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STEROIDAL SAPONINS FROM THE SUBTERRANEAN PART OF *ALLIUM FISTULOSUM*

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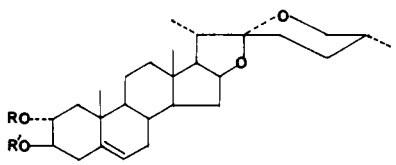
ABSTRACT.—Structures of three new yuccagenin glycosides, named fistulosides A [**1**], B [**2**], and C [**3**], isolated from the subterranean part of *Allium fistulosum*, were determined by chemical and spectral means. Two known diosgenin glycosides, dioscin and saponin P-d, were also isolated and identified.

Allium fistulosum L. (Liliaceae) is a perennial herb that is cultivated widely. The leaves are used for food. According to the dictionary of Chinese drugs (1), the bulbs and roots of this plant have been used for treatment of febrile disease, headache, abdominal pain, diarrhea, snakebite, ocular disorders, and habitual abortion, as well as having antifungal and antibacterial effects. There have been reports on various volatile flavor compounds and sugars from *A. fistulosum* (2). A survey of the literature showed that various steroidal saponins have been reported in the genus *Allium* (3), although no chemical work has been done on the saponins of *A. fistulosum*. The present paper describes isolation and structural characterization of three new yuccagenin glycosides **1–3** and two known diosgenin glycosides from the subterranean part of *A. fistulosum*.

RESULTS AND DISCUSSION

Two known diosgenin glycosides, dioscin and saponin P-d, were identified by comparison of their physico-chemical properties and spectroscopic evidence with those reported in the literature (4,5).

Compound **1**, mp 238–240°, gave a positive Liebermann-Burchard test and showed characteristic absorption of the 25(*R*)-spiroketal moiety at 982, 920, 900, and 866 cm^{-1} (intensity of absorption 900>920 cm^{-1}) in the ir spectrum (6). Acid hydrolysis of **1** yielded aglycone **4** along with galactose and rhamnose. Compound **4** was identified as yuccagenin on the basis of spectroscopic (ms, ^1H- and ^{13}C-nmr) evidence. Acetylation of **4** yielded di-*O*-acetyl yuccagenin [**5**], which was also characterized from its ir, ms, and ^1H-nmr spectra. The fabms spectrum of **1** exhibited a cationized molecular ion $[M + Na]^+$ at *m/z* 761 and a $[genin + H]^+$ ion at *m/z* 431, suggesting that **1** was a yuccagenin disaccharide. The ^1H-nmr spectrum of **1** showed β configuration for one galactose unit and α configuration for one rhamnose unit (Table 1). Partial hydrolysis of **1** with mild acid afforded one prosapogenin **6** with yuccagenin. Compound **6** afforded galactose on acid hydrolysis, and the ^1H-nmr spectrum of **6** showed one anomeric proton doublet ($J = 8.5$ Hz) at δ 5.01. In the ^{13}C-nmr spectrum, the signals due to C-2, -3, and -4 of yuccagenin revealed significant glycosidation shifts at C-2 (−2.5 ppm), C-3 (+8.5 ppm), and C-4 (−3.1 ppm), indicating that the galactose unit was attached at C-3 of yuccagenin. In light of the above evidence, the structure of **6** was established as yuccagenin 3-*O*-β-D-galactopyranoside. On comparison of the ^{13}C-nmr spectrum of **1** with that of **6**, the C-2 signal of the galactopyranosyl moiety of **1** was more deshielded (+4.1 ppm) than that of **6**, and the C-1 and C-3 signals exhibited upfield (−2.2 ppm) and downfield shifts (+0.4 ppm), respectively. Consequently, the structure of **1** was established as yuccagenin 3-*O*-α-L-rhamnopyranosyl(1↦2)-β-D-galactopyranoside. This saponin has not been reported previously and has been named fistuloside A.



