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Studies on the Constituents of *Xanthoceras sorbifolia* BUNGE. IV.[1] Structures of the Minor Prosapogenins

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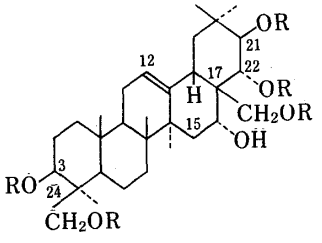
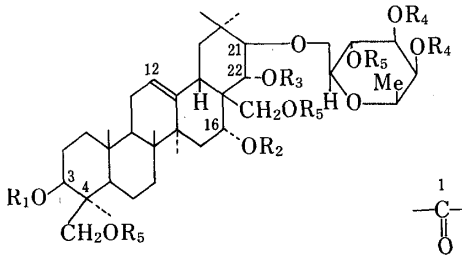
The prosapogenins from the partial hydrolysate of fruit saponin of *Xanthoceras sorbifolia* BUNGE (Sapindaceae) were examined. On the basis of chemical and spectral analyses, compound G was identified as protoaescigenin (**1**). Two new prosapogenins were characterized as 16-*O*-acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-*β*-D-fucopyranosylprotoaescigenin (**5**) and 22-*O*-acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-*β*-D-fucopyranosylprotoaescigenin 3-*O*-*β*-D-glucuronopyranoside (**7**).

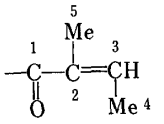
Keywords——*Xanthoceras sorbifolia*; Sapindaceae; protoaescigenin; protoaescigenin fucoside; protoaescigenin glucuronide

Previously, we reported the isolation and characterization of 21,22-di-*O*-angeloyl-R_1-barrigenol, napoleogenin B and three other prosapogenins from the fruits of *Xanthoceras sorbifolia* BUNGE.[1] Further studies on the saponins of fruits have led to the isolation of two new prosapogenins and a known compound, protoaescigenin, from the partial hydrolysate of saponins. We wish to report here the structure elucidation of the two new prosapogenins along with the known compound, protoaescigenin.

On acid hydrolysis, the crude saponin fraction, obtained from a methanolic extract of fruits of *Xanthoceras sorbifolia* 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 A, B, C, D, E, F, G and H. Compound A (21,22-di-*O*-angeloyl R_1-barrigenol) and four other prosapogenins B, C, E and F were characterized previously.[1] Compound G (**1**) was identified as 3*β*,16*α*,21*β*,22*α*,24,28-hexahydroxyolean-12-ene (pro-







1: R=H protoaescigenin
2: R=Ac protoaescigenin pentaacetate

	R_1	R_2	R_3	R_4	R_5
3	H	H	H	H	H
4	H	H	H	angeloyl	H
5	H	Ac	H	angeloyl	H
6	Ac	Ac	H	angeloyl	Ac
7	glc–UA	H	Ac	angeloyl	H

