Triterpene Glycosides from the Seeds of *Astragalus sinicus* L.[1)]

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From the seeds of *Astragalus sinicus* L. (Leguminosae), seven triterpene glycosides were isolated and identified as soyasaponin I—III methyl esters (1—3) which were treated with CH_2N_2 during the separation procedure, soyasaponin IV (4), soyasapogenol B 3-*O*-β-D-glucuronopyranoside (5), 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-xylopyranosyl(1→2)-β-D-glucuronopyranosyl 3β,22β,24-trihydroxy-11-oxoolean-12-ene (6), whose sapogenol (8) was obtained by enzymatic hydrolysis using glycyrrhizinic acid hydrolase, unambiguously characterized and designated as complogenin, and 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl complogenin (7).

Keywords *Astragalus sinicus*; Leguminosae; complogenin; soyasapogenol B; soyasaponin; glucuronide; oleanene glycoside; glycyrrhizinic acid hydrolase

In the course of our systematic studies on leguminous plants, we reported the constituents of Astragali Semen, the seeds of *Astragalus complanatus*.[2-6)] In connection with this study, we have investigated the triterpene glycosides of *Astragalus sinicus* L. The methanol extract of the seeds of *A. sinicus* was separated by normal and reversed phase column chromatographies to provide seven compounds **1**—**7**, among which compounds **1**—**3** were isolated as the corresponding methyl esters treated with CH_2N_2 during the separation procedure.

Compounds **1**—**4** were shown to be identical with soyasaponin I—III methyl esters[7,8)] and soyasaponin IV,[9)] respectively, according to the *Rf* values on thin layer chromatography (TLC), positive fast atom bombardment mass spectra (FAB-MS), and proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra.

Compound **5** obtained as a white powder, mp 144—146 °C, $[\alpha]_D$ +13.5° (pyridine), showed a peak at *m/z* 657 due to $[M+Na]^+$ in the positive FAB-MS. Acid hydrolysis of **5** provided soyasapogenol B as sapogenol. The ^{1}H-NMR spectrum of **5** displayed the presence of seven tertiary methyl groups at δ 0.84, 1.00, 1.01, 1.23, 1.30×2 and 1.45 (all 3H, s), along with an anomeric proton signal at δ 5.17 (1H, d, J=7.7 Hz) and an olefinic proton signal at δ 5.31 (1H, br s). In the ^{13}C-NMR spectrum of **5** as listed in Table I, signals caused from the sugar moiety were assignable to the *O*-β-D-glucuronopyranosyl moiety, and others due to the aglycone part showed a downfield shift at the C-3 by +8.2 ppm as compared with that of soyasapogenol B.[10)] Consequently, the structure of **5** was characterized as soyasapogenol B 3-*O*-β-D-glucuronopyranoside, whose methyl ester was obtained as a prosapogenol from soybean saponin by mild acid hydrolysis.[11)]

