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Steroidal Saponins from the Rhizomes of *Smilax china*

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Abstract—Five known diosgenin glycosides have been isolated from the MeOH extract of *Smilax china* rhizomes and characterized as prosapogenin A of dioscin, dioscin, gracillin, methyl protogracillin, methyl protodioscin and its corresponding 22-hydroxy analog. This is the first isolation of the former four compounds from this plant. β-Sitosterol glucoside was also isolated and identified.

Keywords—*Smilax china* • Liliaceae • steroidal saponin • prosapogenin A of dioscin • dioscin • gracillin • methyl protogracillin • methyl protodioscin • protodioscin • β-sitosterol glucoside

The rhizomes of *Smilax china* L. (Liliaceae) has been used in treating gout, scrofula, frambesia, and menorrhagia.[1] Phytochemical work on this plants has been done and the isolation of smilax saponin B as a major component has been reported.[2] However, no detailed chemical investigation appears to have been performed on *Smilax china* rhizomes. This paper reports the isolation and characterization of five steroidal saponins together with β-sitosterol glucoside.

The BuOH soluble fraction after defatted with benzene from the MeOH extract of the rhizomes of *Smilax china*, on repeated chromatographic purification, afforded six glycosides, tentatively designated as compounds I~VI in increasing order of polarities on silica gel TLC.

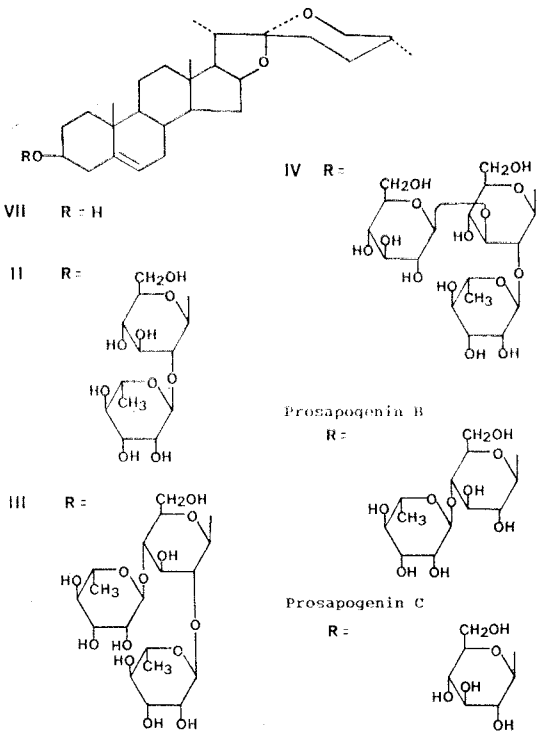
Compound I, mp 298~300°, showed a strong absorption band of hydroxyl groups at 3420 cm^{-1} in its IR spectrum. On acid hydrolysis, I gave β-sitosterol and glucose. Accordingly, compound I was considered to be β-sitosterol glucoside. Acetylation of I with Ac_2O/pyridine gave tetraacetate, mp 163~4°, which was identical with an authentic sample by its mp and IR and ^{1}H-NMR spectra. However, mass spectral data suggested that compound I was a mixture of a small amount of stigmasterol and β-sitosterol glucosides.

Compound II, mp 238~240°, showed characteristic absorption bands of the 25(R)-spiroketal moiety[3] in the IR spectrum at 920, 900, 865 and 837 cm^{-1} (intensity 900>920). Acid hydrolysis of II yielded rhamnose and glucose together with an aglycone, diosgenin (Ⅶ) and ^{1}H-NMR spectrum of II exhibited two anomeric proton signals at δ 4.92 (1 H, d, J=7.2 Hz) and 6.20 (1 H, s) (see Table I) indicating the presence of one mole each of β-glucosyl and α-rhamnosyl linkages in II. ^{13}C-NMR spectrum of II provided the information about the points of attachment in the saccharide part. The presence of an upfield anomeric signal at δ100.3 and the signals due to glucose C-2 (+4.5 ppm) and C-3 (−0.8 ppm) indicated that the terminal rhamnosyl group was linked to

glucose C-2 which in turn attached at C-3 of diosgenin. Therefore the structure of compound II could be designated as diosgenin 3-O-α-L-rhamnopyranosyl (1→2)-β-D-glucopyranoside. This was confirmed by direct comparison with an authentic sample, prosapogenin A which was prepared from dioscin as reported in literature.[4]

Compound III, mp 290~2°, gave quite similar IR spectrum to that of II suggesting to be a spirostanol derivative. It gave also diosgenin (VII), glucose and rhamnose on acid hydrolysis. ^{1}H-NMR spectrum of III showed two rhamnosyl anomeric protons and one glucosyl anomeric proton doublet (see Table II). A direct comparison of compound III with an authentic sample of dioscin showed the two samples to be identical. The ^{13}C-NMR spectral data were also supported the above observations.