glc–UA: glucuronic acid

angeloyl group

Chart 1

TABLE I. Carbon-13 Chemical Shifts (δ) in Pyridine-d_5

Carbon	1	3	4	5	7
1	39.0	38.9	38.9	38.8	38.9
2	28.5	28.5	28.5	28.4	27.0
3	80.2	80.1	80.1	80.0	89.1
4	43.2	43.2	43.2	43.1	44.3
5	56.4	56.4	56.4	56.3	56.1
6	19.2	19.1	19.1	19.1	19.1
7	33.6	33.5	33.5	33.4	33.2
8	40.1	40.1	40.2	40.1	40.0
9	47.3	47.2	47.2	47.1	47.0
10	37.0[a]	37.2[a]	37.2[a]	37.1[a]	36.5[a]
11	24.2	24.1	24.2	24.1	24.1
12	123.8	123.8	123.7	123.8	123.8
13	144.0	143.9	143.8	141.7	143.0
14	42.1	42.0	41.9	41.3	41.6
15	34.4	34.5	34.5	31.2	34.6
16	67.9	68.0	68.0	70.7	68.7
17	47.4	47.9	48.2	47.1	47.8
18	41.3	40.6	40.5	39.3	40.0
19	48.3	48.3	47.9	47.9	47.8
20	36.5[a]	37.0[a]	37.0[a]	37.0[a]	37.8[a]
21	78.7	92.2	92.1	90.5	85.7
22	77.3	74.0	73.6	71.9	74.4
23	23.6	23.5	23.5	23.5	23.3
24	64.6	64.6	64.6	64.5	63.3
25	16.3[b]	16.2[b]	16.2[b]	16.3[b]	16.1[b]
26	16.9[b]	16.8[b]	16.8[b]	16.7[b]	16.7[b]
27	27.3	27.5	27.5	27.0	27.5
28	68.4	67.4	66.9	64.5	64.0
29	30.6	30.0	29.9	29.9	30.2
30	19.5	20.4	20.3	19.5	20.1
Fuc. 1′		106.7	106.1	105.9	105.4
2′		72.5	70.0	69.9	70.0
3′		75.3	74.3	74.2	74.0
4′		72.7	71.1	71.0	71.6
5′		71.6	69.5	69.6	69.0
6′		17.0	16.4	16.3	16.7
Glc-UA 1″					106.4
2″					75.0
3″					78.1
4″					73.0
5″					76.6
6″					176.8
Ang. 1			167.3	167.3	167.4
			167.3	167.3	167.4
2			127.9	127.8	127.9
			128.1	128.0	128.2
3			138.3	138.4	138.1
			138.8	138.9	138.9
4			20.5	20.5	20.5
			20.8	20.7	20.8
5			15.9	15.9	15.6
			16.0	16.0	15.9
Ac. COMe				169.3	171.7
COMe				22.1	22.0

Assignments indicated by *a*) or *b*) may be reversed in each column. The carbons bearing an OH group were assigned by means of selective proton decoupling experiments. Fuc., fucose; Glc-UA, glucuronic acid; Ang., angeloyl group; Ac., acetoxyl group.

TABLE II. Values of Molecular Rotation

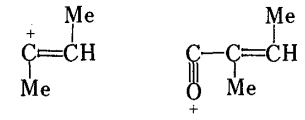
Compound	$[\alpha]_D^{20}$ (°)	$[M]_D^{20}$ (°)	$-\Delta[M]_D$ (°)
3	+9.4	+60.6	−49.2
1	+21.7	+109.8	

The following $[M]_D$ values were used: methyl β-D-fucopyranoside −29°;[12] methyl α-D-fucopyranoside +309°;[12] methyl α-L-fucopyranoside −309°.[12]

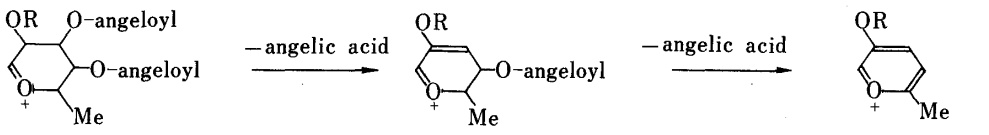
toaescigenin)[2] by comparison with an authentic sample.

Compound D (**5**), on acid hydrolysis, furnished fucose and an aglycone (**1**) identical with protoaescigenin, suggesting that **5** is a triterpenoidal prosapogenin composed of protoaescigenin linked with fucose. On alkaline hydrolysis, **5** gave compound **3**. Comparison of the carbon 13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **3** with that of **1** showed that the C-21 signal of **3** is shifted downfield by 13.5 ppm, while the C-22 signal is shifted upfield by 3.3 ppm (Table I). These shifts can be regarded as glycosidation shifts[3] and thus the location of fucose is assigned to C-21 of protoaescigenin. The β-glycosidic linkage of the fucose was deduced on the basis of application of Klyne's rule[4] to the $[M]_D$ value due to the fucose moiety calculated from the $[M]_D$ values of **1** and **3** (Table II). In the ^{13}C-NMR spectrum of **3**, the signals at 106.7, 72.5, 75.3, 72.7, 71.6 and 17.0, assignable to C-1′, C-2′, C-3′, C-4′, C-5′ and C-6′ of fucose, are coincident with those for methyl β-D-fucopyranoside.[5] It is thus clear that **3** is a protoaescigenin 21-*O*-β-D-fucopyranoside. This was further confirmed by the finding that **3** is identical with the compound obtained by alkaline hydrolysis of napoleogenin B (**4**), whose structure was established by X-ray diffraction analysis.[1]