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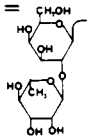
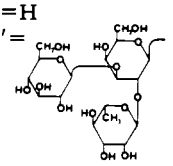
5 R=R′=Ac
1 R=H
R′= 

8 R=Me, R′=H
2 R=H
R′= 

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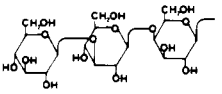
R′= 

6 R=H
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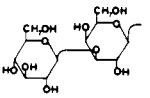
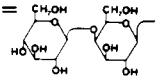
R′= 

9 R=H
R′= 

Compound **2**, mp >300°, showed characteristic absorption of a 25(*R*)-spiroketal moiety in the ir spectrum. On acid hydrolysis, **2** gave galactose, glucose, rhamnose, and yuccagenin, which were identified by direct comparison with authentic samples. Compound **2** showed a cationized molecular ion $[M + Na]^+$ at *m/z* 923 and a $[genin + H]^+$ ion at *m/z* 431 in the fabms spectrum, indicating that **2** was a triglycoside of yuccagenin possessing one mole each of glucose, galactose, and rhamnose. Partial hydrolysis of **2** gave three prosapogenins with the aglycone, yuccagenin. Two of the prosapogenins were identified by direct comparison (co-tlc, mmp) with authentic samples as **6** and **1**. On acid hydrolysis, the third prosapogenin **7** yielded galactose and glucose as sugar components, and in the ^{1}H-nmr spectrum, the β linkages of the sugars were revealed by the coupling constants of two anomeric proton signals at δ 5.02 (J = 7.7 Hz), and 5.45 (J = 7.8 Hz). On comparison of the ^{13}C-nmr spectrum of **7** with that of

TABLE 1. Partial ^{1}H-nmr Spectral Data for **1–3** in Pyridine-d_5.[a]

Proton	Compound		
	1	**2**	**3**
Me-18	0.82 s	0.82 s	0.82 s
Me-19	0.96 s	0.96 s	0.95 s
Me-21	1.13 d (6.8)	1.14 d (6.8)	1.14 d (6.8)
Me-27	0.71 d (5.5)	0.71 d (5.0)	0.70 d (5.5)
H-6	5.32 br d (4.8)	5.32 br d (4.6)	5.31 br d (4.8)
Rha-Me	1.61 d (6.2)	1.61 d (5.8)	
Anomeric protons	4.97 d (7.8)	4.95 d (7.7)	4.97 d (7.8)
	6.30 s	5.16 d (7.6)	5.16 d (7.7)
		6.29 s	5.28 d (7.5)

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

6, the C-3 signal of the galactopyranosyl moiety of **7** was more deshielded (+10.1 ppm) than that of **6**. Consequently, the structure of **7** was determined to be yuccagenin 3-*O*-β-D-glucopyranosyl(1↦3)-β-D-galactopyranoside. In light of the above findings, the structure of **2** was established as yuccagenin 3-*O*-α-L-rhamnopyranosyl(1↦2)-[β-D-glucopyranosyl(1↦3)]-β-D-galactopyranoside. Glycosides **2** and **7** have not been reported previously in the literature, and **2** has been named fistuloside B. The sugar moiety of **2**, solatriose, was identical to that of aculeatiside B from *Solanum aculeatissimum* (7), and the ^{13}C-nmr chemical shifts of the latter were also superimposable with those of solatriose.