Compound IV, mp 296~8°, on acid hydrolysis, yielded diosgenin (VII) along with glucose and rhamnose, like compound II. The ^{1}H-NMR specral data show that compound IV was comprised of two moles of glucose and one mole of rhamnose in its structure: two doublets at δ 4.84(1 H, J=7.3 Hz) and 4.97 (1 H, J=7.7 Hz) and a singlet at δ 6.18 (1 H). On comparison of the ^{13}C-NMR spectrum (see Table II) of the sugar moiety of IV with that of II, an additional set of signals due to a terminal β-glucopyranosyl unit appeared in the spectrum of IV and further, the signals due to the inner β-glucopyranosyl moiety revealed significant glycosidation shifts at C-2 (−1.5 ppm), C-3 (+11.5 ppm) and C-4(−2.4 ppm) signals indicating that the terminal glucose unit was attached at C-3 of the inner glucoside.[5] Therefore, compound IV could be designated as diosgenin 3-O-α-L-rhamnopyranosyl (1→2)-[β-D-glucopyranosyl (1→3)]-β-D-glucopyranoside (=diosgenin 3-O-gracillimatrioside, gracillin). Finally, comparison of physicochemical and spectral data of IV with those of the reported in literature[6] confirmed its identity.



Compound V, mp 180~198°, showed absorptions due to hydroxyls, but no spiroketal side chain absorptions in its IR spectrum, and was positive result to the Ehrlich reagent[7] suggesting that V is a furostanol glycoside. On enzymatic hydrolysis with almond emulsin, V liberated a glycoside, mp 290~93°, and glucose. The former was identical with III in every respect. Therefore, compound V was deduced to be a furostanol glycoside corresponding to compound III. However, ^{1}H- and ^{13}C-NMR spectral data showed that compound V was a mixture of 22-hydroxy and 22-methoxyfurostanosides, *i.e.* protodioscin and methyl protodioscin(see Table I and II). On refluxing in aqueous acetone, compound V was converted to protodioscin, while it was converted to methyl protodioscin on refluxing in MeOH; such chemical transformations are well known in oligofurostanoides[8]. The intensity ratio of the signals due to the proto- and methyl proto derivatives in the NMR spectra was approxi-

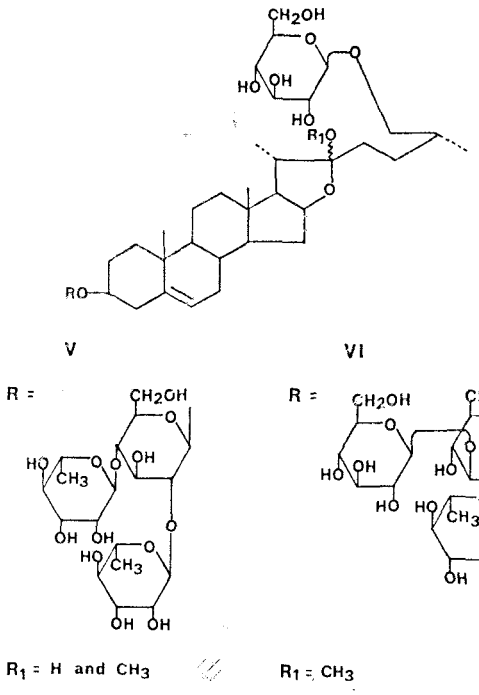
Table I—Partial ^{1}H-NMR spectral data for II, III, IV, V, and VI in pyridine-d_5[1]

