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STEROIDAL SAPONINS FROM THE RHIZOMES OF *POLYGONATUM SIBIRICUM*

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ABSTRACT.—Investigation of the rhizomes of *Polygonatum sibiricum* led to the isolation of the previously reported neoprazerigenin A 3-*O*-β-lycotetraoside [**3**], its methyl proto-type congener **2**, and two new steroidal saponins, sibiricosides A [**1**] and B [**4**]. The structures have been determined by spectral means and by comparison with literature data and authentic samples.

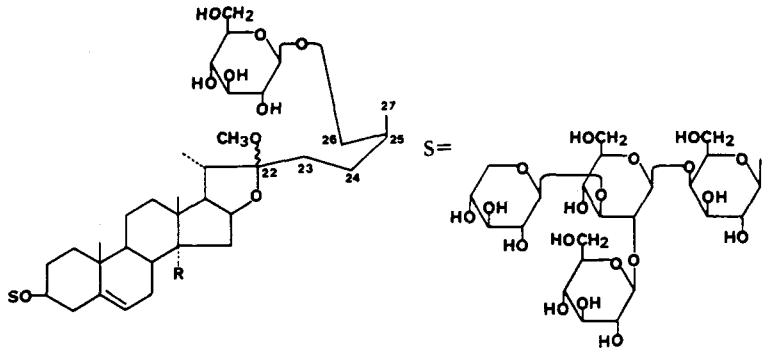
The rhizomes of *Polygonatum sibiricum* Redoute (Liliaceae) have been used in traditional Chinese medicine for treatment of fevers of influenza, mastitis, coughs, and lung trouble. A tincture, made by soaking two parts rhizome in one part wine, is used as a tonic for heart and lungs and a stimulant acting on the secretion of saliva and digestive juices. It is especially good for tubercular patients (1). A survey of the literature showed that various steroidal saponins have been reported from several *Polygonatum* species (2,3), although no chemical work has been done on *P. sibiricum*. The present paper describes the isolation and structural characterization of four steroidal saponins.

RESULTS AND DISCUSSION

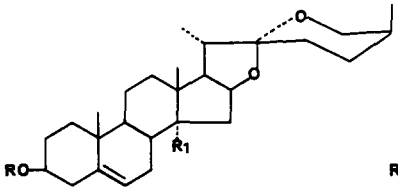
The MeOH extract of the rhizomes of *P. sibiricum*, on repeated chromatographic separation, gave two furostanol glycosides, compounds **1** and **2**, and two spirostanol glycosides, compounds **3** and **4**.

The major compound, designated PS-I [**1**], mp 218–221°, reacted positively to Ehrlich's reagent (4) and showed a strong absorption band due to hydroxy groups but no spiroketal side chain absorptions in the ir spectrum, suggesting that **1** is a furostanol glycoside. ^{1}H- and ^{13}C-nmr spectra (Tables 1–3) exhibited the presence of a methoxyl group and resonances typical of furostanol carbons. Enzymatic hydrolysis with almond emulsin yielded a glycoside **5**, mp 278–279°, and glucose. On acidic hydrolysis with 2 N HCl/dioxane, **5** liberated xylose, glucose, galactose, and an aglycone, which was identified as yamogenin [**6**] by direct comparison with an authentic sample. The fabms spectrum of **5** showed a cationized molecular ion $[M+Li]^+$ at *m/z* 1039, indicating that **5** was a yamogenin tetraoside having three moles of hexose and one mole of xylose. The permethylether of **5**, prepared by Hakomori's method (5), showed terminal permethylated pentosyl and hexosyl cations at *m/z* 175 and 219, respectively, in its eims spectrum, and four doublet signals (all $J=7$ Hz) at δ 4.25, 4.66, 4.86, and 4.95 ascribable to anomeric protons in the ^{1}H-nmr spectrum, suggesting that all the glycosidic linkages are β.

