °C, $[\alpha]_D$ +22.6° (c=0.93%, MeOH). $C_{32}H_{50}O_7$. Pos. HR-SIMS: m/z 547.3627 [$(M+H)^+$], error: −0.5 (m mass). SIMS: m/z 547 [$(M+H)^+$], 569 [$(M+Na)^+$] .IR ($CHCl_3$) cm^{-1}: 3500—3200 (OH), 1733 (OAc). ^{1}H- and ^{13}C-NMR (pyridine-d_5) δ: Tables 1 and 2.

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References and Notes

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