Studies on the Constituents of *Cimicifuga* Species. XV.[1] Two New Diglycosides from the Aerial Parts of *Cimicifuga simplex* WORMSK.

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Two new diglycosides (I, II) were isolated from the aerial parts of *Cimicifuga simplex* (Ranunculaceae), and their structures were determined to be 25-*O*-acetylcimigenol 3-*O*-*β*-D-glucopyranosyl-(1→3)-*β*-D-xylopyranoside (I) and 23-*O*-acetylshengmanol 3-*O*-*β*-D-glucopyranosyl-(1→3)-*β*-D-xylopyranoside(II). Two known xylosides (Ia, IIa) were also isolated and identified as 25-*O*-acetylcimigenol 3-*O*-*β*-D-xylopyranoside (Ia) and 23-*O*-acetylshengmanol 3-*O*-*β*-D-xylopyranoside (IIa). Cellulase A [Amano] 3 hydrolyzed I and II to afford Ia and IIa respectively, while Cellulase T [Amano] 4 hydrolyzed I and II to afford 25-*O*-acetylcimigenol (Ib) and 23-*O*-acetylshengmanol (IIb) as the aglycones, respectively.

Keywords *Cimicifuga simplex*; Ranunculaceae; cycloartane; glucosyl xyloside; cellulase

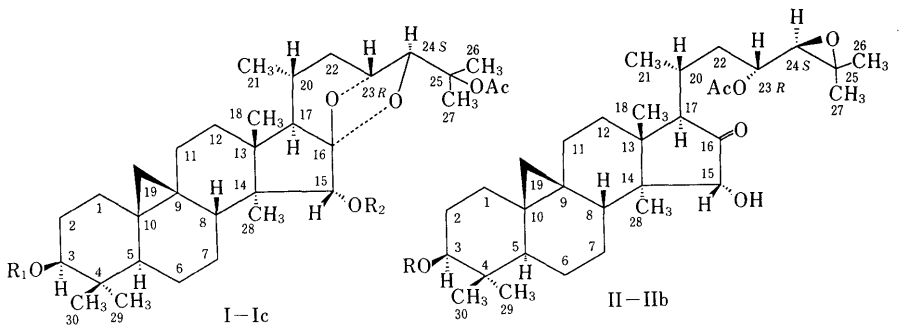
We recently reported on the isolation of a new triterpenic xyloside, 7*β*-hydroxy-23-*O*-acetylshengmanol 3-*O*-*β*-D-xyloside, from the aerial parts of *Cimicifuga simplex*.[1] In our continuing work, we isolated two new diglycosides (I, II) along with the two known xylosides (Ia, IIa) from the same herb. This paper deals with the structure elucidation of I and II as 25-*O*-acetylcimigenol 3-*O*-*β*-D-glucopyranosyl-(1→3)-*β*-D-xylopyranoside and 23-*O*-acetylshengmanol 3-*O*-*β*-D-glucopyranosyl-(1→3)-*β*-D-xylopyranoside, and the identification of Ia and IIa to 25-*O*-acetylcimigenol 3-*O*-*β*-D-xylopyranoside and 23-*O*-acetylshengmanol 3-*O*-*β*-D-xylopyranoside . This is the first report on the isolation of diglycosides from the *Cimicifuga* species, although triterpenol bisdesmosides have been reported recently.[2] This paper also describes that Cellulase A [Amano] 3 hydrolyzed I and II to afford Ia and IIa, respectively, while Cellulase T [Amano] 4 hydrolyzed I and II to afford the aglycones Ib and IIb, respectively.

The new diglycosides (I, II) and the xylosides (Ia, IIa) were obtained as described in the experimental section after repeated chromatographies on octadecylsilanized silicic acid (ODS) and silica gel columns of a water soluble portion shaken with *n*-butanol about the methanolic extracts of the aerial parts.