Compound **6** was obtained as a white powder, $[\alpha]_D$ −7.0° (pyridine), showed a peak at *m/z* 927 due to $[M+H]^+$ in the positive FAB-MS. Acid hydrolysis of **6** resulted in the production of a complex hydrolysate, meanwhile, enzymatic hydrolysis of **6** with glycyrrhizinic acid hydrolase (GH)[12)] yielded a homogeneous sapogenol **8**, colorless needles (MeOH), mp 256—258 °C, $[\alpha]_D$ +83.6° ($CHCl_3$), which exhibited an absorption peak at λ_{max}(nm) 250 (log ε 4.86) in the ultraviolet (UV) spectrum and infrared (IR) absorptions at 3432 cm^{-1} (OH) and 1652 cm^{-1} (α,β-unsaturated carbonyl). The EI-MS of **8** showed a molecular ion peak at *m/z* 472 and other characteristic peaks at *m/z* 289 and 135 due to the McLafferty rearrangement,[13)] and at *m/z* 248 and 224 due to the retro Diels–Alder fission,[14)] which suggested the occurrence of two hydroxyl groups in the A/B ring, a partial structure of the 11-oxo-12-ene system and one hydroxyl group in the D/E ring on the oleanene skeleton. The ^{13}C-NMR spectrum (Table I) of **8** displayed signals which arose from C-11, 12 and 13 at δ 199.5, 128.4 and 169.7, respectively, and the ketonization shifts[15)] at C-8, 9, 14, 25, 26 and 27 by +3.8, +14.1, +3.1, +1.0, +1.6 and −2.7 ppm, respectively, in comparison with those of soyasapogenol B,[10)] suggesting the presence of a carbonyl group at C-11. The triacetate (**8a**) of **8** obtained as colorless plates (MeOH), mp 265—267 °C, $[\alpha]_D$ +128.8° ($CHCl_3$), showed a molecular ion peak at *m/z* 598 being higher by 126 mass units than that of **8**. The ^{1}H-NMR spectrum of **8a** exhibited signals due to seven tertiary methyl groups at δ 0.84, 0.93, 1.02×2, 1.14, 1.18 and 1.37 (each 3H, s), three acetyl groups at δ 2.04, 2.05 and 2.07 (each 3H, s), two methine protons at δ 2.37 (1H, s) and 2.84 (1H, br d, J=13.6 Hz), a hydroxymethyl group at δ 4.19, 4.34 (2H, ABq, J=11.7 Hz), two oxygenated methine protons at δ 4.60 (1H, dd, J=4.4, 12.1 Hz) and 4.69 (1H, t, J=3.5 Hz), along with an olefinic proton signal at δ 5.66 (1H, s). From the above evidence, the structure of **8** was represented as 3β,22β,24-trihydroxy-11-oxoolean-12-ene and named as complogenin which was identical with the sapogenol of saponins-V and VI isolated from the seeds of *A. complanatus*.[4)] In addition, this sapogenol had been synthetically derived from hederagenin by Kitagawa *et al.*[16)] Since this aglycone had not been obtained by acid hydrolysis, no datum was described in the preceding paper.[4)] Here, the new sapogenol, complogenin (**8**), was the first to be unambiguously characterized.

In the ^{1}H-NMR spectrum of **6**, three anomeric proton signals appeared at δ 5.03 (1H, d, J=8.1 Hz), 5.71 (1H, d, J=7.7 Hz) and 6.37 (1H, br s), together with signals that arose from seven tertiary methyl groups at δ 0.97, 1.10, 1.14, 1.18, 1.24, 1.45, 1.56 (all 3H, s), a secondary methyl group at δ 1.84 (3H, d, J=6.2 Hz) and an olefinic proton at δ 5.82 (1H, s). Moreover, signals derived from the sapogenol moiety suggested that **6** was a 3-*O*-monodesmoside in comparison with those of **8**, and that others caused from the sugar part were superimposable on those of astragaloside VIII[17)] in the ^{13}C-NMR spectrum (Table I) of **6**. The methyl ester (**6a**) of **6** was obtained as a white powder, $[\alpha]_D$ +1.2° (pyridine), showing a peak due to $[M+H]^+$ at *m/z* 941 in the positive FAB-MS, was iden-

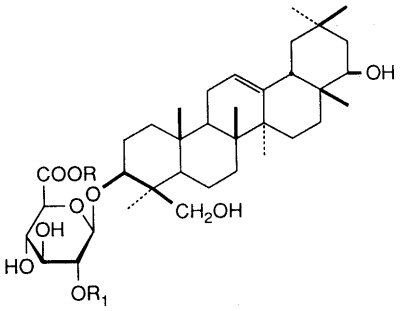
TABLE I. ^{13}C-NMR Spectral Assignments for Compounds **1**—**7**, **6a**, **7a** and Complogenin **8** (in Pyridine-d_5)