Proton	Compound					
	II	III	IV	V		VI
				22-OH	22-OCH_3	
H-18	0.80, s	0.81, s	0.82, s	0.87, s	0.81, s	0.81, s
H-19	1.01, s	1.01, s	1.04, s	1.01, s	1.02, s	1.03, s
H-21	1.09, d(6.9)	1.09, d(6.9)	1.11, d(6.9)	1.25, d(6.9)	1.13, d(6.8)	1.14, d(6.8)
H-27	0.68, d(5.7)	0.69, d(5.2)	0.71, d(5.7)	0.95, d(6.8)	0.98, d(6.7)	0.98, d(6.6)
H-6	5.28, brd(4.8)	5.30, brd(4.6)	5.32, brd(4.8)	5.31, brs	5.31, brs	5.32, brd(4.1)
OCH_3	—	—	—	—	3.22, s	3.23, s
Rha-CH_3	1.67, d(6.3)	1.52, d(6.2)	1.66, d(6.1)	1.50, d(6.2)		1.65, d(6.2)
		1.66, d(6.1)		1.64, d(6.2)		
Anomeric	4.92, d(7.2)	4.82, d(7.4)	4.84, d(7.3)	4.78, d(7.2)		4.82, d(7.2)
protons	6.20, s	5.62, brs	4.97, d(7.7)	5.56, s		4.96, d(7.7)
		6.17, s	6.18, s	6.10, s		6.17, s

[1]Data are δ (ppm), multiplicity, and J (in parentheses) in Hz.

mately 1 : 1. In the light of the above observations, compound V was deduced to be a mixture of methyl protodioscin and protodioscin.

Compound VI, mp 230~32°, was also considered to be a furostanol glycoside from the IR and positive colorization with the Ehrlich reagent. On enzymatic hydrolysis in the same manner as for compound V gave a spirostanol glycoside, mp 296~8°, together with glucose. The physicochemical and spectral data of the above mentioned glycoside were superimposable with those of gracillin (IV)[6] in every respect. Consequently the structure of VI could be assigned as methyl protogracillin.



In 1966, Kawasaki *et al.* reported the isolation of uncharacterized steroidal saponins, smilax saponins A, B and C from the same plant[2]. Among those saponins, the structure of the major saponin smilax saponin B was revised as methyl protodioscin in 1974[9]. Therefore, other saponins from this plant are the first report of the isolation. Other furostanol glycoside corresponding to methyl proto compound II was also isolated in impure state. However, we could not obtain it in pure state due to the short of sample but enzymatic hydrolysis of this sample afforded compound II which was identified by direct comparison with an authentic sample.

Experimental

Mps were determined on a Mitamura-Riken apparatus and are uncorrected. The IR spectra were obtained on a Perkin-Elmer 283B spectrophotometer. ^{1}H-NMR spectra were obtained on

Table II—^{13}C-NMR spectral data for II, III, IV, V, and VI in pyridine-d_5

carbon No.	compound II	III	IV	V 22-OH	V 22-OCH_3	VI	carbon No.	compound II	III	IV	V	VI
1	37.4	37.4	37.5	37.5		37.4	Glc C-1	100.3	100.1	100.0	100.2	99.8
2	30.0	29.9	30.0	30.0		29.9	2	79.3	79.5	77.8	79.4	77.7
3	77.9	78.0	78.4[a]	78.3		78.3[a]	3	77.8[a]	76.5	89.3	76.5	89.2
4	38.8	38.8	38.7	40.0	39.8	39.7	4	71.8	77.7[a]	69.4[c]	77.7	69.3[b]
5	140.8	140.7	140.8	140.9		140.7	5	77.9[a]	77.6[a]	77.6	77.7	77.5
6	121.5	121.5	121.7	121.6		121.6	6	62.6	61.8	62.4	61.4	62.4
7	32.0	32.0	32.2[b]	32.1		32.0	Rha C-1	101.7	101.7	102.0	101.7	101.9
8	31.6	31.6	31.8	31.7		31.6	(→^{2}Glc)2	72.2	72.1	72.2	72.2	72.1
9	50.2	50.6	50.3	50.4		50.3	3	72.6	72.2	72.6	72.5	72.5
10	37.0	37.0	37.1	37.1		37.0	4	73.9	73.9	74.0	73.9	73.9
11	20.9	20.9	21.1	21.1		20.9	5	69.2	70.1	69.5[c]	70.3	69.4[b]
12	39.8	39.8	39.9	38.9		38.6	6	18.4	18.2	18.6	18.4	18.4
13	40.3	40.3	40.4	40.8		40.7	Rha C-1		102.7		102.8	
14	56.5	56.5	56.7	56.6		56.5	(→^{4}Glc)2		72.4		72.2	
15	32.2	32.2	32.3[b]	32.3		32.2	3		72.5		72.4	
16	80.9	80.9	81.0	81.0	81.2	81.2	4		73.6		73.6	
17	62.8	62.8	62.9	63.7	64.1	64.0	5		69.2		69.2	
18	16.1	16.2	16.2	16.4	16.2	16.2	6		18.3		18.4	
19	19.2	19.3	19.3	19.3		19.3	Glc C-1			104.3		104.2
20	41.8	41.8	41.9	40.5	40.4	40.3	(→^{3}Glc)2			74.8		74.7
21	14.8	14.8	14.9	16.2	16.1	16.1	3			77.0		76.9
22	109.0	109.0	109.2	110.6	112.6	112.5	4			71.4		71.3
23	31.7	31.7	31.7	36.9	30.7	30.6	5			78.3[a]		78.2[a]
24	29.1	29.1	29.2	28.1		28.1	6			62.4		62.4
25	30.4	30.4	30.5	34.1		34.1	26-O-Glc					
26	66.7	66.7	66.8	75.1		75.1	C-1				104.6	104.7
27	17.1	17.1	17.2	17.3	17.2	17.1	2				74.9	74.9
OCH_3					47.2	47.2	3				78.0	78.0
							4				71.7	71.7
							5				78.3	78.3
							6				62.9	62.8