Compound **3**, mp 230–233°, gave a positive Liebermann-Burchard test and showed characteristic absorption of a 25(*R*)-spiroketal moiety in the ir spectrum, suggesting that **3** was a spirostanol derivative. On acid hydrolysis, **3** liberated glucose, galactose, and an aglycone which was identified as yuccagenin [**4**] by direct comparison with an authentic sample. The fabms spectrum of **3** showed a cationized molecular ion $[M+Na]^+$ at *m/z* 937 and a $[genin+H]^+$ ion at *m/z* 431, indicating that **3** was a yuccagenin trioside possessing 3 mol of hexoses. The permethylether of **3**, prepared by Hakomori's method (8), showed eleven singlet signals at δ 3.35–3.60 due to methoxyl protons and three doublet signals at δ 4.33 ($J=7.7$ Hz), 4.69 ($J=7.4$ Hz), and 4.80 ($J=7.6$ Hz) ascribable to anomeric protons in the ^{1}H-nmr spectrum, suggesting that all the glycosidic linkages are β. Methanolysis of the permethylether of **3** gave methyl 2,3,4,6-tetra-*O*-methylglucopyranoside, methyl 2,4,6-tri-*O*-methylglucopyranoside, methyl 2,3,6-tri-*O*-methylgalactopyranoside, and yuccagenin 2-*O*-methylether [**8**], mp 244–245°. Partial hydrolysis of **3** afforded two prosapogenins with the aglycone yuccagenin. One prosapogenin was identified by direct comparison with an authentic sample of **6**. On acid hydrolysis, the other prosapogenin **9** yielded galactose, glucose, and yuccagenin. The ^{1}H-nmr spectrum of **9** showed the presence of two anomeric proton doublets at δ 4.95 ($J=7.7$ Hz) and 5.29 ($J=7.8$ Hz), suggesting the β configuration for each sugar. On comparison of the ^{13}C-nmr spectrum of **9** with that of **6**, the C-4 signal of galactopyranosyl moiety of **9** was more deshielded (+9.9 ppm) than that of **6**. Therefore, the structure of **9** was determined as yuccagenin 3-*O*-β-D-glucopyranosyl(1↦4)-β-D-galactopyranoside. In the ^{13}C-nmr spectrum of **3**, the C-2, -3, and -4 signals of the inner glucopyranosyl moiety revealed significant glycosidation shifts at C-2 (−0.3 ppm), C-3 (+7.3 ppm), and C-4 (−1.8 ppm), suggesting that the terminal glucose unit of **3** was attached to C-3 of the inner glucose moiety. From the above data, the structure of **3** was determined to be yuccagenin 3-*O*-β-D-glucopyranosyl(1↦3)-β-D-glucopyranosyl(1↦4)-β-D-galactopyranoside. The new saponin, **3**, was named fistuloside C.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were taken on a Yanaco apparatus and are uncorrected. Optical rotations were measured on a Rudolph Autopol III or Jasco DIP 360 automatic polarimeters. Ir spectra were determined in KBr on a Mattson Polaris TM (FT-IR) spectrophotometer. Elemental analysis was performed on a Perkin-Elmer 240C instrument. Nmr spectra were obtained on a Bruker AM-300 (300 MHz for ^{1}H nmr and 75.5 MHz for ^{13}C nmr) spectrometer using TMS as an internal standard and measured at room temperature. Chemical shifts are given as ppm. Eims and fabms were recorded on a Kratos MS 25 RFA mass spectrometer. Glc was run on a Shimadzu GC-9AM gas chromatograph. Tlc was carried out on precoated Si gel 60 F_{254} sheets (Merck), and detection was achieved by spraying 10% H_2SO_4 followed by heating. Sugars were run on precoated cellulose plates (Merck) and detected by aniline phthalate. Cc utilized Merck Si gel.

PLANT MATERIAL.—The bulbs and roots of *A. fistulosum* were collected in Kyong Bug province of Korea in the summer season of 1989. A voucher specimen is deposited in the College of Pharmacy, Yeungnam University.

EXTRACTION AND FRACTIONATION.—The dried chopped bulbs and roots (10 kg) were refluxed with hot MeOH (3 times, 12 h for each extraction) and evaporated in vacuo to give a residue (615 g), which was suspended in H_2O and extracted successively with $CHCl_3$ and *n*-BuOH. The *n*-BuOH solution was concentrated to give the *n*-BuOH-soluble fraction (165 g).

ISOLATION.—A portion of the *n*-BuOH-soluble fraction was subjected to cc over Si gel eluted with EtOAc saturated with H_2O/MeOH (gradient 0 to 10%) to give six fractions. The third fraction was rechromatographed over Si gel with $CHCl_3$-MeOH-H_2O (7:3:1) (lower layer) to give dioscin and fistuloside A [**1**]. The fifth fraction was subjected to repeated cc over Si gel using EtOAc saturated with H_2O/MeOH (gradient 0 to 8%) as eluent to yield saponin P-d, fistuloside B [**2**], and fistuloside C [**3**]. The physicochemical and spectral data of dioscin and saponin P-d were identical with those previously published (4,5).