I was obtained as colorless needles, mp 285—286 °C, $[\alpha]_D$ +11.6°, and the molecular formula was determined to be $C_{43}H_{68}O_{15}$, by the FAB-MS [$(M+1)^+$; *m/z* 825]. The IR spectrum exhibited strong hydroxyl and ester carbonyl bands at 3550—3480 and 1738 cm^{-1}. The ^{1}H-NMR (Table I) and the ^{13}C-NMR (Table II) spectra were similar to those of cycloartane derivatives previously isolated from the *Cimicifuga* species.[1-6]

I was hydrolyzed with Cellulase A [Amano] 3 to afford Ia, mp 224—225 °C, $C_{37}H_{58}O_{10}$, $[\alpha]_D$ +25.2°, whereas when I was hydrolyzed with Cellulase T [Amano] 4, it afforded Ib, mp 191—192 °C, $C_{32}H_{50}O_6$, $[\alpha]_D$ +34.1°. By direct comparison with authentic specimens, Ia was identified to 25-*O*-acetylcimigenol 3-*O*-*β*-D-xyloside,[5] and Ib was identified to 25-*O*-acetylcimigenol.[5]

D-Glucose, $[\alpha]_D$ +60.8° and a mixture of methyl-*α*-D xyloside and methyl-*β*-D-xyloside, $[\alpha]_D$ +61.1° were



I : R_1=*β*-D-Glc(p)-(1→3)-*β*-D-Xyl(p), R_2=H
Ia : R_1=*β*-D-Xyl(p), R_2=H
Ib : R_1=R_2=H
Ic : R_1=hexa-*O*-Ac-*β*-D-Glc(p)-(1→3)-*β*-D-Xyl(p)
R_2=Ac