[a,b,c] Assignments in each column may be reversed.

Varian FT-80A(80 MHz) or Bruker AM-300 (300 MHz) instrument and ^{13}C-NMR spectra were recorded on a Bruker AM-300(75.5 MHz) spectrometer using TMS as an internal standard. Mass spectra were measured on a Hewlett-Packard 5985B GC/MS system equipped with a direct inlet system. Optical rotations were recorded on a Rudolph Autopol III automatic polarimeter. TLC chromatography was perfo-rmed on precoated Kieselgel 60F_{254} plates(Merck, 5715) and spots were detected by Ehrlich reagent, and by 10% H_2SO_4 followed by heating. Sugars were runned on precoated cellulose plates (Merck, 5552) and detected by aniline

hydrogen phthalate.

Plant material—The rhizomes of *Smilax china* were collected in south Jeonra Bug Do province in the summer season of 1986. Specimens have been deposited in College of Pharmacy, Yeungnam University.

Extraction and Isolation—The chopped, dried samples(15kg) were extracted with MeOH and concentrated *in vacuo* to yield MeOH extract. The MeOH extract was defatted with benzene and the insoluble substance was partitioned between BuOH and H_2O. The BuOH soluble portion was washed with 1% KOH solution and then H_2O, and evaporated *in vacuo* to afford BuOH extract (320 g). A portion of BuOH extract thus obtained was subjected to column chromatography over silica gel eluted with $CHCl_3$-MeOH-H_2O(75 : 25 : 3) to yield three fractions. Fr. 1 was purified by chromatography on silica gel with EtOAc and then EtOAc saturated with H_2O to give compound I. Fr. 2 was purified by column chromatography on silica gel with EtOAc saturated with H_2O-MeOH (gradient, 94 : 4 to 94 : 6) to yield compounds II, III and IV. Fr. 3 was further purified by column chromatography over silica gel using $CHCl_3$-MeOH-H_2O(70 : 30 : 4) as eluent to afford compounds V and VI.

Compoud I: amorphous white from MeOH. Mp 298~300°, $[\alpha]_D^{25}$=−41.7°(c, 0.2, pyridine); IR ν_{max}^{KBr} cm^{-1} 3420(OH), 1650(C=C), 1075, 1025(C−O), 835, 800(CH=C); MS(30 eV), *m/z*(rel. int.) M^+(not observed), 414 (13.1), 412(6.7), 397(60.4), 396(100), 396 (44.5), 382(28.5), 381(17.1), 329(7.0), 303 (10.7), 275(20.8), 273(16.7), 271(10.8), 255 (69.8), 229(13.5), 213(38.0).

Compound II: amorphous white from MeOH. Mp 238~240°, $[\alpha]_D^{25}$=−120.5° (c, 0.4, MeOH); IR ν_{max}^{KBr} cm^{-1} 3410(OH), 1650(C=C), 1100−1000(C−O), 920, 900, 865, 837 [900> 920, 25(R)-spiroketal], 811; ^{1}H-NMR(300 MHz, pyridine-d_5) and ^{13}C-NMR(75.5 MHz, pyridine-d_5): see Table I and II, respectively.

Compound III: colorless needles from MeOH. Mp 290~2°, $[\alpha]_D^{25}$=−112.3° (c, 0.3, MeOH); IR ν_{max}^{KBr} cm^{-1} 3420(OH), 1640(C=C), 1100−1000(C−O), 920, 900, 866, 838[900> 920, 25(R)-spiroketal], 811; ^{1}H-NMR(300 MHz, pyridine-d_5) and ^{13}C-NMR(75.5 MHz, pyridine-d_5): see Table I and II, respectively.