Fistuloside A [**1**].—White amorphous powder from MeOH: mp 238–240°; $[\alpha]^{21}D$ −64.0° (c = 0.08, MeOH); ir ν max (KBr) 3416, 1052, 982, 920, 900, 866 cm^{-1} [intensity of absorption 900>920 cm^{-1}, 25(*R*)-spiroketal]; fabms *m/z* (rel. int.) $[M + Na]^+$ 761 (5.2), [genin + H]$^+$ 431 (2.5); ^1H nmr see Table 1; ^{13}C nmr see Table 2. *Anal.* calcd for $C_{39}H_{62}O_{13}\cdot 2H_2O$, C 60.44, H 8.59; found C 60.68, H 8.30.

Fistuloside B [**2**].—White amorphous powder from MeOH: mp >300°; $[\alpha]^{21}D$ −98.0° (c = 0.16, pyridine); ir ν max (KBr) 3420, 1053, 981, 920, 900, 865 cm^{-1} [intensity of absorption 900>920 cm^{-1}, 25(*R*)-spiroketal]; fabms *m/z* (rel. int.) $[M + Na]^+$ 923 (0.9), [genin + H]$^+$ 431 (1.0); ^1H nmr see Table 1; ^{13}C nmr see Table 2. *Anal.* calcd for $C_{45}H_{72}O_{18}$, C 59.98, H 8.05; found C 60.12, H 7.90.

Fistuloside C [**3**].—White needles from MeOH: mp 230–233°; $[\alpha]^{21}D$ −48.0° (c = 0.15, pyridine); ir ν max (KBr) 3413, 1075, 982, 920, 900, 866 cm^{-1} [intensity of absorption 900>920 cm^{-1}, 25(*R*)-spiroketal]; fabms *m/z* (rel. int.) $[M + Na]^+$ 939 (4.1), [genin + H]$^+$ 431 (4.1); ^1H nmr see Table 1; ^{13}C nmr see Table 2. *Anal.* calcd for $C_{45}H_{72}O_{19}\cdot 2H_2O$, C 56.71, H 8.04; found C 54.98, H 7.81.

ACID HYDROLYSIS OF **1–3**.—Solutions of each glycoside (30 mg each) in 4 N HCl-dioxane (1:1) (9 ml) were refluxed for 30 min, and each reaction mixture was diluted with ice-H_2O. Precipitates were collected by filtration and purified by recrystallization from MeOH to afford the same aglycone, yuccagenin [**4**], as colorless needles: mp 245–247°; $[\alpha]^{23}D$ −118° (c = 0.4, $CHCl_3$); ir ν max (KBr) 3415, 1053, 982, 921, 900, 865 cm^{-1} [intensity of absorption 900>921 cm^{-1}, 25(*R*)-spiroketal]: ms *m/z* (rel. int.) 430 (7.7), 371 (3.7), 358 (11.1), 316 (16.4), 301 (8.5), 298 (25.7), 287 (14.8), 280 (4.2), 269 (5.0), 139 (100.0), 115 (22.1); ^1H nmr ($CDCl_3$) δ 0.79 (3H, d, J = 5.6 Hz, Me-27), 0.79 (3H, s, Me-18), 0.97 (3H, d, J = 6.7 Hz, Me-21), 1.06 (3H, s, Me-19), 3.30 (1H, m, H-3), 3.38–3.53 (2H, m, CH_2-26), 3.66 (1H, m, H-2), 4.41 (1H, m, H-16), 5.39 (1H, br d, J = 4.6 Hz, H-6); ^{13}C nmr see Table 2. Each filtrate was evaporated, and the residue was examined by tlc. Galactose and rhamnose from the hydrolysate of **1**, galactose, rhamnose, and glucose from that of **2**, and galactose and glucose from that of **3** were detected as the sugar components.