	1	**2**	**3**	**4**	**5**	**6**	**6a**	**7**	**7a**	**8**
C- 1	38.6	38.7	38.6	38.7	38.7	39.5	39.2	39.3	39.2	39.5
C- 2	26.5[a]	26.4[a]	26.3[a]	26.4[a]	26.5[a]	26.7	26.6[a]	26.7	26.6	28.4
C- 3	91.3	91.0	90.7	90.5	89.0	91.0	90.9	91.1	91.2	79.8
C- 4	44.0	44.0	43.8	44.1	44.4	44.7	44.5	44.3	44.2	43.5
C- 5	56.2	56.1	56.1	56.1	56.1	56.1	56.0	55.8	55.8	55.9
C- 6	18.6	18.6	18.6	18.7	18.9	17.9	17.7	17.7	17.7	18.3
C- 7	33.3	33.3	33.3	33.3	33.5	33.2	33.1	33.1	33.0	33.4
C- 8	40.0	40.0	39.8	40.0	40.0	44.0	44.0	44.0	43.9	43.9
C- 9	47.9	47.8	47.8	47.8	47.8	61.8	61.6	61.7	61.7	62.1
C-10	36.5	36.5	36.4	36.5	36.6	37.0	36.8	36.8	36.8	37.3
C-11	24.1	24.0	24.0	24.0	24.1	199.4	199.4	199.3	199.3	199.5
C-12	122.9	122.4	123.2	122.4	122.5	128.5	128.2	128.4	128.3	128.4
C-13	144.8	144.8	144.8	144.8	144.8	169.7	169.9	169.8	169.9	169.7
C-14	42.4	42.4	42.3	42.4	42.4	45.4	45.4	45.4	45.3	45.5
C-15	26.7[a]	26.7[a]	26.6[a]	26.7[a]	26.9[a]	26.7	26.7[a]	26.7	26.6	26.6
C-16	28.6	28.6	28.7	28.7	28.7	27.9	27.9	27.9	27.8	27.9
C-17	38.0	38.0	37.9	38.0	38.0	37.8	37.7	37.8	37.7	37.7
C-18	45.3	47.8	45.4	47.8	45.4	45.2	45.2	45.5	45.4	45.5
C-19	46.8	46.8	46.7	46.8	46.8	45.2	45.0	45.2	45.1	45.2
C-20	30.9	30.9	30.8	30.9	30.9	30.9	30.8	30.9	30.9	30.8
C-21	42.4	42.4	42.0	42.3	42.3	42.0	42.0	42.0	42.0	42.0
C-22	75.6	75.6	75.0	75.6	75.6	74.9	74.8	74.8	74.8	74.8
C-23	23.0	23.0	22.6	22.6	22.7	23.1	22.9	23.0	23.0	23.5
C-24	63.6	63.5	63.3	63.3	63.3	62.8	62.6	63.5	63.4	62.1
C-25	15.8	15.8	15.7	15.8	15.8	16.6	16.5	16.9	16.8	17.3
C-26	17.0	17.0	17.0	17.0	17.1	19.0	18.8	19.0	18.8	18.7
C-27	25.7	25.7	25.5	25.7	25.7	23.0	23.0	23.1	22.9	23.0
C-28	28.7	28.7	28.7	28.7	28.7	28.3	28.2	28.3	28.1	28.4
C-29	33.3	33.3	33.0	33.3	33.3	33.1	33.0	33.1	33.0	33.0
C-30	21.2	21.2	21.0	21.2	21.2	21.7	21.6	21.7	21.6	21.6
Glc A										
C-1	105.5	105.5	104.8	105.3	106.5	105.5	105.4	105.5	105.5	
C-2	78.3	78.2	78.2	78.9	75.4	78.7	78.7	78.5	78.1	
C-3	76.6[b]	76.6	76.8	76.8	78.1	76.6	76.7	76.5[b]	76.5[b]	
C-4	73.6	74.0	73.2	73.6	73.5	73.9	73.4	73.8	73.4	
C-5	77.7	77.7	77.6	77.9	78.1	77.7	77.4	77.8	77.7	
C-6	170.4	170.3	170.4	172.4	172.6	172.4	170.3	172.3	170.2	
COOMe	52.2	52.1	52.3				52.1		52.1	
Gal										
1	101.8		104.8					101.7	101.7	
2	76.6[b]		72.5					76.6[b]	76.5[b]	
3	76.7[b]		75.5					76.5[b]	76.4[b]	
4	71.2		70.5					71.2	71.1	
5	77.0		77.0					77.0	76.9	
6	61.7		62.1					61.8	61.6	
Ara										
1		101.8		104.9						
2		77.7		73.3						
3		75.8		75.0						
4		70.6		70.3						
5		66.9		67.5						
Xyl										
1						102.6	102.4			
2						79.5	79.1			
3						78.2	77.7			
4						70.9	70.6			
5						66.8	66.6			
Rha										
1	102.4	102.4				102.4	102.2	102.5	102.4	
2	72.4	72.4				72.4	72.2	72.4	72.3	
3	72.8	72.7				72.8	72.5	72.8	72.5	
4	74.4	74.3				74.4	74.2	74.4	74.3	
5	69.4	69.5				69.5	69.3	69.4	69.0	
6	19.0	18.9				19.0	18.7	18.7	18.7	

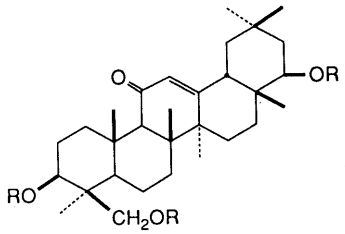
a, *b*) In each vertical column may be interchanged.

tical with saponin-V[4] by comparing their TLC, ^{1}H- and ^{13}C-NMR (Table I) spectra. Based on the above evidence, the structure of **6** was thus constructed as 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-xylopyranosyl(1→2)-β-D-glucuronopyranosyl complogenin.

