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Studies on the Constituents of *Xanthoceras sorbifolia* BUNGE. II. Major Sapogenol and a Prosapogenin from the Fruits of *Xanthoceras sorbifolia* BUNGE[1)]

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The main sapogenol and a prosapogenin from the fruits of *Xanthoceras sorbifolia* BUNGE (Sapindaceae) were examined. On the basis of chemical and spectral analyses, the structure of the new sapogenol obtained by acid hydrolysis of crude saponin fraction was established to be 21β,22α-diangeloyloxy-3β,15α,16α,28-tetrahydroxyolean-12-ene (=21,22-di-*O*-angeloyl-R_1-barrigenol) (**1**). The structure of the prosapogenin was identified as 21β-(3,4-di-*O*-angeloyl-β-D-fucopyranosyl)oxy-3β,16α,22α,24,28-pentahydroxyolean-12-ene (napoleogenin B) (**6**) on the basis of spectral and X-ray crystal diffraction analyses.

Keywords——*Xanthoceras sorbifolia*; Sapindaceae; X-ray diffraction; R_1-barrigenol; 21,22-di-*O*-angeloyl-R_1-barrigenol; napoleogenin B

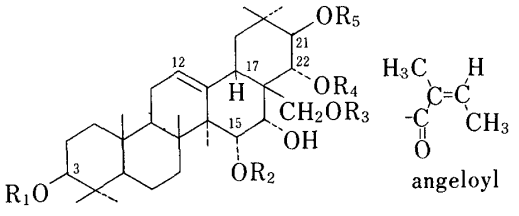
Xanthoceras sorbifolia BUNGE (Sapindaceae) is a shrub mainly growing in Inner mongolia, China. Its bark and fruits are used to treat rheumatism and enuresis of children as a folk medicine in China. We have previously studied the constituents of the fruits of this plant and identified phenolic acid, coumarin and coumarin glucoside constituents.[1)] This paper deals with the structure elucidation of the main sapogenol and a prosapogenin isolated from the hydrolyzates of the crude saponin fraction.

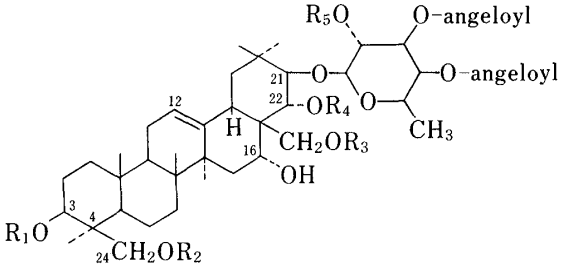
In regard to the saponin constituents, xanthoceras-saponin was isolated by Chirva.[2)] The sapogenol was gypsogenin and the sugar were arabinose, galactose, glucose and glucuronic acid.

We have examined the sapogenol and prosapogenin constituents of the fruits and identified a new sapogenol, 21,22-di-*O*-angeloyl-R_1-barrigenol (**1**) and a prosapogenin, napoleogenin B (**6**).

On acid hydrolysis, the crude saponin fraction, obtained from a methanolic extract of fruits of *Xanthoceras sorbifolia* BUNGE by droplet counter-current chromatography (d.c.c.), afforded a mixture of sapogenols and prosapogenins. The mixture was chromatographed on silica gel to give compounds **1** and **6** in yields of 5 and 4%, respectively (calculated from the crude saponin) as well as another 8 minor sapogenols and prosapogenins.

Compound **1** was obtained as colorless needles. The high resolution mass spectrum (MS) and elemental analysis of **1** suggested the molecular formula $C_{40}H_{62}O_8$. On acetylation under usual conditions, it furnished a triacetate (**2**), in which one hydroxyl group was unaffected.[3)] The nuclear magnetic resonance (NMR) spectrum and MS indicated that **2** possesses an olean-12-ene skeleton. In the ^{1}H-NMR spectrum of **2**, a triplet-like signal at 4.53 ppm can be assigned to $C_{(3)}$-α-H geminal to an acetoxyl.[4)] An acetoxyl and the unaffected hydroxyl form a