ACETYLATION OF YUCCAGENIN [**4**].—Yuccagenin (20 mg) was treated with Ac_2O in pyridine (1 ml each) at room temperature for 24 h. Workup in the usual manner gave **5**, which was recrystallized from MeOH as colorless needles: mp 170–171°; $[\alpha]^{23}D$ −128° (c = 0.36, $CHCl_3$); ir ν max (KBr) 1739, 1235, 975, 915, 893, 860 cm^{-1}; ms *m/z* (rel. int.) 514 (6.0), 455 (51.6), 445 (3.5), 395 (9.7), 394 (10.3), 385 (12.0), 382 (45.5), 379 (3.4), 371 (2.5), 340 (92.1), 325 (20.0), 322 (3.9), 311 (8.6), 280 (91.7), 251 (18.8), 139 (100.0); ^1H nmr ($CDCl_3$) δ 0.79 (3H, d, J = 5.9 Hz, Me-27), 0.79 (3H, s, Me-18), 0.97 (3H, d, J = 6.8 Hz, Me-21), 1.12 (3H, s, Me-19), 2.01, 2.02 (3H each, s, 2Ac), 3.33–3.48 (2H, m, CH_2-26), 4.41 (1H, m, H-16), 5.44 (1H, br d, J = 4.8 Hz, H-6).

PARTIAL HYDROLYSIS OF **1** AND **2**.—Compound **1** (50 mg) was refluxed with 1% H_2SO_4 in MeOH (12 ml) for 10 min. After cooling, the reaction mixture was diluted with ice-H_2O, and the precipitate was collected by filtration and dried. Tlc [EtOAc-MeOH-H_2O (100:16.5:13.5)] of the residue showed three spots, and the residue (30 mg) was subjected to cc over Si gel with hexane-EtOAc (8:5) and then EtOAc saturated with H_2O/MeOH (gradient 0 to 4%) to afford **4** (6 mg), **6** (7 mg), and recovered **1** (10 mg) in the order of elution. Compound **4** and recovered **1** were identified by comparison with the previously obtained samples of yuccagenin and fistuloside A. The recovered **6** was refluxed with acid in the same manner as described above. Galactose from **6** was detected by tlc. Compound **6** was recrystallized from MeOH as colorless needles: mp 268–272°; $[\alpha]^{23}D$ −20° (c = 0.21, MeOH); ^1H nmr (pyridine-d_5) δ 0.70 (3H, d, J = 5.3 Hz, Me-27), 0.82 (3H, s, Me-18), 0.97 (3H, s, Me-19), 1.14 (3H, d, J = 6.9 Hz, Me-21), 5.01 (1H, d, J = 8.5 Hz, anomeric H), 5.31 (1H, br d, J = 4.8 Hz, H-6); ^{13}C nmr see Table 2. Compound **2** (100 mg) was hydrolyzed in the same manner. The precipitate (60 mg) was chromatographed to give **4** (5 mg), prosapogenins **6** (3 mg), **1** (11 mg), **7** (16 mg), and recovered **2** (25 mg) with hexane-EtOAc (8:5) and then EtOAc saturated with H_2O/MeOH (gradient 0 to 8%). The prosapogenins were identified as yuccagenin 3-*O*-β-D-galactopyranoside and fistuloside A by direct comparison with **6** and **1**, respectively. Prosapoge-

TABLE 2. ^{13}C-nmr Chemical Shifts of Yuccagenin and its Glycosides in Pyridine-d_5.[a]