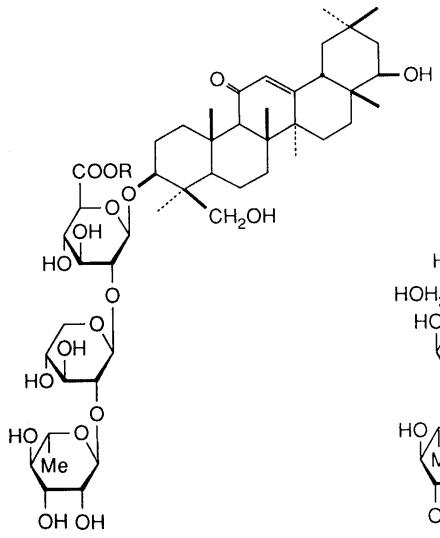
Compound **7** obtained as a white powder, $[\alpha]_D$ −5.0°



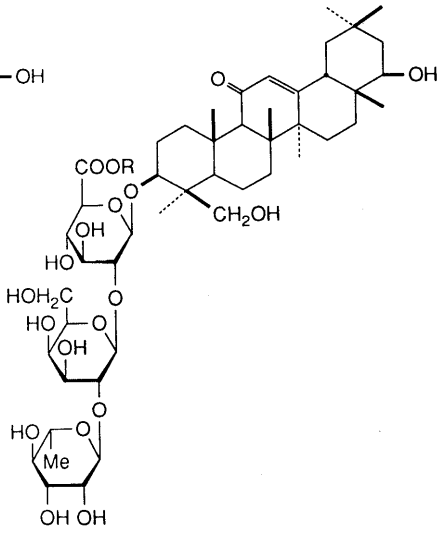
	R	R_1
1	CH_3	-gal$\overset{2}{-}$rha
2	CH_3	-ara$\overset{2}{-}$rha
3	CH_3	gal
4	H	ara
5	H	H



		R
complogenin	(8)	H
	8a	Ac



6 : R=H
6a : R = CH_3



7 : R=H
7a : R = CH_3

(pyridine), showed a peak due to $[M+H]^+$ at *m/z* 957, which was higher by 30 mass units than that of **6** in the positive FAB-MS. Enzymatic hydrolysis of **7** afforded complogenin (**8**) as sapogenol in respect to TLC and ^{1}H-NMR spectrum. Three anomeric proton signals were observed at δ 4.98 (1H, d, J=7.3 Hz), 5.82 (1H, d, J=7.3 Hz) and 6.31 (1H, br s) in the ^{1}H-NMR spectrum of **7**. A comparative study of the ^{13}C-NMR spectrum (Table I) of **7** with that of soyasaponin I led to the identification at the sugar moiety, that is, the sugar moiety of **7** possessed an α-L-rhamnopyranosyl(1→2)-β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl group. The methyl ester (**7a**) of **7**, a white powder, $[\alpha]_d$ +9.6° (MeOH), showing a peak due to $[M+H]^+$ at *m/z* 971 in the positive FAB-MS, was identified with saponin-VI[4] according to TLC, ^{1}H- and ^{13}C-NMR (Table I) spectra. Therefore, the structure of **7** could be represented as 3-*O*-α-L-rhamnopyranosyl(1→2)-β-D-galactopyranosyl(1→2)-β-D-glucuronopyranosyl complogenin.

Experimental

Optical rotations were measured on a JASCO DIP-360 automatic digital polarimeter. The IR spectra were recorded with a Hitachi IR spectrometer, model 270-30. 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- and EI-MS were recorded with a JEOL DX-303 HF spectrometer and taken in a glycerol matrix containing NaI. Thin layer chromatography was performed on precoated Kieselgel 60 F_{254} plate (0.2 mm Merck) and detection was achieved by spraying 10% H_2SO_4 followed by heating. Column chromatography was carried out with MCI gel CHP 20P (Mitsubishi Chem. Ind. Co., Ltd.), Bondapak C_{18} (Waters Associates) and Kieselgel 60 (70—230 and 230—400 mesh, Merck).