Compound IV: colorless needles from MeOH. Mp 296~8°, $[\alpha]_D^{25}$=−95°(c, 0.4, pyridine); IR ν_{max}^{KBr} cm^{-1} 3420(OH), 1640(C=C), 1100−1000(C−O), 920, 900, 866, 836 [900> 920, 25(R)-spiroketal], 812; ^{1}H-NMR(300 MHz, pyridine-d_5) and ^{13}C-NMR(75.5 MHz, pyridine-d_5): see Table I and II, respectively.

Compound V: colorless needles from MeOH. Mp 180~198°; IR ν_{max}^{KBr} cm^{-1} 3400(OH), 1635(C=C), 1100−1000(C−O), 905, 883, 820, 805; ^{1}H-NMR(300 MHz, pyridine-d_5) and ^{13}C-NMR(75.5 MHz, pyridine-d_5): see Table I and II, respectively.

Compound VI: colorless needles from MeOH. Mp 230~2°, $[\alpha]_D^{25}$=−82°(c, 0.3, pyridine); IR ν_{max}^{KBr} cm^{-1} 3400(OH), 1640(C=C), 1100-1000(C−O), 915, 890, 838, 811; ^{1}H-NMR (300 MHz, pyridine-d_5) and ^{13}C-NMR(75.5 MHz, pyridine-d_5): see Table I and II, respectively.

Acid hydrolysis of compounds—Compounds I~VI (*ca* 30 mg each) were separately hydrolyzed with 5% H_2SO_4-60% dioxane (10 ml) by refluxing for 3 hr on a water bath, and each reaction mixture was poured onto crushed ice and filtered. The precipitate from compound I was crystallized from MeOH to give an aglycone, mp 134~8°, as amorphous white which was identified as β-sitosterol by direct comparison with an authentic sample. Each

precipitate from compounds II～VI was repeatedly recrystallized from acetone to yield the common aglycone, diosgenin (VII), mp 205～7°, as colorless needles which was identified by direct comparison with an authentic sample. Each aqueous layer was neutralized with $BaCO_3$, filtered and the solution was evaporated to dryness under reduced pressure. Each residue was examined by TLC (solvent; pyridine-EtOAc-HOAc-H_2O=36 : 36 : 7 : 21). D-Glucose was identified from the hydroysate of compound I and D-glucose and L-rhamnose were detected from the hydrolysate of compounds II～VI as the common sugars.

Enzymatic hydrolysis of compounds V and VI—Aqueous solutions of compound V (10mg) and VI (10 mg) were separately incubated with almond emulsin (1 mg each) at 37～40° for 24 hr, then MeOH was added and the whole was evaporated *in vacuo* to give a residue, which was examined by TLC in the same manner as described above. D-Glucose was found to be present in each case. After identification of sugar, the residue was separately subjected to chromatography over silica gel with EtOAc saturated with H_2O-MeOH (95 : 5) to give compound III, mp 290～3°, from V and compound IV, mp 296～8°, from VI, which were identified by direct comparison with authentic samples.

Acetylation of compound I—A sample of I (20 mg) was treated with Ac_2O/pyridine (1ml each) at room temperature overnight. Work-up in the usual manner followed by recrystallization from MeOH afforded compound I acetate as leaflet, mp 163～4°; IR ν_{max}^{KBr} cm^{-1} 1740, 1239 (OAc); ^{1}H-NMR (80 MHz, $CDCl_3$): 0.67 (3 H, s, 18-CH_3), 0.97(3 H, s, 19-CH_3), 1.99, 2.00, 2.03, 2.05 (3H each, s, OAc), 4.58 (1 H, d, J=7.4 Hz, anomeric H), 5.34 (1H, br d, J=3.2Hz, H-6).

Partial hydrolysis of compound III—Compound III (300 mg) was refluxed with 0.5 N-HCl-50% EtOH for 1 hr. The reaction mixture was treated as described in literature[4] to furnish prosapogenins A, B and C.