In the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **5**, the signals at 1.90 (6H, br s), 1.99 (6H, d, J=7 Hz) and 5.97 ppm (2H, q, J=7 Hz) can be assigned to α-Me, β-Me and β-H of two angeloyl functions,[6] respectively. The presence of two angeloyl groups was supported by the ^{13}C-NMR spectrum of **5**, which shows sets of signals for two angeloyl groups (Table I). The fragment ions at m/z 311 in the mass spectrum (MS) of **5** and at 353 in the MS of **6** (pentaacetate of **5**) suggest that the two angeloyl groups are in the fucose moiety (Chart 2).[7] Further comparison of the ^{13}C-NMR data of **5** with those of **4** showed that the signals for two angeloyl groups and fucose in **5** coincide well with those in **4**, indicating the



m/z 55 m/z 83



m/z 311 (R=H)
m/z 353 (R=Ac)

m/z 211 (R=H)
m/z 253 (R=Ac)

m/z 111 (R=H)
m/z 153 (R=Ac)

Chart 2

angeloyl groups to be located at C-3′ and C-4′ of fucose, respectively. The ^{1}H-NMR (2.31 ppm 3H, s, OCOMe) and ^{13}C-NMR (169.3 ppm, OCOMe and 22.1 ppm, OCOMe) spectra suggest the existence of an acetoxyl group in **5**, and this was shown to be located at C-

16 based on the observation of acetylation shifts of the signals due to C-16 (2.7 ppm downfield shift), C-15 (3.3 ppm upfield shift) and C-17 (1.1 ppm upfield shift) in comparison with **4**. On the basis of these observations, compound D (**5**) was established to be 16-*O*-acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-*β*-D-fucopyranosylprotoaescigenin.

Compound H (**7**) contains two sugars, based on the existence of signals of two anomeric carbons at 105.4 and 106.4 ppm in the ^{13}C-NMR spectrum of **7**. Acid hydrolysis of **7** furnished fucose, glucuronic acid and protoaescigenin. On mild acid hydrolysis, **7** gave napoleogenin B (**4**), indicating that a 3,4-di-*O*-angeloyl-*β*-D-fucopyranose moiety is linked to C-21 of protoaescigenin and suggesting **7** to be a glucuronide derivative of **4**. A comparison of the ^{13}C-NMR spectrum of **7** with that of **4** showed that a set of signals assignable to glucuronic acid appeared in the spectrum of **7**. The uronic acid was shown to be linked to C-3 of **4**, based on the observation of glycosidation shifts of the signals due to C-3 (downfield shift by 9.0 ppm) and C-2 (upfield shift by 1.5 ppm). The *β*-configuration of the two sugars, fucose and glucuronic acid, was indicated by the $^1J_{CH}$ values of 153.8 Hz (for the peak at 105.4 ppm) and 158.7 Hz (for the peak at 106.4 ppm), respectively.[8] The ^{1}H-NMR (2.34 ppm, 3H, s, OCOMe) and ^{13}C-NMR (171.7 ppm, OCOMe, 22.0 ppm, OCOMe) spectra indicated the presence of an acetoxyl group in **7**. The position of this group was determined by ^{13}C-NMR analysis. A downfield shift of the signal of C-22 to 74.4 ppm and an upfield shifts of that of C-21 to 85.7 ppm, compared with **4**, showed the acetoxyl group to be located at C-22, according to the acetylation shift rule.[9] This was confirmed by comparison of the C-21 signal of **7** (85.7 ppm) with that of the hexaacetate of napoleogenin [21*β*-(6-deoxy-3,4-diangelate-*β*-glucopyranosyl)oxy-3*β*,16*α*,22*α*,24,28-pentahydroxy-olean-12-ene] (84.3 ppm)[10] and pentaacetate of napoleogenin B (85.9 ppm).[7] On acetylation of 22-OH of napoleogenin, the C-21 signal was shifted upfield by 6.9 ppm (from 91.2 to 84.3 ppm). A similar result was observed in **5** with an upfield shift of 6.4 ppm (from 92.1 ppm in **4** to 85.7 ppm in **7**), indicative of the presence of an acetoxyl group at C-22.