Carbon	Compound					Carbon	Compound	
	4	1	2	6	7		3	9
C-1	46.6	45.9	45.8	45.9	45.8	C-1	45.8	45.8
C-2	72.7	70.3	70.2	70.2	70.1	C-2	70.1	70.1
C-3	76.8	85.7	85.0	85.3	84.9	C-3	84.8	84.9
C-4	40.9	37.4	37.1	37.8	37.8	C-4	37.7	37.7
C-5	141.3	140.1	140.0	140.2	140.1	C-5	140.1	140.1
C-6	121.3	121.9	121.9	121.9	121.9	C-6	121.9	121.9
C-7	32.3[b]	32.1	32.1	32.2	32.2	C-7	32.2	32.2
C-8	31.2	31.2	31.1	31.1	31.1	C-8	31.1	31.1
C-9	50.4	50.2	50.1	50.2	50.1	C-9	50.2	50.2
C-10	38.6	37.9	37.9	37.9	37.9	C-10	37.9	37.9
C-11	21.3	21.2	21.1	21.2	21.2	C-11	21.2	21.2
C-12	39.9	39.8	39.7	39.8	39.8	C-12	39.8	39.8
C-13	40.5	40.5	40.4	40.5	40.4	C-13	40.5	40.5
C-14	56.7	56.5	56.5	56.5	56.5	C-14	56.5	56.5
C-15	32.2[b]	32.2	32.2	32.2	32.2	C-15	32.2	32.2
C-16	81.1	81.1	81.1	81.1	81.1	C-16	81.1	81.1
C-17	62.9	62.9	62.8	62.9	62.8	C-17	62.9	62.9
C-18	16.4	16.3	16.3	16.4	16.3	C-18	16.3	16.3
C-19	20.7	20.4	20.3	20.4	20.4	C-19	20.4	20.4
C-20	42.0	42.0	41.9	42.0	41.9	C-20	42.0	42.0
C-21	15.0	15.0	14.9	15.0	15.0	C-21	15.0	15.0
C-22	109.3	109.2	109.2	109.3	109.2	C-22	109.3	109.3
C-23	31.6	31.6	31.8	31.8	31.8	C-23	31.8	31.8
C-24	29.3	29.3	29.2	29.3	29.2	C-24	29.3	29.3
C-25	30.6	30.6	30.5	30.6	30.6	C-25	30.6	30.6
C-26	66.8	66.7	66.8	66.9	66.8	C-26	66.9	66.9
C-27	17.3	17.3	17.3	17.3	17.3	C-27	17.3	17.3
Gal C-1		102.0	101.4	104.2	103.6	Gal C-1	103.4	103.6
C-2		76.5	74.7	72.4	71.5	C-2	72.8	73.1
C-3		75.7	85.0	75.3	85.4	C-3	75.5	75.8[b]
C-4		70.7	70.1	70.2	69.7	C-4	80.8	80.1
C-5		76.9	76.6	77.2	76.9	C-5	75.5	75.9[b]
C-6		62.1	62.5[b]	62.3	62.5[b]	C-6	60.4	60.7
Rha C-1		102.0	102.0			Glc C-1	106.8	107.1
(↦^{2}Gal) C-2		72.5[b]	72.4[c]			(↦^{4}Gal) C-2	74.9	75.2
C-3		72.8[b]	72.7[c]			C-3	85.9	78.6
C-4		74.1	74.0			C-4	70.5	72.3
C-5		69.4	69.4			C-5	78.4	78.7
C-6		18.5	18.4			C-6	61.8	63.1
Glc C-1			105.7		106.6	Glc C-1	105.1	
(↦^{3}Gal) C-2			74.9		75.9	(↦^{3}Glc) C-2	75.5	
C-3			78.4		78.7	C-3	78.2	
C-4			71.5		71.5	C-4	71.7	
C-5			78.3		78.4	C-5	78.4	
C-6			62.2[b]		62.2[b]	C-6	63.2	

[a]Chemical shifts are reported in ppm from TMS. Assignments were made by comparison with model compounds and DEPT spectra.

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

nin **7** was refluxed with acid, and galactose and glucose were detected by tlc. Compound **7** was recrystallized from MeOH as white needles: mp 266–268°; $[\alpha]^{17}D$ −48° (c = 0.1, pyridine); ^{1}H nmr (pyridine-d_5) δ 0.70 (3H, d, J = 5.4 Hz, Me-27), 0.82 (3H, s, Me-18), 0.96 (3H, s, Me-19), 1.14 (3H, d, J = 6.9 Hz, Me-21), 5.02 (1H, d, J = 7.7 Hz, anomeric H), 5.33 (1H, br d, J = 4.5 Hz, H-6), 5.45 (1H, d, J = 7.8 Hz, anomeric H); ^{13}C nmr see Table 2.