Extraction and Separation The dried seeds of *Astragalus sinicus* (15 kg) were extracted with MeOH and then the MeOH extract (383 g) was partitioned between *n*-hexane and 80% MeOH. The 80% MeOH layer was poured into 40% MeOH solution which was further extracted with AcOEt. The 40% MeOH layer was concentrated and subjected to a MCI gel CHP 20P gel column eluting with $H_2O \rightarrow H_2O$–MeOH to afford a number of fractions. A part of the triterpene fractions were treated with excess diazomethane and chromatographed over MCI gel CHP 20P, Bondapak C_{18} and silica gel column chromatographies to give compounds **1** (60 mg), **2** (34 mg), **3** (16 mg), **6a** (175 mg) and **7a** (97 mg). On the other hand, other triterpene fractions were separated by normal and reversed phase column chromatographies to provide compounds **4** (33 mg), **5** (17 mg), **6** (163 mg) and **7** (18 mg).

Compound 1 A white powder, $[\alpha]_D^{25}$ −8.9° (c=0.50, pyridine). Positive FAB-MS *m/z*: 979 $[M+Na]^+$, 957 $[M+H]^+$. ^{1}H-NMR (pyridine-d_5) δ: 0.72, 0.96, 1.00, 1.23, 1.28, 1.30, 1.45 (each 3H, s, *tert*-Me×7), 1.78 (3H, d, J=6.2 Hz, rha Me-6), 3.76 (3H, s, COOMe), 5.31 (1H, br s, H-12), 5.80

(1H, d, J=7.0 Hz, gal H-1), 6.31 (1H, br s, rha H-1), glc A H-1: hidden by H_2O signal. ^{13}C-NMR (pyridine-d_5): Table I. Compound **1** on acid hydrolysis provided a sapogenol identical with soyasapogenol B on TLC. Identified with soyasaponin I methyl ester.

Compound 2 A white powder, $[\alpha]_D^{25}$ −5.3° (c=0.40, pyridine). Positive FAB-MS m/z: 949 $[M+Na]^+$, 649 $[M-rha-ara+H]^+$. ^{1}H-NMR (pyridine-d_5) δ: 0.74, 0.97, 1.01, 1.23, 1.29, 1.31, 1.44 (each 3H, s, *tert*-Me×7), 1.77 (3H, d, J=6.2 Hz, rha Me-6), 3.76 (3H, s, COOMe), 4.95 (1H, d, J=7.3 Hz, glc A H-1), 5.31 (1H, br s, H-12), 5.59 (1H, d, J=7.3 Hz, ara H-1), 6.25 (1H, br s, rha H-1). ^{13}C-NMR (pyridine-d_5): Table I. Compound **2** on acid hydrolysis provided a sapogenol identical with soyasapogenol B on TLC. Identified with soyasaponin II methyl ester.

Compound 3 A white powder, $[\alpha]_D^{25}$ +8.2° (c=0.40, pyridine). Positive FAB-MS m/z: 833 $[M+Na]^+$, 811 $[M+H]^+$, 810 $[M]^+$. ^{1}H-NMR (pyridine-d_6) δ: 0.73, 0.95, 1.00, 1.24, 1.25, 1.30, 1.38 (each 3H, s, *tert*-Me×7), 3.79 (3H, s, COOMe), 4.95 (1H, d, J=8.1 Hz, glc A H-1), 5.28 (1H, br s, H-12), 5.43 (1H, d, J=7.0 Hz, gal H-1). ^{13}C-NMR (pyridine-d_5): Table I. Compound **3** on acid hydrolysis provided a sapogenol identical with soyasapogenol B on TLC. Identified with soyasaponin III methyl ester.

Compound 4 A white powder, $[\alpha]_D^{25}$ +3.0° (c=0.80, pyridine). Positive FAB-MS m/z: 767 $[M+H]^+$, 635 $[M-ara+H]^+$, 456. ^{1}H-NMR (pyridine-d_5) δ: 0.75, 0.96, 1.00, 1.22, 1.28, 1.29, 1.30 (each 3H, s, *tert*-Me×7), 4.95 (1H, d, J=7.3 Hz, glc A H-1), 5.30 (1H, br s, H-12), 5.49 (1H, d, J=7.3 Hz, ara H-1). ^{13}C-NMR (pyridine-d_5): Table I. Compound **4** on acid hydrolysis provided a sapogenol identical with soyasapogenol B on TLC. Identified with soyasaponin IV.