	R_1	R_2	R_3	R_4	R_5
1:	H	H	H	angeloyl	angeloyl
2:	Ac	Ac	Ac	angeloyl	angeloyl
3:	H	H	H	H	H
4:	Ac	Ac	Ac	Ac	Ac
5:	Ac	Ac	Ac	H	Ac

6: $R_1=R_2=R_3=R_4=R_5=H$
7: $R_1=R_2=R_3=R_4=R_5=Ac$

Chart 1

monoacetylated α-glycol system at $C_{(15)}$ and $C_{(16)}$ on the basis of two doublets at 5.12 and 4.28 ppm with $J=4$ Hz.[3] The AB quartet signals at 3.80 and 3.96 ppm (2H, each $J=12$ Hz) indicate the presence of an equatorial primary carbinol at $C_{(17)}$.[4,5] Another AB quartet at 5.58 and 5.88 ppm with $J=10$ Hz, assigned to $C_{(22)}$ and $C_{(21)}$ protons, indicated the existence of ester groups at $C_{(21)}$ and $C_{(22)}$. On irradiating the signal of $C_{(28)}\underline{H}_2OAc$, the integral area of $C_{(22)}H$ increased by 46%, so the $C_{(22)}$ proton should be β-proton and the $C_{(21)}$ proton, which is coupled to $C_{(22)}$β-H with $J=10$ Hz, should be an α-proton in axial orientation. Therefore the two ester groups at $C_{(21)}$ and $C_{(22)}$ constitute a diesterified *trans*-diequatorial α-glycol moiety. This result is consistent with the work of Kitagawa *et al.*[6,7] Based on these observations, the skeleton of compound **1** can be assigned as 3β,15α,16α,21β,22α,28-hexahydroxyolean-12-ene (R_1-barrigenol).

The infrared (IR) spectrum of **1** reveals the existence of an α,β-unsaturated ester (1700, 1635 cm^{-1}) and the NMR data of **2** suggested the presence of two angeloyl functions: two olefinic protons at 6.00 ppm (2H, diffused quartet, $J=7$ Hz), two vinylic methyls at 1.95 ppm (6H, d, $J=7$ Hz) and other two vinylic methyls at 1.85 ppm (6H, br s) can be assigned to the β-H, β-CH_3 and α-CH_3 of two angeloyl functions, respectively.[8] The presence of two angeloyl groups is supported by the ^{13}C-NMR data for **1** as follows: the signals at 168.1 and 167.7 ppm showed the presence of two ester carbonyl groups. The signals at 128.9, 129.1, 135.8 and 137.4 ppm are due to α- and β-vinylic carbons of two α,β-unsaturated esters. It has become clear that compound **1** is R_1-barrigenol esterified by two angelic acid moieties and the structure of **1** is very similar to that of 21-*O*-angeloyl-R_1-barrigenol established by Kitagawa *et al.*[3] The positions to which the angeloyl groups are linked to R_1-barrigenol were established by comparison of the NMR data of **1** and its triacetate (**2**). The results showed that only the two protons at $C_{(21)}$ and $C_{(22)}$ exhibit no acetylation shifts (Table I), so R_1-barrigenol is esterified through the $C_{(21)}$β- and $C_{(22)}$α-hydroxyl groups by two angelic acid moieties. Therefore the structure of compound **1** is determined to be 21β,22α-diangeloyloxy-3β,15α,16α,28-tetrahydroxyolean-12-ene (21,22-di-*O*-angeloyl-R_1-barrigenol).

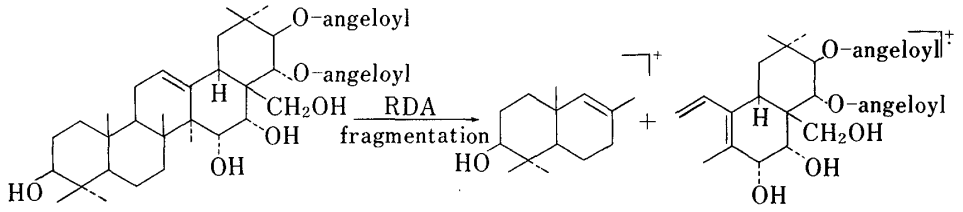
This structure was confirmed by the MS analyses and the alkaline hydrolysis of **1**. The MS of **1** exhibits two sets of characteristic fragments derived from a primarily retro Diels–Alder cleavage,[9] together with their secondary fragment ions as given in Fig. 1. The presence of angeloyl groups was also verified by the base peak at *m/z* 83 ($C_4H_7CO^+$).