Based on these analyses, **7** was characterized as 22-*O*-acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-*β*-D-fucopyranosylprotoaescigenin 3-*O*-*β*-D-glucuronopyranoside (= 22-*O*-acetylnapoleogenin B 3-*O*-*β*-D-glucuronopyranoside).

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 JNM MH-100 spectrometer and ^{13}C-NMR spectra were measured on a JEOL FX-100 spectrometer using tetramethylsilane (TMS) as an internal standard; chemical shifts are given in δ (ppm). Gas liquid chromatography (GLC) were performed on a Shimadzu GC-6A gas chromatography apparatus, using 2% OV-17 on Chromosorb VAN-DMCS (3 mm × 2 m column) for analysis of TMS-sugars.

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 water (1 l). The BuOH-soluble portion was fractionated 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 Prosapogenins——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)] to give the following compounds:

1) $CHCl_3$–MeOH (200 : 1): Compound A (30 mg) (21,22-di-*O*-angeloyl R_1-barrigenol.[1])

2) $CHCl_3$–MeOH (100 : 1): Compound B (20 mg) [21-*O*-(3′,4′-di-*O*-angeloyl)-*β*-D-fucopyranosylbarringtogenol C].[1]

3) $CHCl_3$–MeOH (50 : 1): a) Compound C (10 mg) [21-*O*-(4′-*O*-acetyl-3′-*O*-angeloyl)-*β*-D-fucopyranosylbarringtogenol C].[1] b) Compound D (**5**) (15 mg). c) Compound E (24 mg) (napoleogenin B).[1]

4) $CHCl_3$–MeOH (25 : 1): Compound F (19 mg) [22-*O*-acetyl-21-*O*-(4′-*O*-acetyl-3′-*O*-angeloyl)-*β*-D-fuco-

pyranosylprotoaescigenin].[1)]

5) $CHCl_3$–MeOH (7:3): a) Compound G (**1**) (10 mg). b) Compound H (**7**) (13 mg).

Protoaescigenin[2)]——Colorless needles, mp over 300 °C. $[\alpha]_D^{20}$ +21.7° (c=0.2, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3430, 2930, 2870, 1635, 1443, 1385, 1375, 1260, 1030, 703. ^{1}H-NMR (pyridine-d_5) δ: 0.95 (6H, s), 1.36, 1.42, 1.57, 1.87 (3H, each s, Me), 3.68 (1H, t-like, H-3), 3.73, 4.06 (2H, ABq, J=11 Hz, H_2-24), 3.70, 4.54 (2H, ABq, J=11 Hz, H_2-28), 4.65 (1H, d, J=10 Hz, H-22), 4.82 (1H, d, J=10 Hz, H-21), 5.06 (1H, m, H-16), 5.46 (1H, m, H-12). ^{13}C-NMR data are given in Table I.