Compound 5 A white powder, $[\alpha]_D^{25}$ +13.5° (c=0.92, pyridine). Positive FAB-MS m/z: 657 $[M+Na]^+$. ^{1}H-NMR (pyridine-d_5) δ: 0.84, 1.00, 1.01, 1.23, 1.30×2, 1.45 (each 3H, s, *tert*-Me×7), 5.17 (1H, d, J=7.7 Hz, glu A H-1), 5.31 (1H, br s, H-12). ^{13}C-NMR (pyridine-d_5): Table I. Compound **5** on acid hydrolysis provided a sapogenol identical with soyasapogenol B on TLC.

Compound 6 A white powder, $[\alpha]_D^{25}$ −7.0° (c=0.50, pyridine). Positive FAB-MS m/z: 949 $[M+Na]^+$, 927 $[M+H]^+$, 781 $[M-rha+H]^+$, 649 $[M-rha-xyl+H]^+$. ^{1}H-NMR (pyridine-d_5) δ: 0.97, 1.10, 1.14, 1.18, 1.24, 1.45, 1.56 (each 3H, s, *tert*-Me×7), 1.84 (3H, d, J=6.2 Hz, rha Me-6), 2.52 (1H, s, H-9), 3.01 (1H, br d, J=13.6 Hz, H-18), 3.44 (1H, dd, J=4.4, 11.7 Hz, H-3), 5.03 (1H, d, J=8.1 Hz, glc A H-1), 5.71 (1H, d, J=7.7 Hz, xyl H-1), 5.82 (1H, s, H-12), 6.37 (1H, br s, rha H-1). ^{13}C-NMR (pyridine-d_5): Table I.

Enzymatic Hydrolysis of 6 To a solution of **6** (130 mg) in acetate buffer (pH=4.2, 8 ml) was added glycyrrhizinic acid hydrolase (GH) (4 ml) and the mixture was incubated at 40 °C for 4 h. When the hydrolysis had been completed, the hydrolysate was subjected to a MCI gel CHP 20P column eluted with H_2O and MeOH. The MeOH fraction was evaporated to dryness and purified over silica gel column chromatography with *n*-hexane–acetone (2 : 1) to yield **8** (42 mg), colorless needles (MeOH), mp 256—258 °C, $[\alpha]_D^{26}$ +83.6° (c=0.96, $CHCl_3$). UV λ_{max} nm (log ε): 250 (4.86). IR ν_{max}^{KBr} cm^{-1}: 3432 (OH), 1652 (α,β-unsaturated carbonyl). *Anal.* Calcd for $C_{30}H_{48}O_4 \cdot H_2O$: C, 73.47; H, 10.20. Found: C, 73.65; H, 9.95. EI-MS m/z: 472 $[M]^+$, 454 $[M-H_2O]^+$, 289, 135 [McLafferty rearrangement]$^+$ and 248, 224 [retro Diels–Alder fission]$^+$. ^{1}H-NMR ($CDCl_3$) δ: 0.90, 0.94, 1.06, 1.09, 1.11, 1.25, 1.34 (each 3H, s, *tert*-Me×7), 2.33 (1H, s, H-9), 2.80 (1H, br d, J=13.9 Hz, H-18), 3.34, 4.21 (2H, ABq, J=11.0 Hz, H_2-24), 3.46 (1H, dd, J=4.1, 12.0 Hz, H-3), 3.47 (1H, br s, H-22), 5.63 (1H, s, H-12). ^{13}C-NMR (pyridine-d_5): Table I.