The alkaline hydrolysis of **1** furnished **3**, the ^1H-NMR data of which are fully consistent with those of R_1-barrigenol.[10] On usual acetylation, **3** afforded **4** and **5**. The ^1H-NMR data of

TABLE I. ^{1}H-NMR Data for **1**, **2** and **3** in Pyridine-d_5

	1	**2**	**3**	$\Delta\delta$ (**2**−**1**)	$\Delta\delta$ (**1**−**3**)
$C_{(3)}\alpha$-H	3.48 (1H, t-like)	4.63 (1H, t-like)	3.44 (1H, t-like)	+1.15	+0.04
$C_{(15)}\beta$-H	4.27 (1H, d, J=4 Hz)	5.45 (1H, d, J=4 Hz)	4.44 (1H, d, J=4 Hz)	+1.18	−0.17
$C_{(16)}\beta$-H	4.45 (1H, d, J=4 Hz)	4.92 (1H, d, J=4 Hz)	4.96 (1H, d, J=4 Hz)	+0.47	−0.51
$C_{(21)}\alpha$-H	6.70 (1H, d, J=11 Hz)	6.62 (1H, d, J=11 Hz)	4.84 (1H, d, J=10 Hz)	−0.08	+1.86
$C_{(22)}\beta$-H	6.28 (1H, d, J=11 Hz)	6.00 (1H, d, J=11 Hz)	4.61 (1H, d, J=10 Hz)	−0.28	+1.67
$C_{(28)}\beta$-H_2	3.55 (1H, d, J=12 Hz)	4.24 (1H, d, J=12 Hz)	3.80 (1H, d, J=12 Hz)	+0.69	−0.25
	3.80 (1H, d, J=12 Hz)	4.52 (1H, d, J=12 Hz)	4.12 (1H, d, J=12 Hz)	+0.72	−0.32

$\Delta\delta$ (**2**−**1**): acetylation shift = δ (compound **2**) − δ (compound **1**).
$\Delta\delta$ (**1**−**3**): upfield shift = δ (compound **1**) − δ (compound **3**).



m/z 670 (1) *m/z* 207 (a) *m/z* 462 (b)

m/z	intensity (%)	assignment	*m/z*	intensity (%)	assignment
670	0.2	M^+	462	1.5	b
652	0.5	$M-H_2O$	444	1.0	$b-H_2O$
634	0.4	$M-2H_2O$	207	11.0	a
570	1.5	652 − angeloyl + H	189	6.6	$a-H_2O$
569	1.5	652 − angeloyl	83	100.0	angeloyl
552	1.6	634 − angeloyl + H	55	46.8	$Me-\overset{+}{C}=CH-Me$

Fig. 1. Mass Fragmentation of **1**

4 are identical with those of the pentaacetate of R_1-barrigenol.[3,10] The positions of the two angeloyl groups were further confirmed by comparison of NMR data for **3** with those for **1**. The results showed that the two protons at $C_{(21)}$ and $C_{(22)}$ have the largest up-field shifts on going from **1** to **3** (Table I).

Compound **6**, $C_{46}H_{72}O_{12}$, colorless needles. On acetylation, **6** furnished a pentaacetate (**7**), in which one OH was unaffected. The NMR spectra suggest that both **6** and **7** possesses an olean-12-ene skeleton. Thus the signals at 143.8 and 123.7 ppm in the ^{13}C-NMR spectrum of **6** indicate the presence of a double bond between $C_{(12)}$ and $C_{(13)}$.[11] In the ^{1}H-NMR spectrum of **7**, the peaks at 4.61 (1H, m, $C_{(3)}\alpha$–H), 4.24 (1H, m, $C_{(16)}\beta$–H), 5.41 (1H, d, J=10 Hz, $C_{(22)}\beta$–H) and 3.90 ppm (1H, d, J=10 Hz, $C_{(21)}\alpha$–H) indicate the presence of $C_{(3)}\beta$–OAc, $C_{(16)}\alpha$–OH, $C_{(22)}\alpha$–OAc and a 21β-oxygen group. The ABq signals at 4.13, 4.44 ppm (2H, J= 12 Hz) and the broad singlet (2H) at 3.84 ppm were assigned to $C_{(24)}\underline{H}_2$ OAc and $C_{(28)}\underline{H}_2$OAc, respectively.