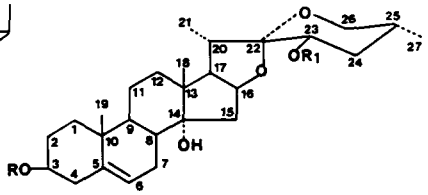
Methanolysis of the permethylether of **5** gave methyl 2,3,4,6-tetra-*O*-methylglucopyranoside, methyl 2,3,4-tri-*O*-methylxylopyranoside, methyl 4,6-di-*O*-methylglucopyranoside, and methyl 2,3,6-tri-*O*-methylgalactopyranoside. These results strongly suggested the sugar moiety to be β-lycotetraose, a well-known tetrasaccharide from various plant sources, as a sugar moiety of saponins (2). Thus, the structure of **5** could be assigned as yamogenin 3-*O*-β-lycotetraoside. This result was further supported by the fact that the ^{13}C-nmr spectra of **5** were in good agreement with literature data (6). Accordingly, the structure of **1** was determined to be 26-*O*-β-D-glucopyranosyl-22-*O*-



1 R=H
2 R=OH



3 R=S, R_1=OH
5 R=S, R_1=H
6 R=R_1=H
7 R=H, R_1=OH



4 R=S, R_1=H
8 R=R_1=H
9 R=R_1=Ac

methyl-25(*S*)-furost-5-ene-3β,26-diol 3-*O*-β-lycotetraoside. Although **5** has recently been isolated from another plant of the same genus, *Polygonatum odoratum* var. *pluriflorum* (6), its methyl prototype congener **1** appears not to have been described previously and has been named sibiricoside A.

PS-II [**2**], mp 202–204°, seemed to be a furostanol glycoside from the ir and positive colorization with Ehrlich's reagent. On enzymatic hydrolysis, **2** afforded glucose and a spirostanol glycoside **3**, mp 262–266°, identical in all respects with the PS-III

TABLE 1. Partial ^{1}H-nmr Spectral Data for Compounds **1–5** in Pyridine-d_5.[a]

Proton	Compound				
	1[b]	**2**[b]	**3**[b]	**4**[b]	**5**[c]
Me-18	0.69 s	0.84 s	0.96 s	0.91 s	0.82 s
Me-19	0.75 s	0.92 s	1.07 s	1.25 s	0.93 s
Me-21	1.06 d (6.7)	1.10 d (6.7)	1.20 d (6.8)	1.23 d (6.8)	1.13 d (6.9)
Me-27	0.94 d (6.3)	0.96 d (6.4)	1.08 d (6.8)	0.71 d (5.2)	1.09 d (7.1)
H-6	5.34 m	5.33 m	5.38 m	5.36 m	5.36 m
OMe	3.14 s	3.12 s	—	—	—
Anomeric protons	4.75 d (7.8)	4.76 d (7.7)	4.87 d (7.4)	4.83 d (7.3)	4.87 d (7.8)
	5.09 d (7.8)	5.08 d (8.2)	5.17 d (7.8)	5.13 d (7.9)	5.11 d (7.9)
	5.14 d (7.8)	5.13 d (7.6)	5.23 d (7.6)	5.19 d (7.0)	5.17 d (7.8)
	5.47 d (6.8)	5.47 d (6.6)	5.56 d (7.0)	5.55 d (7.3)	5.57 d (8.1)

[a]Data are δ (ppm), multiplicity, and *J* (in parentheses) in Hz.
[b]Measured with a Bruker AM-200 instrument.
[c]Measured with a Bruker AM-300 instrument.

TABLE 2. ^{13}C-nmr Chemical Shifts of Aglycone Moieties in Pyridine-d_5.[a]

Carbon No.	Compound						
	1	**2**	**3**	**4**	**5**	**7**[b]	**8**
C-1	37.6	37.9	37.7	37.7	37.5	38.1	38.0
C-2	30.3	30.4	30.2	30.1	30.1	32.7	32.6
C-3	78.8	78.8	78.6	78.5	78.7	71.3	71.3
C-4	39.4	40.2	39.9	39.7	39.3	43.5	43.5
C-5	141.2	140.5	140.5	140.5	141.1	141.6	141.5
C-6	121.8	122.4	122.2	122.2	121.6	121.6	121.6
C-7	32.4	26.8	30.0	26.6	32.2	26.3	26.7
C-8	31.8	35.7	35.6	35.5	31.7	35.7	35.6
C-9	50.4	43.7	43.6	43.5	50.3	43.7	43.7
C-10	37.1	37.6	37.4	37.3	37.1	37.4	37.4
C-11	21.2	20.2	20.4	20.2	21.1	20.5	20.5
C-12	39.9	32.0	32.0	32.2	39.9	32.1	32.3
C-13	40.9	45.6	45.1	45.6	40.5	45.1	45.7
C-14	56.7	86.9	86.6	86.6	56.7	86.5	86.6
C-15	32.4	39.5	39.3	39.2	32.2	39.9	39.8
C-16	81.5	82.3	82.0	82.4	81.2	82.0	82.5
C-17	64.3	61.3	59.7	59.5	62.7	59.8	59.6
C-18	16.4	20.1	20.0	20.2	16.3	20.1	20.3
C-19	19.5	19.5	19.3	19.2	19.4	19.5	19.4
C-20	40.6	40.6	42.6	35.8	42.5	42.6	35.8
C-21	16.5	16.8	15.2	15.0	14.9	15.2	15.0
C-22	112.9	113.5	110.1	111.8	109.7	110.1	112.0
C-23	31.2	31.2	26.7	67.5	26.4	26.7	67.6
C-24	28.4	28.4	26.3	38.7	26.2	26.6	38.9
C-25	34.7	34.7	27.6	31.6	27.6	27.6	31.7
C-26	75.1	75.2	65.1	65.9	65.1	65.1	65.9
C-27	17.7	17.7	16.3	16.8	16.3	16.4	16.9
OMe	47.5	47.5					