16-*O*-Acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-β-D-fucopyranosylprotoaescigenin (5)——A white powder (MeOH), mp 232—235 °C (dec.). $[\alpha]_D^{19}$ +44.4° (c=0.14, MeOH). *Anal.* Calcd for $C_{48}H_{74}O_{13}\cdot 1/2H_2O$: C, 66.44; H, 8.65. Found: C, 66.12; H, 8.59. UV λ_{max}^{MeOH} nm (log ε): 215 (4.22). IR ν_{max}^{KBr} cm^{-1}: 3430, 2930, 2870, 1740, 1720, 1640, 1450, 1375, 1355, 1235, 1150, 1064, 1040, 845, 752. ^{1}H-NMR (pyridine-d_5) δ: 0.84, 0.91, 1.31, 1.45, 1.51, 1.57 (3H, each s, Me), 1.23 (3H, d, J=7 Hz, Me of fucose), 2.31 (3H, s, OCOMe), 3.66 (1H, t-like, H-3), 4.20 (1H, d, J=10 Hz, H-22), 4.61 (1H, d, J=10 Hz, H-21), 5.46 (1H, m, H-12), 5.73 (1H, m, H-16), 1.90 (6H, br s, α-Me of angeloyl), 1.99 (6H, d, J=7 Hz, β-Me of angeloyl), 5.97 (2H, q, J=7 Hz, β-H of angeloyl). ^{13}C-NMR data are given in Table I. MS m/z (%): 55 (100), 71 (59), 83 (38), 107 (72), 111 (14), 171 (18), 189 (46), 205 (6), 211 (6), 281 (25), 311 (14), 411 (14), 473 (3).

Acid Hydrolysis of 5——A solution of **5** (10 mg) in HCl–H_2O–EtOH (2:1:2) mixture (5 ml) was heated on a water bath for 2 h, then diluted with water (5 ml) and extracted with EtOAc. The water layer was trimethylsilylated and analyzed by GC; TMS-fucose was identified by comparison with an authentic sample (GC, retention time: 3.26 and 3.96 min). The EtOAc extract was chromatographed on a silica gel column with $CHCl_3$–MeOH (15:1) to give **1** (identical with authentic protoaescigenin).

Alkaline Hydrolysis of 5——A solution of **5** (10 mg) in 5% KOH/MeOH was refluxed for 30 min and then the solution was diluted with water (10 ml) and neutralized with hydrochloric acid. The solution was extracted with EtOAc. The EtOAc extract thus obtained was chromatographed on a silica gel column with $CHCl_3$–MeOH (20:1) to give **3** (4 mg) as colorless needles (pyridine–water), mp 297—300 °C. $[\alpha]_D^{20}$ +9.4° (c=0.2, pyridine). *Anal.* Calcd for $C_{36}H_{60}O_{10}\cdot 2H_2O$: C, 62.79; H, 9.30. Found: C, 62.92; H, 9.27. IR ν_{max}^{KBr} cm^{-1}: 3420, 2970, 2930, 2870, 1635, 1443, 1385, 1375, 1175, 1075, 1030, 990, 900, 855, 750, 705. ^{1}H-NMR (pyridine-d_5) δ: 0.95 (6H, s), 1.37 (3H, s), 1.57 (6H, s), 1.88 (3H, s, Me), 3.67 (1H, m, H-3), 3.70, 4.52 (2H, ABq, J=11 Hz, H_2-28), 3.72, 4.04 (2H, ABq, J=11 Hz, H_2-24), 4.62 (1H, d, J=10 Hz, H-22), 4.80 (1H, d, J=10 Hz, H-21), 5.06 (1H, m, H-16), 5.48 (1H, m, H-12). ^{13}C-NMR data are given in Table I.