Next, the peaks at 1.79 (6H, br s, α-CH_3), 1.99 (6H, d, J=7 Hz, β-CH_3) and 6.14, 6.16 ppm (1H, each, q, J=7 Hz, β-H) indicate the presence of two angeloyl groups in **7**. On acid hydrolysis, **6** gave fucose. Thus it become clear that **6** is a prosapogenin which consists of 3β,16α,21β,22α,24,28-hexahydroxyolean-12-ene linked with fucose and two angeloyl groups. The full structure of **6** was definitively established by X-ray diffraction analysis utilizing direct methods for 4151 observed reflections (Fig. 2). The crystal data were: formula= $C_{46}H_{72}O_{12}\cdot 2H_2O$, orthorhombic, space group $P2_12_12_1$, Z=4. Lattice constants, a=19.942

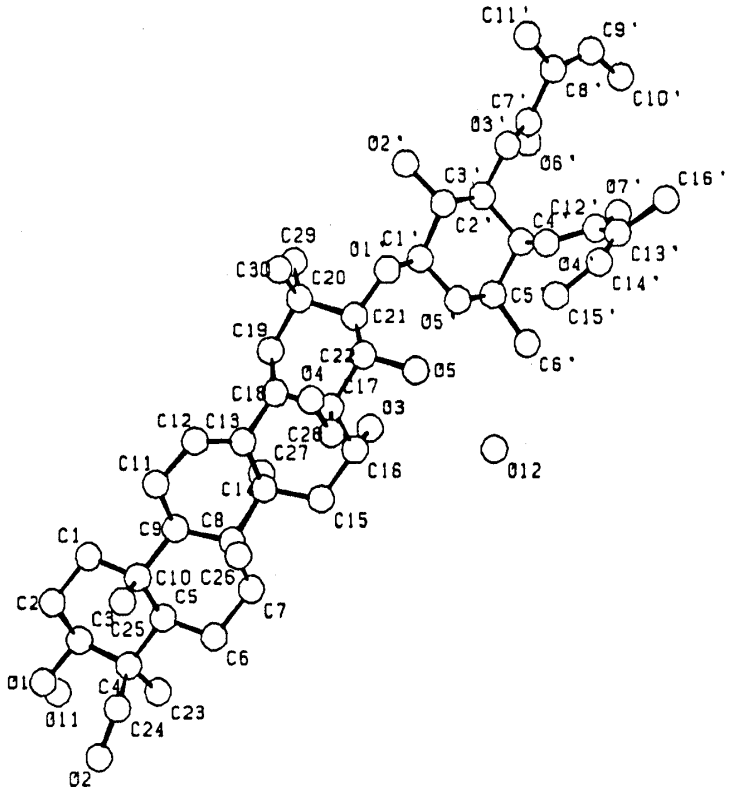


Fig. 2. X-Ray Structure of **6**

(10), $b=33.359$ (16), $c=6.998$ (4) Å, $V=4655$ Å^3. The final R value was 0.067, including 60 heavier atoms and 76 hydrogen atoms. Consequently the structure of **6** was characterized as 21β-(3,4-di-*O*-angeloyl-β-D-fucopyranosyl)oxy-3β,16α,22α,24,28-pentahydroxyolean-12-ene(napoleogenin B). Napoleogenin B has been isolated by Kapundu *et al.* from the seeds of *Napoleonaea vogelii* in acetylated form.[12] This is the first report of isolation of th free form from the fruits of *Xanthoceras sorbifolia.*

Experimental

All melting points were measured on a Yanagimoto microscope hot plate and are uncorrected. Ultraviolet (UV) spectra were taken with a Shimadzu UV-240 spectrometer. MS were recorded on a JEOL DX-300 mass spectrometer. ^{1}H-NMR spectra were determined on a MH-100 spectrometer and ^{13}C-NMR spectra were measured on a JEOL JNM-FX-100 spectrometer using tetramethylsilane (TMS) as internal standard; chemical shifts are given in δ (ppm). Gas-liquid chromatography (GLC) were performed on a Shimadzu GC-6A gas chromatograph, using 2% OV-17 on Chromosorb VAN-DMCS (3 mm × 2 m column) for analysis of TMS-sugar.