II : R=*β*-D-Glc(p)-(1→3)-*β*-D-Xyl(p)
IIa : R=*β*-D-Xyl(p)
IIb : R=H

Fig. 1. Structures of I, II and Their Derivatives

TABLE I. ^{1}H-NMR Chemical Shifts of I, II and the Derivatives in Pyridine-d_5

	I	Ia	Ib	Ic[a]	II	IIa	IIb
1	1.17, 1.51	1.18, 1.51	1.18, 1.51		1.20, 1.55	1.18, 1.50	1.15, 1.53
2	1.88, 2.32	1.90	1.86 dddd		1.90	1.95, 2.32	1.84, 1.95
		2.30 dd (3.5, 12.5)	(4.0, 11.5, 12.5, 12.5)		2.30 ddd		
			2.00		(4.0, 4.0, 13.0)		
3	3.48 dd (4.0, 11.5)	3.46 dd (4.0, 12.0)	3.49 dd (4.5, 11.5)	3.06 dd (9.5, 5.0)	3.48 dd (4.0, 11.5)	3.50 dd (4.0, 11.5)	3.52 dd (4.5, 12.0)
5	1.25	1.25	1.24 dd (4.0, 13.0)		1.28	1.27	1.28
6	0.65, 1.50	0.67 ddd	0.71 dddd		0.73 ddd	0.74 ddd	0.77 ddd
		(12.0, 12.0, 12.0)	(2.5, 13.0, 13.0, 13.0)		(12.0, 12.0, 12.0)	(12.0, 12.0, 12.0)	(12.0, 12.0, 12.0)
		1.48	1.50		1.58	1.50	1.56
7	1.15, 2.05	1.15, 2.05	1.15, 2.05		1.18, 2.05	1.18, 2.00	1.18, 2.00
8	1.63	1.63	1.62		1.78	1.78	1.85
11	1.15, 2.05	1.15, 2.05	1.15, 2.05		1.15, 2.10	1.15, 2.10	1.11, 2.12
12	1.50, 1.62	1.51, 1.61	1.50, 1.60		1.75 (2H)	1.75 (2H)	1.75 (2H)
15	4.26 s	4.23 s	4.22 s	4.26	4.36 s	4.35 s	4.33 s
17	1.41 d (11.0)	1.41 d (11.0)	1.41 d (11.0)		2.35 d (6.2)	2.34 d (6.5)	2.31 d (6.6)
18	1.10 s	1.10 s	1.11 s		1.37 s	1.37 s	1.35 s
19	0.23 d (4.0)	0.25 d (4.0)	0.27 d (4.0)	0.38 d (4.0)	0.33 d (4.0)	0.34 d (4.0)	0.33 d (4.0)
	0.48 d (4.0)	0.48 d (4.0)	0.51 d (4.0)	0.63 d (4.0)	0.56 d (4.0)	0.57 d (4.0)	0.58 d (4.0)
20	1.62	1.60	1.65		2.10	2.05	2.08
21	0.81 d (7.0)	0.81 d (6.7)	0.82 d (6.5)	0.90 d (7.5)	1.26 d (6.7)	1.26 d (7.0)	1.23 d (7.5)
22	0.95	0.94 dd (12.5, 12.5)	0.94 dd (13.0, 13.0)		1.78	1.75	1.76
	2.25	2.24 ddd	2.25 ddd		2.60 ddd	2.62 ddd	2.62 dd (11.0, 12.5)
		(7.5, 10.0, 12.5)	(7.0, 9.5, 13.0)		(2.0, 12.0, 12.0)	(2.0, 12.0, 12.0)	
23	4.63 d (9.2)	4.56 d (9.2)	4.56 d (9.5)	4.30 d (9.0)	5.36 ddd	5.36 ddd	5.35 ddd
					(2.0, 8.3, 9.2)	(2.5, 8.5, 11.0)	(2.5, 8.8, 11.0)
24	4.13 s	4.08 s	4.07 s	3.68 s	3.06 d (8.3)	3.05 d (8.5)	3.00 d (8.8)
26	1.67 s	1.62 s	1.61 s	1.45 s	1.29 s	1.30 s	1.24 s
27	1.71 s	1.65 s	1.64 s	1.40 s	1.44 s	1.42 s	1.38 s
28	1.15 s	1.15 s	1.14 s	0.86	1.21 s	1.21 s	1.18 s
29	1.26 s	1.26 s	1.16 s	0.93	1.33 s	1.30 s	1.17 s
30	1.01 s	1.01 s	1.03 s	0.75	1.05 s	1.06 s	1.06 s
$COCH_3$	1.95 s	1.95 s	1.96 s	2.12, 2.08	2.12 s	2.12 s	2.04 s
				2.04(4Ac) 1.98(2Ac)			
1′-H	4.81 d (7.5)	4.81 d (7.5)		4.95 d (8.5)	4.83 d (8.0)	4.84 d (8.0)	
2′-H	4.03 dd (7.5, 9.0)	3.99 dd (7.5, 9.0)		4.99 dd (8.5, 8.5)	4.04 dd (9.0, 8.0)	4.02 dd (8.0, 8.5)	
3′-H	4.19 dd (9.0, 9.0)	4.13 dd (9.0, 9.0)		3.80 dd (8.5, 8.5)	4.21 dd (9.0, 9.0)	4.18 dd (8.5, 8.5)	
4′-H	4.08 ddd	4.19 ddd		4.86 dd (8.5, 8.5)	4.10 ddd	4.22 ddd	
	(5.0, 9.0, 9.0)	(5.5, 9.0, 9.0)			(5.5, 9.0, 9.0)	(5.0, 8.5, 9.0)	
5′-H	3.69 dd (9.0, 11.5)	3.69 dd (9.0, 11.0)		3.25 dd (10.0, 12.5)	3.71 dd (9.0, 11.3)	3.74 dd (9.0, 11.5)	
5′-H	4.28 dd (5.0, 11.5)	4.31 dd (5.0, 11.0)		4.01 dd (8.5, 12.5)	4.30 dd (5.5, 11.3)	4.35 dd (5.0, 11.5)	
1″-H	5.32 d (7.7)			4.36 d (8.5)	5.32 d (8.0)		
2″-H	4.05 dd (7.7, 9.0)			5.04 dd (8.5, 8.5)	4.05 dd (8.0, 8.0)		
3″-H	4.22 dd (8.5, 8.5)			5.12 dd (8.5, 8.5)	4.03 dd (8.0, 8.0)		
4″-H	4.06 dd (8.5, 8.5)			4.93 dd (8.5, 8.5)	4.06 dd (8.0, 8.0)		
5″-H	4.02 ddd			3.66 m	4.02 ddd		
	(2.0, 5.0, 8.5)				(2.0, 5.0, 8.0)		
6″-H	4.19 dd (5.0, 11.5)			3.83 dd (4.0, 12.5)	4.20 dd (5.0, 11.3)		
6″-H	4.54 dd (2.0, 11.5)			4.06 dd (4.0, 12.5)	4.53 dd (2.0, 11.3)		

a) The data in $CDCl_3$.