[a]All spectra run at 50.3 MHz except for **8** (75.5 MHz). Chemical shifts are reported in ppm from TMS. Multiplicities were obtained by DEPT spectra. Assignments were based on comparison to model compounds.

[b]Data for compound **7** are taken from Sugiyama *et al.* (6).

isolated from this plant. Compound **3** gave xylose, glucose, galactose, and uncharacterized resinous material on acid hydrolysis. Smith-de Mayo degradation (7) of **3** yielded a genuine sapogenin **7**, mp 208–210°, which was identified as neoprazerigenin A on the basis of spectroscopic and chemical evidence (6). The fabms spectrum of **3** exhibited a cationized molecular ion $[M+Li]^+$ at *m/z* 1055 suggesting that **3** was a neoprazerigenin A tetraoside. A detailed comparison of ^{1}H- and ^{13}C-nmr data (Tables 1 and 3) for **3** and **5** showed that the saccharide chain is identical in both compounds. From the above findings, the structure of **3** (=PS-III) was determined to be neoprazerigenin A 3-*O*-β-lycotetraoside. Finally, PS-II [**2**] was assigned to be 26-*O*-β-D-glucopyranosyl-22-*O*-methyl-25(*S*)-furost-5-ene-3β,14α,26-triol 3-*O*-β-lycotetraoside. PS-II [**2**] and PS-III [**3**] were isolated from *P. odoratum* var. *pluriflorum* (6) as a mixture of 25(*R*)- and 25(*S*)-epimeric pairs. However, we excluded the possibility that **2** and **3** are the mixture of 25(*R*) and 25(*S*) epimers by ^{1}H- and ^{13}C-nmr spectra.

PS-IV [**4**], mp 227–230°, was positive in the Liebermann-Burchard reaction and negative in the Ehrlich reaction. It showed a strong absorption band due to hydroxy groups in its ir spectrum. Acid hydrolysis of **4** afforded xylose, glucose, galactose, and uncharacterized resinous material. Smith-de Mayo degradation of **4**, followed by

TABLE 3. ^{13}C-nmr Chemical Shifts of Sugar Moieties in Pyridine-d_5.[a]

Carbon No.	Compound				
	1	2	3	4	5
Gal C-1	102.9	102.9	102.7	102.6	102.8
C-2	73.4	73.4	73.2	73.1	73.1
C-3	75.4	75.4	75.1	75.2	75.1
C-4	80.1	80.1	79.8	79.8	79.9
C-5	76.4	76.4	76.2	76.0	76.2
C-6	60.7	60.7	60.6	60.6	60.6
Glc C-1	105.1	105.1	104.7	104.6	104.8
($\rightarrow^{4}$Gal) C-2	81.5	81.5	81.3	81.2	81.3
C-3	86.9	86.9	86.9	87.0	86.9
C-4	70.9	70.9	70.7	70.6	70.8
C-5	78.8	78.8	78.6	78.5	78.7
C-6	62.6	62.6	62.5	62.3	62.5
Xyl C-1	105.3	105.4	105.1	104.8	105.1
($\rightarrow^{3}$Glc) C-2	75.7	75.7	75.5	75.4	75.6
C-3	77.8	77.8	77.5	77.4	77.6
C-4	70.7	70.7	70.4	70.3	70.5
C-5	67.5	67.5	67.3	67.2	67.3
Glc C-1	105.3	105.4	104.9	104.8	105.1
($\rightarrow^{2}$Glc) C-2	75.4	75.4	75.3	75.2	75.3
C-3	78.3	78.4	78.3	78.2	78.2
C-4	71.2	71.2	71.1	71.0	71.1
C-5	77.8	77.8	77.8	77.7	77.8
C-6	63.1	63.1	63.0	62.9	63.0
26-*O*-Glc C-1	105.3	105.4			
C-2	75.4	75.3			
C-3	78.8	78.8			
C-4	71.9	71.9			
C-5	78.3	78.4			
C-6	63.1	63.1			