Isolation of Saponin from Fruits of *Xanthoceras sorbifolia* BUNGE——Fruits (2.5 kg) were extracted with MeOH (5 l × 6) at room temperature. The combined extracts (193 g) were partitioned between *n*-BuOH (1 l) and H_2O (1 l). The *n*-BuOH soluble portion was fractioned by d.c.c. using a $CHCl_3$–MeOH–H_2O (35 : 65 : 40) solvent system (upper layer as the mobile phase, lower layer as the stationary phase). The saponin fractions were collected and combined. Removal of the solvents by evaporation gave the crude saponins (6 g).

Isolation of Sapogenol and Prosapogenin——A) A solution of crude saponin (600 mg) in EtOH (15 ml), H_2O (15 ml) and conc. HCl (7.5 ml) was refluxed for 3 h. The precipitate produced was collected and washed with water to give a crude mixture of sapogenols and prosapogenins (250 mg). The crude mixture was chromatographed on silica gel (20 g) and eluted in a stepwise manner with $CHCl_3$–MeOH mixtures [200 : 1 (600 ml), 100 : 1 (250 ml), 50 : 1 (500 ml), 25 : 1 (250 ml), 7 : 3 (100 ml)]. A product obtained by elution with $CHCl_3$–MeOH (200 : 1) mixture was crystallized from MeOH to afford compound **1** (30 mg). A substance obtained by elution with $CHCl_3$–MeOH (50 : 1) mixture was crystallized from MeOH to give compound **6** (24 mg).

B) Crude saponin (250 mg) and snail enzyme (300 mg), prepared from snails according to the method of Schindler *et al.*,[13] were dissolved in NaOAc–HOAc buffer (pH 5, 300 ml) and incubated at 37 °C for 3 d. The

precipitate produced was collected and chromatographed according to the method described above. Compounds **1** (10 mg) and **6** (5 mg) were obtained.

21,22-Di-*O*-angeloyl-R_1-barrigenol (1)——Colorless needles, mp 282—284 °C. $[\alpha]_D^{31}$ +30° (c=0.2, MeOH). *Anal.* Calcd for $C_{40}H_{62}O_8 \cdot H_2O$: C, 69.72; H, 9.29. Found: C, 69.69; H, 9.08. UV λ_{max}^{MeOH} nm (log ε) 215 (4.39). IR ν_{max}^{KBr} cm^{-1}: 3500, 2960, 2930, 2870, 1720, 1700, 1648, 1460, 1385, 1357, 1240, 1165, 1072, 1040, 972, 950, 845, 753, 660. ^{1}H-NMR (pyridine-d_5) δ: 1.01, 1.07 (3H, each s), 1.15 (6H, s), 1.26, 1.36, 1.85 (3H, each, s), 1.78 (6H, br s), 2.00 (6H, d, J=7 Hz). Other signals are given in Table I. ^{13}C-NMR (pyridine-d_5) δ: 168.1, 167.7, 143.6, 137.4, 135.8, 129.1, 128.9, 125.5, 78.6, 78.0, 73.6, 73.4, 67.6, 63.2, 55.6, 48.4, 47.8, 47.3, 47.1, 46.9, 41.5, 41.1, 39.4, 37.4, 36.9, 36.4, 30.0, 29.5, 28.7, 28.2, 24.0, 21.2, 21.0, 20.6, 20.2, 19.1, 17.7, 16.6, 15.9, 15.7. MS m/z (%) 670.4443 (Calcd 670.4444) (M^+, 0.2), 652 ($M-H_2O$, 0.5), 634 ($652-H_2O$, 0.4), 570 (652 − angeloyl + H, 1.5), 569 (652 − angeloyl, 1.5), 552 (634 − angeloyl + H, 1.6), 521 (0.6), 470 (1.0), 462 (b, 1.5), 444 (b − H_2O, 1.0), 362 (5.7), 345 (1.3), 331 (2.7), 313 (5.7), 231 (5.5), 207 (a, 11.0), 190 (7.7), 189 (a − H_2O, 6.6), 147 (5.1), 135 (6.5), 121 (6.2), 119 (5.8), 107 (6.4), 95 (7.6), 83 (angeloyl, 100), 81 (8.6), 55 ($Me-\overset{+}{C}=CH-Me$, 46.8).