Acetylation of 8 A solution of **8** (15 mg) in Ac_2O–pyridine (1 : 1, 2 ml) was allowed to stand at room temperature overnight. The reaction mixture was evaporated by blowing with N_2 gas to afford a residue which was purified by silica gel column chromatography with *n*-hexane–acetone (5 : 1) to yield the triacetate (**8a**, 8 mg), colorless plates (MeOH), mp 265—267 °C, $[\alpha]_D^{26}$ +128.8° (c=0.84, $CHCl_3$). EI-MS m/z: 598 $[M]^+$, 583 $[M-CH_3]^+$, 538 $[M-AcOH]^+$, 478 $[M-2\times AcOH]^+$, 331, 135 [McLafferty rearrangement]$^+$, 290, 247 [retro Diels–Alder fission]$^+$. ^{1}H-NMR ($CDCl_3$) δ: 0.84, 0.93, 1.02×2, 1.14, 1.18, 1.37 (each 3H, s, *tert*-Me×7), 2.04, 2.05, 2.07 (each 3H, s, AcO×3), 2.37 (1H, s, H-9), 2.84 (1H, br d, J=13.6 Hz, H-18), 4.19, 4.34 (2H, ABq, J=11.7 Hz, H_2-24), 4.60 (1H, dd, J=4.4, 12.1 Hz, H-3), 4.69 (1H, t, J=3.5 Hz, H-22), 5.66 (1H, s, H-12).

Compound 6 Methyl Ester (6a) A white powder, $[\alpha]_D^{25}$ +1.2° (c=0.50, pyridine). Positive FAB-MS m/z: 963 $[M+Na]^+$, 941 $[M+H]^+$. ^{1}H-NMR (pyridine-d_5) δ: 0.97, 1.08, 1.14, 1.15, 1.22, 1.43, 1.52 (each 3H, s, *tert*-Me×7), 1.84 (1H, d, J=6.2 Hz, rha Me-6), 2.50 (1H, s, H-9), 3.00 (1H, br d, J=13.6 Hz, H-18), 3.43 (1H, dd, J=4.4, 11.7 Hz, H-3), 3.77 (3H, s, COOMe), 4.98 (1H, d, aJ=7.7 Hz, glc A H-1), 5.82 (1H, br s, H-12), 6.29 (1H, br s, rha H-1), xyl H-1: hidden by H_2O signal. ^{13}C-NMR (pyridine-d_5): Table I.

Compound 7 A white powder, $[\alpha]_D^{26}$ −5.0° (c=0.50, pyridine). Positive FAB-MS m/z: 957 $[M+H]^+$, 811 $[M-rha+H]^+$, 649 $[M-rha-gal+H]^+$. ^{1}H-NMR (pyridine-d_5) δ: 0.97, 1.09, 1.11, 1.15, 1.24, 1.44, 1.47 (each 3H, s, *tert*-Me×7), 1.81 (3H, d, J=6.2 Hz, rha Me-6), 2.50 (1H, s, H-9), 2.99 (1H, br d, J=13.6 Hz, H-18), 3.40 (1H, dd, J=4.4, 11.7 Hz, H-3), 4.98 (1H, d, J=7.3 Hz, glc A H-1), 5.81 (1H, s, H-12), 5.82 (1H, d, J=7.3 Hz, gal H-1), 6.31 (1H, br s, rha H-1). ^{13}C-NMR (pyridine-d_5): Table I.

Enzymatic Hydrolysis of 7 To a solution of **7** (10 mg) in acetate buffer (pH=4.2, 2 ml) was added GH (1 ml) treated in the same manner as described for **6** to afford a sapogenol, which was identical with complogenin (**8**) by TLC and ^{1}H-NMR spectrum.

Compound 7 Methyl Ester (7a) A white powder, $[\alpha]_D^{26}$ +9.6° (c=0.50, MeOH). Positive FAB-MS m/z: 971 $[M+H]^+$, 825 $[M-rha+H]^+$, 663 $[M-rha-gal+H]^+$, 473 $[M-rha-gal-glc\ A\ (Me)+H]^+$. ^{1}H-NMR (pyridine-$d_5$) δ: 0.97, 1.09, 1.10, 1.15, 1.23, 1.43, 1.45 (each 3H, s, *tert*-Me×7), 1.80 (1H, d, J=6.2 Hz, rha Me-6), 2.49 (1H, s, H-9), 3.00 (1H, br d, J=13.6 Hz, H-18), 3.40 (1H, dd, J=4.0, 11.7 Hz, H-3), 3.75 (3H, s, COOMe), 4.94 (1H, d, J=7.3 Hz, glc A H-1), 5.76 (1H, d, J=7.3 Hz, gal H-1), 5.81 (1H, s, H-12), 6.26 (1H, br s, rha H-1). ^{13}C-NMR (pyridine-d_5): Table I.

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