[a]All spectra run at 50.3 MHz. Chemical shifts are reported in ppm from TMS. Multiplicities were obtained by DEPT spectra. Assignments were based on comparison to model compounds.

chromatographic purification, liberated a sapogenin **8**, mp 147–149°, which exhibited a molecular ion peak at *m/z* 446. It has three hydroxy groups in its structure, as may be deduced from the presence of the fragments at *m/z* 428, 410, and 392. However, **8** formed a diacetate **9**, mp 192–193° (*m/z* 530 for $[M]^+$; δ 2.02, s, 6H), upon acetylation, whose mass spectrum still exhibited the presence of a hydroxyl that presumably is tertiary as it resisted acetylation. The tertiary hydroxy group in **8** could be allocated to the C-14 position by the observation of peaks at *m/z* 301 and 287 as observed in **7** and isoplexigenin derivatives (8). The ^{13}C-nmr spectral data of **8** were very close to those of **7** except for the chemical shifts of carbons on rings E and F, indicating the presence of 3β,14α-hydroxy functionalities. The mass spectrum of **8** showed other important peaks at *m/z* 361, 155, and 131 with great relative abundance which are characteristic of 23-hydroxy spirostane sapogenins (9,10). A comparison of the ^{13}C-nmr spectra of **7** and **8** showed the expected downfield shifts for the absorptions due to C-22 (+1.9 ppm), C-23 (+40.9 ppm), and C-24 (+12.3 ppm), and an upfield shift for the C-20 (−6.8 ppm) due to the γ-gauche effect (11,12) exerted by the α-oriented hydroxyl group at C-23. The carbon resonances of the rings E and F were in close agreement with those of hongguanggenin (13) (the assignments for C-20 and -24 signals may need to be revised), confirming the α hydroxyl at C-23. Evidence for the presence of an equatorial

Me-27 was obtained from its chemical shift (δ 0.82 in $CDCl_3$ and δ 0.71 in pyridine-d_5) as well as from the position and the coupling pattern of the signal for H-26 (14,15). From the above data, the structure of **8** was assigned to be (23*S*,25*R*)-spirost-5-ene-3β,14α,23-triol, which has not been previously reported and has been named sibiricogenin. The fabms spectrum of **4** showed a cationized molecular ion $[M + Li]^+$ at *m/z* 1071, indicating that **4** was a sibiricogenin tetraoside. As shown in Table 3, ^{13}C-nmr spectral data of the sugar moiety in **4** were superimposable on those of **3** and **5**. In light of the above findings, the structure of PS-IV [**4**] was determined as sibiricogenin 3-*O*-β-lycotetraoside. This saponin has not been reported previously and has been named sibiricoside B.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined on a Yanaco or Mitamura-Riken apparatus and are uncorrected. Optical rotations were measured on a Rudolph Autopol III automatic polarimeter. Ir spectra were recorded on a Perkin-Elmer 283B spectrophotometer. Elemental analysis was performed on a Perkin-Elmer 240DS instrument. ^1H-nmr spectra were obtained on either a Varian FT-80A (80 MHz), a Bruker AM-200 (200 MHz), or a Bruker AM-300 (300 MHz) spectrometer using TMS as an internal standard. ^{13}C-nmr spectra were recorded with a Bruker AM-200 (50.3 MHz) or a Bruker AM-300 (75.5 MHz) instrument. Eims were determined on a Hewlett-Packard 5985B GC/MS System equipped with direct inlet system. For tlc, Kieselgel 60 F_{254} sheets (Merck) were used.

PLANT MATERIAL.—The rhizomes of *P. sibiricum* were collected in Kyong Bug province of Korea in the summer season of 1986, and authenticated by Prof. Weon Kim, College of Natural Sciences, Kyongbug National University, Korea. A voucher specimen is in College of Pharmacy, Yeungnam University.