21,22-Di-*O*-angeloyl-R_1-barrigenol Triacetate (2)——A solution of 21,22-di-*O*-angeloyl-R_1-barrigenol (**1**) (15 mg) in Ac_2O (1 ml) and pyridine (1 ml) was allowed to stand at room temperature for 16 h. The reaction mixture was poured into ice water and the precipitate formed was chromatographed on silica gel (15 g) with benzene–acetone (15 : 1). The eluate was evaporated and the residue was crystallized from EtOH–H_2O to give the triacetate as colorless needles (15 mg). mp 255—258 °C. ^{1}H-NMR ($CDCl_3$) δ: 0.88, 0.91, 0.96, 0.99, 1.01, 1.12, 1.58 (3H, each, s, $\rangle C-CH_3$), 2.04, 2.07, 2.10 (3H, each, s, $-OCOCH_3$), 4.53 (1H, t-like, $C_{(3)}\underline{H}OAc$), 5.12 (1H, d,[14] J=4 Hz, $C_{(15)}\underline{H}OAc$), 4.28 (1H, d,[15] J=4 Hz, $C_{(16)}\underline{H}OH$), 5.88 (1H, d,[14] J=10 Hz, $C_{(21)}\underline{H}$–O-angeloyl), 5.58 (1H, d,[14] J=10 Hz, $C_{(22)}\underline{H}$–O-angeloyl), 3.80, 3.96 (2H, ABq, J=12 Hz, $C_{(28)}\underline{H}_2OAc$), 5.50 (1H, br s, $C_{(12)}H$), 6.00 (2H, q,[14] J=7 Hz, β-H of two angeloyl moieties), 1.95 (6H, d,[14] J=7 Hz, β-CH_3 of two angeloyl moieties), 1.85 (6H, br s,[14] α-CH_3 of two angeloyl moieties). ^{1}H-NMR (pyridine-d_5): 0.91 (12H, s), 1.09, 1.12, 1.29 (3H, each, s, $\rangle C-CH_3$), 2.01, 2.09, 2.17 (3H, each, s, $-OCOCH_3$), 4.63, (1H, t-like, $C_{(3)}\underline{H}OAc$), 5.45 (1H, d, J=4 Hz, $C_{(15)}\underline{H}OAc$), 4.92 (1H, d, J=4 Hz, $C_{(16)}\underline{H}OH$), 6.62 (1H, d, J=11 Hz, $C_{(21)}\underline{H}$O-angeloyl), 6.00 (1H, d, J=11 Hz, $C_{(22)}\underline{H}$O-angeloyl), 4.24, 4.52 (2H, ABq, J=12 Hz, $C_{(28)}\underline{H}_2OAc$), 5.90 (2H, q, J=7 Hz, β-H of two angeloyl moieties), 2.02 (6H, d,[14] J=7 Hz, β-CH_3 of two angeloyl moieties), 1.82 (6H, br s, α-CH_3 of two angeloyl moieties), 5.57 (1H, br s, $C_{(12)}H$), ^{13}C-NMR (pyridine-d_5) δ: 170.6, 167.6, 167.4, 141.5, 138.0, 137.5, 128.7, 128.5, 127.0, 80.7, 77.7, 74.9, 71.8, 69.3, 68.3, 54.9, 47.2, 46.9, 46.5, 42.3, 41.6, 38.5, 37.8, 37.2, 36.1, 35.2, 29.3, 28.1 23.9, 21.6, 21.1, 20.9, 20.6, 20.5, 20.0, 18.9, 17.6, 17.0, 15.8, 15.7, 15.6. MS m/z (%): 796 (M^+, 10), 736 (18), 696 (12), 658 (11), 576 (20), 353 (23), 249 (25), 189 (60), 83 (100), 55 (90).