obtained by HPLC of acidic hydrolysis products of I and identified by comparison of the ^{1}H-NMR spectra. The 1→3 connectivity between D-glucose and D-xylose was established as follows. Acetylation of I with acetic anhydride in pyridine afforded a heptaacetate (Ic), mp 160—161 °C, $C_{57}H_{82}O_{22}$, and in the ^{1}H-NMR spectrum, a triplet which remained at δ 3.80 ppm without acetylation was assigned to 3′-H by the decoupling experiment. Namely, irradiation at 4′-H (4.86 ppm) changed the triplet (3′-H) to a doublet and a pair of dd signals due to 5′-H (3.25) and 5′-H (4.01) to a pair of doublets at the same time. A methine carbon at 87.80 ppm was assigned to 3′-C by a cross peak with the 3′-H in the ^{1}H–^{13}C shift correlation spectroscopy of I, and the glycosylation shift was *ca.* 9 ppm (Table II). The β-D-glucopyranosyl moiety was clarified by the assignment of ^{1}H- and ^{13}C-NMR signals, especially, 1″-H (5.32 ppm, d, J=7.7 Hz) and 1″-C (105.21 ppm), as shown in Tables I and II. Thus, the structure of the new diglycoside (I) should be 25-*O*-acetylcimigenol 3-*O*-β-D-glucopyranosyl-(1→3)-β-D-xylopyranoside.

II was obtained as colorless needles, mp 245—246 °C, $[\alpha]_D$ −38.2°, $[M]_{338}$ −11231°, $[M]_{290}$ +21349°, and the molecular formula was determined to be $C_{43}H_{68}O_{15}$ by the FAB-MS [$(M+1)^+$, *m/z* 825, $(M+Na)^+$, *m/z* 847]. The IR spectrum showed strong hydroxyl bands at 3500—3420 cm^{-1} and an ester carbonyl and five-membered ketone band at 1738 cm^{-1}.

The ^{1}H-NMR (Table I) and ^{13}C-NMR (Table II) spectra were similar to those of 23-*O*-acetylshengmanol derivatives previously isolated from the *Cimicifuga* species.[1,6]

II was hydrolyzed with Cellulase A [Amano] 3 to afford IIa, mp 285—286 °C, $C_{37}H_{58}O_{10}$, $[\alpha]_D$ −45.5°, $[M]_{338}$ −12372°, $[M]_{290}$ +14246°; II was also hydrolyzed with Cellulase T [Amano] 4 to afford IIb, mp 175—176 °C, $C_{32}H_{50}O_6$, $[\alpha]_D$ −44.1°. By direct comparison with authentic specimens, IIa was identified to 23-*O*-acetyl

TABLE II. ^{13}C-NMR Chemical Shifts of I, II and Their Derivatives in Pyridine-d_5