Acetylation of 5——A solution of **5** (2 mg) in Ac_2O (1 ml) and pyridine (1 ml) was allowed to stand at room temperature for 30 h and treated in the usual manner. The crude product obtained was purified by thin layer chromatography (TLC) with benzene–acetone (10:1) to give the pentaacetate of **5** (1 mg) as colorless needles, mp 160—162 °C. *Anal.* Calcd for $C_{56}H_{82}O_{17}\cdot 1/2H_2O$: C, 64.36; H, 8.05. Found: C, 64.17; H, 8.04. UV λ_{max}^{MeOH} nm (log ε): 215 (4.19). ^{1}H-NMR ($CDCl_3$) δ: 0.90, 0.96 (3H, each), 1.00, 1.25 (6H, each s, Me), 1.20 (3H, d, J=7 Hz, Me of fucose), 1.75, 1.86 (3H, each br s, α-Me of angeloyl), 1.98 (6H, d, J=7 Hz, β-Me of angeloyl) 2.05 (12H, s), 2.06 (3H, s, OCOMe), 3.56 (1H, t-like, H-3), 3.86 (2H, br s, H_2-28), 4.08, 4.36 (2H, ABq, J=12 Hz, H_2-24), 6.06 (2H, q, J=7 Hz, β-H of angeloyl). MS m/z (%) 55 (44), 83 (100), 153 (7), 187 (10), 205 (1), 253 (3), 307 (3), 353 (10), 506 (0.6), 519 (0.8), 536 (1), 579 (0.8), 694 (0.3), 738 (0.3), 795 (0.6), 855 (0.1).

22-*O*-Acetyl-21-*O*-(3′,4′-di-*O*-angeloyl)-β-D-fucopyranosylprotoaescigenin 3-*O*-β-D-Glucuronopyranoside (7)——A white powder (MeOH), mp 271—273 °C. $[\alpha]_D^{25}$ +14.7° (c=0.1, pyridine). *Anal.* Calcd for $C_{54}H_{82}O_{19}\cdot 2H_2O$: C, 60.56; H, 8.04. Found: C, 60.42; H, 8.01. UV λ_{max}^{MeOH} nm (log ε): 215 (4.01). IR ν_{max}^{KBr} cm^{-1}: 3430, 2930, 2850, 1737, 1720, 1700, 1635, 1460, 1386, 1260, 1160, 1066, 1040, 980. ^{1}H-NMR (pyridine-d_5) δ: 0.89 (6H, s), 1.02, 1.34, 1.39, 1.88 (3H, each s, Me), 1.20 (3H, d, J=7 Hz, Me of fucose), 2.34 (3H, s, OCOMe), 1.87, 1.96 (3H, each br s, α-Me of angeloyl), 1.94, 2.00 (3H, each d, J=7 Hz, β-Me of angeloyl), 5.92, 6.10 (1H, each q, J=7 Hz, β-H of angeloyl). ^{13}C-NMR data are given in Table I. MS m/z (%): 43 (84), 55 (76), 83 (100), 111 (52), 205 (13), 211 (65), 311 (75), 453 (6), 482 (2), 493 (1.4), 508 (1.6), 513 (2.1), 555 (0.7), 637 (0.1).

Acid Hydrolysis of 7——A solution of **7** (5 mg) in HCl–H_2O–EtOH (1:1:3) mixture (10 ml) was refluxed for 6 h and then the solution was neutralized and evaporated to dryness. The residue was partitioned between water (20 ml) and EtOAc (20 ml). The water layer was divided into two parts. One part was evaporated to dryness *in vacuo*. The residue was reacted with TMS reagent and then analyzed by GC; the retention times (3.25, 3.96 min) were in agreement with those of authentic fucose. The other part was analyzed according to Hulyalkar,[11)] and was found to contain glucuronic acid, retention time 10.41 min (2,3,5,6-tetra-*O*-trimethylsilyl-L-gulono-1,4-lactone). The EtOAc extract was chromatographed on a column of silica gel (5 g) with $CHCl_3$–MeOH (30:1) mixture to give compound **1** (1 mg), which was identical with authentic protoaescigenin.

Partial Acid Hydrolysis of 7——A sample of **7** (10 mg) was hydrolyzed by refluxing it with an HCl–H_2O–EtOH (1:2:2) mixture (20 ml) on a water bath for 2 h. The hydrolysate was diluted with water and extracted with EtOAc. The EtOAc extract was chromatographed on a silica gel column with $CHCl_3$–MeOH (25:1) to give **4** (3 mg) and **1** (1.2 mg), which were identified as napoleogenin B and protoaescigenin, respectively.

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References and Notes

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