Alkaline Hydrolysis of 1——A solution of **1** (25 mg) in 5% KOH–MeOH (5 ml) was refluxed for 1 h, then concentrated to 2 ml and diluted with water (10 ml). The aqueous layer was extracted with EtOAc. After removal of the solvent, the residue was chromatographed on silica gel (10 g) with $CHCl_3$–MeOH (30 : 1) to give **3** (15 mg) as a white powder, mp over 300 °C. ^{1}H-NMR (pyridine-d_5) δ: 0.99, 1.06, 1.12, 1.24, 1.35, 1.39, 1.86 (3H, each s), 3.44 (1H, t-like, $C_{(3)}\underline{H}OH$), 3.80, 4.12 (2H, ABq, J=11 Hz, $C_{(28)}\underline{H}_2OH$), 4.44 (1H, d, J=4 Hz, $C_{(15)}\underline{H}OH$), 4.96 (1H, d, J=4 Hz, $C_{(16)}\underline{H}OH$), 4.61 (1H, d, J=10 Hz, $C_{(22)}\underline{H}OH$), 4.84 (1H, d, J=10 Hz, $C_{(21)}\underline{H}OH$). ^{13}C-NMR (pyridine-d_5) δ: 144.8, 123.8, 78.4, 78.1, 77.2, 72.4, 67.7, 67.5, 55.7, 48.2, 47.9, 47.5, 42.1, 41.5, 39.4, 37.5, 36.8, 36.4, 30.6, 28.8, 28.2, 24.1, 21.2, 19.5, 19.2, 17.6, 16.6, 16.0.

Acetylation of 3——**3** (15 mg) was treated with Ac_2O (1 ml) and pyridine (1 ml) at room temperature for 20 h and the mixture was worked up as usual. The crude products were chromatographed on silica gel (15 g) with benzene–acetone (20 : 1) to give the pentaacetate (**4**) (7 mg) and tetraacetate (**5**) (5 mg). R_1-Barrigenol pentaacetate (**4**), a white powder (MeOH), ^{1}H-NMR ($CDCl_3$) δ: 0.86, 0.89, 0.91, 0.97, 0.99, 1.06, 1.53 (3H, each, s, $\rangle C-CH_3$), 2.01 (6H, s), 2.04, 2.06, 2.09 (3H, each, s, $-OCOCH_3$), 3.72, 3.92 (2H, ABq, J=12 Hz, $C_{(28)}\underline{H}_2OAc$) 4.18 (1H, d,[15] J=4 Hz, $C_{(16)}\underline{H}OH$), 4.50 (1H, t-like, $C_{(3)}\underline{H}OAc$), 5.10 (1H, d, J=4 Hz, $C_{(15)}\underline{H}OAc$), 5.36 (1H, d, J=11 Hz, $C_{(22)}\underline{H}OAc$), 5.66 (1H, d, J=11 Hz, $C_{(21)}\underline{H}OAc$), 5.50 (1H, m, $C_{(12)}H$).

R_1-Barrigenol tetraacetate, a white powder (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 0.85, 0.87, 0.95 (3H, each, s), 0.99 (6H, s), 1.01, 1.51 (3H, each, s), 2.04, 2.06, 2.11, 2.12 (3H, each, s), 3.69, 3.93 (2H, ABq, J=12 Hz, $C_{(28)}\underline{H}OAc$), 4.16 (1H, d, J=4 Hz, $C_{(16)}\underline{H}OH$), 5.10 (1H, d, J=4 Hz, $C_{(15)}\underline{H}OAc$), 4.08 (1H, d, J=11 Hz, $C_{(22)}\underline{H}OH$), 5.18 (1H, d, J=11 Hz, $C_{(21)}\underline{H}OAc$), 4.50 (1H, t-like, $C_{(3)}\underline{H}OAc$), 5.50 (1H, m, $C_{(12)}H$).