EXTRACTION AND ISOLATION.—The dried and chopped rhizomes (30 kg) were percolated with MeOH (3 times, 12 h for each percolation) at room temperature. The extracts were combined and concentrated in vacuo to give a residue (7.14 kg), which was suspended in H_2O and extracted with Et_2O and then with *n*-BuOH. The *n*-BuOH solution was concentrated to give the *n*-BuOH-soluble fraction (135 g). A portion (80 g) was developed on Kiesel gel cc with $CHCl_3$-MeOH-H_2O (70:30:2→70:30:4→66:34:7) to give three fractions. The second fraction was rechromatographed over Si gel with EtOAc saturated with H_2O-MeOH (10:1) to give pure **3** and **4**. Similar treatment of the third fraction with EtOAc saturated with H_2O-MeOH (9:1) afforded **1** and **2**.

PS-I [**1**].—PS-I separated from aqueous EtOH as white amorphous powder: mp 218–221°; $[\alpha]^{20}D$ −51.0° (*c* = 0.15, MeOH); ir ν max (KBr) 3400, 1630, 1150, 1060, 1030, 1010, 885, 860 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Tables 2 and 3. *Anal.* calcd for $C_{57}H_{94}O_{28}\cdot 2H_2O$, C 55.78, H 7.72; found C 55.58, H 7.90.

PS-II [**2**].—PS-II separated from aqueous EtOH as white amorphous powder: mp 202–204°; $[\alpha]^{20}D$ −54.2° (*c* = 0.08, MeOH); ir ν max (KBr) 3400, 1620, 1150, 1075, 1040, 1010, 885, 870 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Tables 2 and 3. *Anal.* calcd for $C_{57}H_{94}O_{29}\cdot H_2O$, C 54.27, H 7.67; found C 54.17, H 7.73.

PS-III [**3**].—PS-III crystallized from aqueous MeOH as colorless needles: mp 258–260°; $[\alpha]^{20}D$ −63.0° (*c* = 0.15, MeOH); ir ν max (KBr) 3410, 1075, 1040, 990, 920, 880, 850, 820 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Tables 2 and 3. *Anal.* calcd for $C_{50}H_{80}O_{23}\cdot H_2O$, C 56.27, H 7.75; found C 56.08, H 7.80.

PS-IV [**4**].—PS-IV separated from MeOH as amorphous white powder: mp 227–230°; $[\alpha]^{20}D$ −23.2° (*c* = 0.16, MeOH); ir ν max (KBr) 3400, 1075, 1045, 970, 895, 885, 840, 822 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Tables 2 and 3. *Anal.* calcd for $C_{50}H_{80}O_{24}\cdot 2H_2O$, C 54.53, H 7.32; found C 54.41, H 7.40.

ENZYMATIC HYDROLYSIS OF **1** AND **2**.—Aqueous solutions of **1** (500 mg) and **2** (600 mg) were separately incubated with almond emulsin (70 mg each) at 37–40° for 24 h; then MeOH was added and the mixture filtered. The filtrate was evaporated in vacuo to give a residue, which was examined by tlc using a precoated cellulose plate developed in pyridine-EtOAc-HOAc-H_2O (36:36:7:21). In both residues D-glucose was identified. The residue from **1** was chromatographed on Si gel with EtOAc saturated with H_2O-MeOH (92:8) to afford **5** which crystallized from aqueous MeOH as colorless needles: mp 278–279°; ir ν max (KBr) 3380, 1070, 1045, 982, 890, 843 cm^{-1}; ^1H nmr see Table 1; ^{13}C nmr see Tables 2 and 3.

Similar treatment of the residue from **2** with EtOAc saturated with H_2O-MeOH (91:9) gave pure **3** which crystallized from aqueous MeOH as colorless needles, mp 262–266°; $[\alpha]^{20}D$ −62.7° (c = 0.14, MeOH). It was shown to be identical with an authentic sample of PS-III by co-tlc, mmp, ir, and ^1H and ^{13}C nmr.

ACID HYDROLYSIS OF **5**, **3**, AND **4**.—Compounds **5**, **3**, and **4** (ca. 30 mg each) were separately hydrolyzed with 4 N HCl-dioxane (1:1) (9 ml) by refluxing for 3 h on an H_2O bath, and each reaction mixture was poured into crushed ice and filtered. Each filtrate was neutralized with Ag_2CO_3 and filtered, and the solution was evaporated to dryness under reduced pressure. In the same manner as described above, D-glucose, D-xylose, and D-galactose were detected in each case as the common sugars. The precipitate obtained from **5** was recrystallized from Me_2CO to give **6**, mp 203–205°, as colorless needles; compound **6** was identified as yamogenin by direct comparison with an authentic sample (mmp, ir, and ^1H nmr). The aglycones obtained from **3** and **4** could not be characterized, due to the presence of resinous decomposed impurities, and no further work has been done on either sample.