Prosapogenin A: mp 234～7°; IR ν_{max}^{KBr} cm^{-1} 3400 (OH), 1645 (C=C), 1100-1000 (C—O), 920, 900, 865, 835 [900>920, 25(R)-spiroketal], 810; ^{1}H-NMR (300MHz, pyridine-d_5): 0.71 (3 H, d, J=5.1 Hz, 27-CH_3), 0.83 (3 H s, 18-CH_3), 1.05 (3 H, s, 19-CH_3), 1.13 (3 H, d, J=6.9 Hz, 21-CH_3), 1.74 (3 H, d, J=6.2 Hz, rha-CH_3), 4.99 (1 H, d, J=6.9 Hz, anomeric H), 5.31 (1 H, br d, J=4.1 Hz, H-6), 6.31 (1 H, br s, anomeric H); ^{13}C-NMR (75.5MHz, pyridine-d_5): 37.4, 30.1, 78.1, 38.9, 140.8, 121.6, 32.1, 31.6, 50.2, 37.1, 21.0, 39.8, 40.4, 56.6, 32.2, 81.0, 62.8, 16.2, 19.3, 41.9, 14.9, 109.2, 31.7, 29.2, 30.5, 66.8, 17.2 (aglycone signals C-1 to C-27); 100.2, 79.4, 77.8*, 71.7, 77.9*, 62.6 (glucose signals C-1 to C-6); 101.9, 72.5, 72.7, 74.0, 69.3, 18.5 (rhamnose signals C-1 to C-6).

Prosapogenin B: mp 116～21°; IR ν_{max}^{KBr} cm^{-1} 3400 (OH), 1640 (C=C), 1100-1000 (C—O), 920, 900, 866, 837 [900>920, 25(R)-spiroketal], 812; ^{1}H-NMR (300MHz, pyridine-d_5): 0.71 (3 H, d, J=5.2Hz, 27-CH_3), 0.84 (3 H, s, 18-CH_3), 0.92 (3H, s, 19-CH_3), 1.13 (3 H, d, J=6.9 Hz, 21-CH_3), 1.69 (3 H, d, J=6.1 Hz, rha-CH_3), 4.93(1H, d, J=7.9Hz, anomeric H), 5.33 (1 H, br d, J=4.4 Hz, H-6), 5.83 (1H, br s, anomeric H); ^{13}C-NMR (75.5 MHz, pyridine-d_5): 37.3, 30.0, 78.3*, 39.1, 140.7, 121.5, 32.0, 31.5, 50.1, 36.9, 20.9, 39.7, 40.3, 56.5, 32.1, 80.9, 62.7, 16.2, 19.2, 41.8, 14.8, 109.1, 31.6, 29.1, 30.4, 66.7, 17.1 (aglycone signals C-1 to C-27); 102.5$^+$, 75.2, 76.9, 78.1*, 76.5, 61.3 (glucose signals C-1′ to C-6′); 102.2$^+$, 72.4, 72.6, 73.7, 70.2, 18.3 (rhamnose signals C-1 to C-6).

Prosapogenin C: Mp 247~9°; IR ν_{max}^{KBr} cm^{-1} 3450 (OH), 1650 (C=C), 1070, 1045, 1025 (C—O), 920, 900, 865, 835 [900>920, 25 (R)-spiroketal], 810; ^{1}H-NMR (300 MHz, pyridine-d_5): 0.70 (3H, d, J=5.2 Hz, 27-CH_3), 0.83 (3H, s, 18-CH_3), 0.92 (3H, s, 19-CH_3), 1.13 (3H, d, J=6.9 Hz, 21-CH_3), 5.01 (1H, d, J=7.7Hz, anomeric H), 5.31 (1H, br d, J=4.4 Hz, H-6); ^{13}C-NMR (75.5 MHz, pyridine-d_5): 37.3, 30.0, 78.3*, 39.1, 140.7, 121.5, 32.0, 31.5, 50.1, 36.9, 20.9, 39.7, 40.3, 56.5, 32.1, 80.9, 62.7, 16.2, 19.2, 41.8, 14.8, 109.1, 31.6, 29.1, 30.4, 66.7, 17.1, (aglycone signals C-1 to C-27); 102.4, 75.1, 78.0*, 71.5, 78.2*, 62.7 (glucose signals C-1 to C-6).

Treatment of compound V with aqueous acetone—Compound V (20 mg) was refluxed with 30% aqueous acetone (20 ml) for 10hr on a water bath, and the reaction mixture was evaporated to dryness *in vacuo* to afford a 22-hydroxyfurostanoid (=protodioscin).

Treatment of compound V with MeOH—A solution of compound V (10 mg) in MeOH (10 ml) was refluxed for 15 hr and then concentrated *in vacuo* to yield a 22-methoxyfurostanoid (=methyl protodioscin).

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