PERMETHYLATION OF **3**.—Compound **3** (50 mg) was permethylated with NaH (100 mg) and MeI (6 ml) by Hakomori's method (8). The reaction product was chromatographed over Si gel with hexane-Me_2CO (4:1) to afford the undeca-*O*-methylether as colorless syrup: ir ν max (KBr) 1075, 1072, 985, 920, 898, 850 cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.79 (3H, d, $J = 6.7$ Hz, Me-27), 0.79 (3H, s, Me-18), 0.99 (3H, d, $J = 6.7$ Hz, Me-21), 1.07 (3H, s, Me-19), 3.35, 3.38, 3.44, 3.47, 3.50, 3.52, 3.62, 3.63 (3H each, s, 9Me), 3.60 (6H, s, 2Me), 4.33 (1H, d, $J = 7.7$ Hz, anomeric H), 4.42 (1H, m, H-16), 4.69 (1H, d, $J = 7.4$ Hz, anomeric H), 4.80 (1H, d, $J = 7.6$ Hz, anomeric H), 5.38 (1H, br d, $J = 4.7$ Hz, H-6).

METHANOLYSIS OF THE PERMETHYLETHER OF **3**.—The permethylether of **3** (15 mg) was refluxed with 2% methanolic HCl (15 ml) for 1 h. The reaction mixture was concentrated to half volume and added to crushed ice. The resulting precipitate was filtered and recrystallized from MeOH to afford yuccagenin 2-*O*-methylether [**8**] as colorless needles: mp 244–245°; $[\alpha]^{22}D$ −134° ($c = 0.15$, $CHCl_3$); ir ν max (KBr) 3500, 1070, 985, 920, 900, 855 cm^{-1}; ms *m/z* (rel. int.) 444 (8.8), 426 (2.5), 385 (2.7), 372 (8.9), 330 (10.5), 315 (5.4), 312 (35.3), 301 (8.0), 298 (5.6), 283 (3.9), 280 (8.5), 139 (100.0); ^1H nmr ($CDCl_3$) δ 0.79 (3H, d, $J = 6.0$ Hz, Me-27), 0.97 (3H, s, Me-18), 0.98 (3H, d, $J = 6.8$ Hz, Me-21), 1.05 (3H, s, Me-19), 3.22 (1H, m, H-3), 3.33–3.49 (3H, m, CH_2-26 and H-2), 3.40 (3H, s, Me), 4.42 (1H, m, H-16), 5.40 (1H, br d, $J = 5.0$ Hz, H-6). The filtrate was neutralized with Ag_2CO_3, and the neutral solution was concentrated to dryness. The residue was examined by glc [column 5% DEGS + 1% H_3PO_4 on chromosorb W AW (100–200 mesh) (2.2 mm × 6 ft); column temperature 170°; carrier gas (N_2) 3.35 kg/cm^2], and methylated sugars were identified as methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (Rt 2.63, 3.69), methyl 2,4,6-tri-*O*-methylglucopyranoside (Rt 6.75, 7.72), and methyl 2,3,6-tri-*O*-methylgalactopyranoside (Rt 9.30, 11.34) by comparison with the authentic samples.

PARTIAL HYDROLYSIS OF **3**.—Compound **3** (200 mg) was hydrolyzed by the same method. The precipitate (95 mg) was chromatographed to give **4** (22 mg), two prosapogenins **6** (5 mg) and **9** (20 mg), and recovered **3** (30 mg) in the same order of elution as those of **2**. Prosapogenin **6** was identified as yuccagenin 3-*O*-β-D-galactopyranoside by direct comparison with **6**. Prosapogenin **9** was refluxed with acid, and galactose and glucose were detected in the hydrolysate. Compound **9** was recrystallized from MeOH as white needles: mp 267–271°; $[\alpha]^{22}D$ −70° ($c = 0.25$, MeOH); ^1H nmr (pyridine-d_5) δ 0.70 (3H, d, $J = 5.3$ Hz, Me-27), 0.82 (3H, s, Me-18), 0.96 (3H, s, Me-19), 1.14 (3H, d, $J = 6.8$ Hz, Me-21), 4.95 (1H, d, $J = 7.7$ Hz, anomeric H), 5.29 (1H, d, $J = 7.8$ Hz, anomeric H), 5.32 (1H, br d, $J = 4.4$ Hz, H-6); ^{13}C nmr see Table 2.

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