	I	Ia	Ib	II	IIa	IIb
1	32.08	32.13	32.22	31.70	31.74	32.21
2	29.72	29.81	30.64	29.48	29.51	30.83
3	88.36	88.27	77.57	88.11	88.03	77.63
4	41.00	41.03	40.62	40.82	40.79	40.80
5	47.20	47.27	46.80	46.92	47.96	47.10
6	20.74	20.76	20.91	20.47	20.53	21.00
7	26.12	26.14	25.79	26.17	26.14	26.53
8	48.31	48.34	48.28	47.77	47.72	48.11
9	19.68	19.69	19.54	19.59	19.59	19.80
10	26.32	26.37	26.53	26.25	26.28	26.81
11	26.02	26.05	26.12	25.47	25.47	25.79
12	33.69	33.71	33.62	32.52	32.53	32.81
13	41.50	41.52	41.44	41.06	41.06	41.32
14	46.89	46.90	47.02	45.58	45.58	45.84
15	79.84	79.86	79.63	82.31	82.28	82.57
16	112.10	112.11	112.04	219.64	219.58	219.73
17	59.08	59.09	59.00	59.46	59.46	59.73
18	19.19	19.21	19.10	19.34	19.31	19.60
19	30.60	30.63	30.64	30.01	29.99	30.42
20	23.62	23.64	23.52	27.46	27.46	27.72
21	19.19	19.21	19.10	19.86	19.85	20.09
22	37.59	37.60	37.51	36.44	36.44	36.72
23	71.38	71.39	71.33	71.73	71.74	71.92
24	86.47	86.48	86.39	64.75	64.75	64.96
25	82.94	82.95	82.91	58.35	58.38	58.46
26	21.26	21.26	21.23	24.24	24.21	24.44
27	22.70	23.05	22.89	18.87	18.86	19.10
28	11.50	11.52	11.41	11.52	11.47	11.73
29	25.29	25.41	25.71	25.09	25.17	25.85
30	15.13	15.14	14.45	14.98	14.93	14.61
$\underline{C}OCH_3$	170.08	170.09	170.12	170.49	170.50	170.55
$CO\underline{C}H_3$	22.03	22.03	21.94	20.56	20.53	20.74
1′	106.56	107.16		106.31	106.79	
2′	74.00	75.19		74.93	74.79	
3′	87.80	78.19		87.39	77.67	
4′	71.38	70.88		69.03	70.51	
5′	66.03	66.69		65.81	66.36	
1″	105.21			104.91		
2″	75.23			73.81		
3″	77.90			78.02		
4″	69.27			71.06		
5″	78.29			77.49		
6″	62.26			61.95		

shengmanol 3-*O*-*β*-D-xyloside,[6] and IIb was identified to 23-*O*-acetylshengmanol.[6]

D-Glucose, $[\alpha]_D$ +60.5° and a mixture of methy-*β*-D-xyloside and methyl-α-D-xyloside, $[\alpha]_D$ +66.9° were obtained by HPLC of acidic hydrolysis products of II and identified, similarly to I. The connectivity 1 →3 between D-glucose and D-xylose was confirmed by the definitive assignment of ^{1}H- and ^{13}C-NMR spectra of II (Tables I and II). Thus, the structure of II should be 23-*O*-acetylshengmanol 3-*O*-*β*-D-glucopyranosyl-(1→3)-*β*-D-xylopyranoside.

25-*O*-Acetylcimigenol 3-*O*-*β*-D-xylopyranoside (Ia) and 23-*O*-acetylshengmanol 3-*O*-*β*-D-xylopyranoside (IIa) were also isolated and identified.

Experimental[7]

Extraction and Isolation of I, II, Ia and IIa The dried aerial parts (6.07 kg) of *Cimicifuga simplex*, were collected in August, 1991 in Sendai, Japan and identified by G. Kusano, and the representative samples, which have been deposited at the Department of Pharmacognosy, Osaka University of Pharmaceutical Sciences, were extracted with MeOH (80 l × 3) at room temperature overnight. The MeOH solution was subjected to an activated charcoal column chromatography (250 g, 6.7 cm i.d. × 37 cm) and the passed fraction was concentrated *in vacuo* to gummy extracts (0.5 kg).

The concentrated extracts were shaken with *n*-BuOH (300 ml) three times and the joined *n*-BuOH layer was washed with water (200 ml) twice. The water washings were subjected to a Diaion HP-20 column (5.5 cm i.d. × 30 cm) chromatography and after elution with water (2.0 l), the adsorbed fraction was eluted with MeOH (1.0 l). After evaporation of the MeOH, the residue was kept at room temperature for several weeks to provide crystalline precipitates (3.0 g).

The precipitates were chromatographed on SiO_2 (150 g, 4.0 cm i.d. × 35.0 cm) and eluted with $CHCl_3$–MeOH (10 : 1) [fraction A] and $CHCl_3$–MeOH (5 : 1) [fraction B]. The ODS chromatographies (100 g, 3.5 cm i.d. × 24 cm) were carried out for each fraction. Elution with MeOH–H_2O (5 : 1) afforded Ia (120 mg) and with MeOH–H_2O (2 : 1), IIa (85 mg), from fraction A. Elution with MeOH–H_2O (9 : 1) afforded I (350 mg) and with MeOH–H_2O (2 : 1), II (200 mg), from fraction B.