Napoleogenin B (6)——Colorless needles (MeOH), mp 262—264 °C, $]\alpha]_D^{30}$ +69.0° (c=0.1, MeOH), UV λ_{max}^{MeOH} nm (log ε) 215 (4.04), IR ν_{max}^{KBr} cm^{-1}: 3460, 2970, 2940, 2930, 2860, 1720, 1648, 1460, 1384, 1375, 1364, 1233, 1155, 1065, 1035, 980, 936, 910, 753, 667. ^{1}H-NMR (pyridine-d_5) δ: 0.94 (6H, s), 1.15 (3H, d, J=7 Hz, $C_{(6')}$–CH_3 of fucose), 1.34, 1.48, 1.53, 1.88 (3H, each, s), 1.82, 1.87 (3H, br s), 1.95 (6H, d, diffused, J=7 Hz), 6.02 (2H, q, J=7 Hz). ^{13}C-NMR (pyridine-d_5) δ: 171.8, 167.3, 143.8, 138.8, 138.3, 128.1, 127.9, 123.7, 106.1, 92.1, 80.1, 74.3, 73.6, 71.1, 70.0, 69.5, 68.0, 66.9, 64.6, 56.4, 48.2, 47.9, 47.2, 43.2, 41.9, 40.5, 40.2, 38.9, 37.8, 37.2, 34.5, 33.5, 29.9, 28.5, 27.5, 24.2, 23.5, 20.8, 20.5, 20.3, 19.1, 16.8, 16.4, 16.2, 16.0, 15.9.

Pentaacetate of Napoleogenin B——Treatment of **6** (10 mg) with Ac_2O (1 ml) and pyridine (1 ml) at room temperature for 15 h followed by column chromatography of the mixture on silica gel (solvent: $CHCl_3$–MeOH 200 : 1) and crystallization of the product from EtOH–H_2O afforded **7** (10 mg), colorless, mp 158—160 °C. UV λ_{max}^{MeOH} nm (log ε): 215 (4.31). ^{1}H-NMR ($CDCl_3$) δ: 0.91, 0.93, 0.99 (3H, each, s), 1.05 (6H, s), 1.40 (3H, s) (all $\rangle C-CH_3$), 1.99, 2.04

(3H, each, s), 2.06 (6H, s), 2.07 (3H, s) (all $-OCOCH_3$), 5.38 (1H, m, $C_{(12)}\underline{H}$), 4.13, 4.44 (2H, ABq, $J=12$ Hz, $C_{(24)}\underline{H}_2OAc$), 3.84 (2H, br s, $C_{(28)}\underline{H}_2OAc$) 4.61 (1H, m, $C_{(3)}\underline{H}OAc$), 4.24 (1H, m, $C_{(16)}\underline{H}OH$), 3.90 (1H, d, $J=10$ Hz, $C_{(21)}\underline{H}O-$), 5.41 (1H, d, $J=10$ Hz, $C_{(22)}\underline{H}OAc$), 1.26 (3H, d, $J=6$ Hz, $-CH_3$ of fucose), 1.79 (6H, br s, α-CH_3 of angeloyl), 1.99 (6H, d, $J=7$ Hz, β-CH_3 of angeloyl), 6.14, 6.16 (1H, each, q, $J=7$ Hz, β-H of angeloyl). ^{13}C-NMR ($CDCl_3$) δ: 170.9, 170.8, 170.6, 169.2, 167.1, 166.5, 141.2, 139.8, 139.2, 127.2, 126.9, 124.1, 102.3, 85.9, 80.1, 72.8, 71.4, 70.1, 69.7, 69.2, 68.7, 65.8, 65.4, 55.9, 46.8, 46.0, 41.0, 39.6, 39.3, 38.5, 36.8, 36.2, 33.3, 28.8, 26.6, 23.6, 22.6, 21.2, 20.8, 20.6, 20.2, 19.2, 19.0, 16.8, 16.2, 15.9, 15.7, 15.4. MS *m/z* (%): 858 (3), 696 (27), 536 (13), 354 (29), 353 (37), 187 (85), 83 (40), 55 (80), 43 (100).

Hydrolysis of 6 with 2 N H_2SO_4–Dioxane–H_2O——A solution of **6** (2 mg) in 2 N H_2SO_4–dioxane–H_2O (2 : 1 : 1) (2 ml) was heated at 100 °C for 5 h. The hydrolyzate was neutralized with $BaCO_3$ and filtered. The filtrate was concentrated and the residue was analyzed by thin layer chromatography (TLC) and GLC. Fucose was identified by comparison with an authentic sample (GLC: retention time, 3.06 and 3.71 min).

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References and Notes

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15) This signal appeared as a multiplet before D_2O addition.