I, mp 285—286 °C, *Anal.* Calcd for $C_{43}H_{68}O_{15}\cdot H_2O$: C, 61.12; H, 8.13. Found: C, 60.59; H, 8.46. FAB-MS: *m/z* 825 $[M+1]^+$, $[\alpha]_D$ +11.6° (*c* = 0.30, MeOH). IR (KBr) cm^{-1}: 3550—3480 (OH), 1738 (OAc). ^{1}H- and ^{13}C-NMR (pyridine-d_5) ppm: Tables I and II.

Ia, mp 224—225 °C, $C_{37}H_{58}O_{10}$, FAB-MS: *m/z* 663 $[M+1]^+$, $[\alpha]_D$ +25.2° (*c* = 0.31, MeOH : pyridine = 3 : 1). IR (KBr) cm^{-1}: 3500—3480 (OH), 1735 (OAc). ^{1}H- and ^{13}C-NMR spectra (Table I and II) were identical with those of an authentic specimen of 25-*O*-acetylcimigenol 3-*O*-*β*-D-xyloside.

II, mp 245—246 °C, *Anal.* Calcd for $C_{43}H_{68}O_{15}\cdot H_2O$: C, 61.12; H, 8.13. Found: C, 61.33; H, 8.38. FAB-MS: *m/z* 825 $[M+1]^+$, 847 $[M+Na]^+$, $[\alpha]_D$ −38.2° (*c* = 1.01, MeOH), ORD: $[M]_{338}$ −11231°, $[M]_{290}$ +21349° (*c* = 0.44, MeOH). IR (KBr) cm^{-1}: 3500—3420 (OH), 1738 (OAc, >C=O). ^{1}H- and ^{13}C-NMR (pyridne-d_5) ppm: Tables I and II.

IIa, mp 285—286 °C, $C_{37}H_{58}O_{10}$, FAB-MS: *m/z* 663 $[M+1]^+$, 685 $[M+Na]^+$, ORD: $[M]_{338}$ −12372°, $[M]_{290}$ +14246° (*c* = 0.45, MeOH). IR (KBr) cm^{-1}: 3570—3430 (OH), 1727 (OAc), 1742 (>C=O). ^{1}H- and ^{13}C-NMR (Tables I and II) spectra were identical with those of an authentic specimen of 23-*O*-acetylshengmanol 3-*O*-*β*-D-xylopyranoside.

Hydrolysis of I with Cellulase A [Amano] 3 and T [Amano] 4 I (70 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 A [Amano] 3 (from *Aspergillus niger*, 300 mg) was added and the solution was stirred for 4 d at room temperature. The reaction solution was shaken with EtOAc (50 ml × 3), and after washing of the joined EtOAc layer with water and drying with Na_2SO_4, the solvent was evaporated *in vacuo* to afford a crystalline residue. Elution with *n*-hexane–EtOAc (1 : 2) in SiO_2 (12 g, 2.0 cm i.d. × 9 cm) chromatography afforded Ia (66.3 mg) as colorless needles after recrystallization from a mixture of EtOAc and MeOH. Ia was identified to 25-*O*-acetylcimigenol 3-*O*-*β*-D-xyloside by direct comparison with the ^{1}H- and ^{13}C-NMR spectra of an authentic specimen.

I (100 mg) was dissolved in 1% ethanolic AcOH (20 ml), then water (40 ml) was added as mentioned above, and Cellulase T [Amano] 4 (from *Trichoderma viride*, 300 mg) was added. The solution was stirred for 4 d at room temperature. The reaction solution was shaken with EtOAc (30 ml × 3), and after washing of the joined EtOAc layer with water and drying over Na_2SO_4, the solvent was evaporated *in vacuo*. Recrystallization from a mixture of EtOAc and MeOH afforded Ib (63.4 mg) as colorless needles. Ib was identified to 25-*O*-acetylcimigenol by direct comparison with an authentic specimen by ^{1}H- and ^{13}C-NMR spectra.

Acidic Hydrolysis of I I (45.5 mg) was dissolved in MeOH (1 ml) and 1 N HCl (2 ml) was added, then the reaction solution was refluxed for 2 h. After cooling to room temperature, the reaction solution was shaken with EtOAc (30 ml × 3). The water layer in the partition with EtOAc was subjected to Amberlite IRA-35 column chromatography and the passed fraction was concentrated *in vacuo*. The residue (10.4 mg in CH_3CN 0.6 ml and water 0.3 ml) was subjected to HPLC [column: LiChrosorb NH_2 (5 μm), solvent: CH_3CN–H_2O (4 : 1), rate: 1 ml/min., column temperature: 40 °C], and D-glucose, t_R 9 : 30 and 9 : 40 min, $[\alpha]_D$ +60.8° (*c* = 0.44, 50% MeOH) and a mixture of methyl-*β*-D-xyloside and methyl-α-D-xyloside (5 : 1), t_R 3 : 40 min, $[\alpha]_D$ +61.1° (*c* = 0.26, 50% MeOH) were obtained and identified by comparison of t_R values,

^{1}H-NMR spectra and $[\alpha]_D$ values with authentic specimens. Methyl-α- and -β-D-glucosides, t_R 5:30 min and D-xylose, t_R 5:50 min were not isolated in the HPLC.

Acetylation of I After I (35 mg) was dissolved to pyridine-d_5 (0.4 ml) and the ^{1}H-NMR spectrum was measured, acetic anhydride (0.1 ml) was added and the mixture stood overnight at room temperature. After the usual treatment, the product (Ic, 46 mg) was obtained as a colorless powder, mp 160—161 °C, $C_{57}H_{82}O_{22}$, FAB-MS: m/z 1058 $[M-AcOH]^+$. ^{1}H-NMR ($CDCl_3$) δ: Table I.

Hydrolysis of II with Cellulase A [Amano] 3 and T [Amano] 4 II (60 mg) was dissolved in 1% ethanolic AcOH (20 ml), and water (40 ml) was added. Cellulase A [Amano] 3 (100 mg) was added and the solution was stirred for 3 days at room temperature. The products were treated as in the case of I, and IIa (40 mg) was obtained as colorless needles by recrystallization from MeOH and identified to 23-*O*-acetylshengmanol 3-*O*-β-D-xyloside by direct comparison of ^{1}H- and ^{13}C-NMR spectra with an authentic specimen.[6]

II (30 mg) was dissolved in 1% ethanolic AcOH (20 ml), and water (40 ml) was added. Cellulase T [Amano] 4 (100 mg) was added and the solution was stirred for 2 d at room temperature. The products were treated as above, and IIb was obtained as colorless needles by recrystallization from a mixture of EtOAc and isopropyl ether and identified to 23-*O*-acetylshengmanol by direct comparison of ^{1}H- and ^{13}C-NMR spectra with an authentic specimen.

Acidic Hydrolysis of II II (67 mg) was dissolved in a mixture of MeOH (1 ml) and 1 N HCl (2 ml) and refluxed in a bath for 2 h. The products were treated as mentioned in I. D-Glucose, t_R 9:30 and 9:40 min, $[\alpha]_D$ +60.5° (c=0.24, 50% MeOH) and methyl-α- and -β-D-xylosides, t_R 3:40 min, $[\alpha]_D$ +66.9° (c=0.18, 50% MeOH) were obtained and identified by direct comparison of HPLC and ^{1}H-NMR spectra of authentic specimens. Methyl-α- and -β-D-glucosides, t_R 5:30 min and D-xylose, t_R 5:50 min were not isolated.

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References and Notes

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7) The instruments used in this work were as follows: Yanagimoto micro melting point apparatus (melting points), JACSCO DIP-digital polarimeter (specific rotation), JASCO ORD/UV-5 spectrometer (ORD), Perkin-Elmer Model 1720X-FT-IR spectrometer (IR spectra), Varian Gemini-200, Varian XL-300, General Electric GN-300, GN-500 (NMR spectra), JEOL JMS-300 spectrometers (Mass spectra). Melting points are uncorrected. NMR spectra were measured in pyridine-d_5 and $CDCl_3$ solution, and chemical shifts are expressed in the δ values and coupling constants (J) in Hertz using tetramethylsilane as an internal standard. Column chromatography was carried out on silica gel (Wako gel C-200) and ODS-A YMC. HPLC was carried out using a LiChrosorb NH_2 (Cica-Merck) 5 μ column, 25 cm × 10 mm i.d., on a Gilson 305 pump and Shodex refractometer as a detector.