PERMETHYLATION OF **5** FOLLOWED BY METHANOLYSIS.—Compound **5** (50 mg) was permethylated with NaH (100 mg) and MeI (6 ml) by Hakomori's method (5). The reaction product was chromatographed on Si gel with hexane-EtOAc (1:1) to afford the dodeca-*O*-methylether as a colorless syrup: ^1H nmr ($CDCl_3$, 80 MHz) δ 0.78 (3H, s, Me-18), 0.98 (3H, d, J = 6 Hz, Me-21), 1.01 (3H, s, Me-19), 1.06 (3H, d, J = 7.3 Hz, Me-27), 3.33 (3H, s, OMe), 3.36 (3H, s, OMe), 3.43 (6H, s, 2 × OMe), 3.46 (3H, s, OMe), 3.50 (6H, s, 2 × OMe), 3.55 (6H, s, 2 × OMe), 3.60 (9H, s, 3 × OMe), 4.25, 4.66, 4.86, and 4.95 (each 1H, d, J = 7 Hz, 4 × anomeric H), 5.30 (1H, m, H-6); ms (30 eV) *m/z* (rel. int.) $[M]^+$ (not observed), 409 (0.4), 397 (2.1), 395 (1.1), 391 (6.4), 285 (0.5), 282 (1.4), 253 (1.2), 233 (1.4), 219 (2.3), 205 (2.6), 187 (18.9), 175 (6.4), 173 (3.9), 155 (5.6), 143 (9.8), 139 (5.6), 115 (5.6), 111 (18.2), 101 (20.6), 88 (33.0). The dodeca-*O*-methylether (ca. 10 mg) was refluxed with 3% methanolic HCl (20 ml) for 4 h. The reaction mixture was concentrated to half volume, added to crushed ice, and filtered. The filtrate was neutralized with Ag_2CO_3, filtered, and concentrated. The dried hydrolysate was trimethylsilylated with a mixture of pyridine (0.5 ml), TMCS (0.1 ml) and HMDS (0.2 ml) for 15 min at 60°, subjected to gc, and identified as methyl 2,3,4-tri-*O*-methylxylopyranoside (Rt 1.82, 2.23), methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (Rt 4.02, 5.71), methyl 2,3,6-tri-*O*-methylgalactopyranoside (Rt 4.43, 5.23), and methyl 4,6-di-*O*-methylglucopyranoside (Rt 6.63) by comparison with authentic samples [column 5% NPGS on Chromosorb WHP (2.2 mm × 6 ft); column temperature 155°; flow rate (N_2) 41 ml/min].

SMITH-DE MAYO DEGRADATION OF **3** (7).—Compound **3** (70 mg) in 50% EtOH (14 ml) was oxidized with $NaIO_4$ (140 mg) at room temperature for 24 h. To the reaction mixture KOH (0.7 g) was added, and the reaction mixture was refluxed for 3 h. The solution was poured into crushed ice and filtered, and the precipitate was recrystallized from MeOH to give **7** as colorless needles: mp 209–210° [lit. (6) mp 211–213°]; ir ν max (KBr) 3400, 982, 960, 918, 890, 868, 840, 830, 813 cm^{-1} [intensity 918>890, 25(*S*)-spiroketal]; ^1H nmr ($CDCl_3$, 80 MHz) δ 0.94 (3H, s, Me-18), 1.02 (3H, d, J = 7 Hz, Me-21), 1.05 (3H, s, Me-19), 1.09 (3H, d, J = 5.6 Hz, Me-27), 3.30 (1H, br d, J = 10.9 Hz, H-26α), 3.50 (1H, m, H-3), 3.95 (1H, dd, J = 10.9, 1.8 Hz, H-26β), 4.64 (1H, q, J = 7 Hz, H-16), 5.39 (1H, br d, J = 2.5 Hz, H-6); ms (30 eV) *m/z* (rel. int.) $[M]^+$ 430 (1.0), 412 (91.5), 397 (9.6), 394 (3.3), 379 (34.9), 301 (1.4), 287 (0.9), $[301 - H_2O]^+$ 283 (14.3), $[287 - H_2O]^+$ 269 (13.2), $[287 - 2H_2O]^+$ 251 (13.1), 139 (100.0).

ACETYLATION OF **7**.—Compound **7** (7 mg) was treated with Ac_2O in pyridine (1 drop each) at room temperature for 24 h. Workup in the usual manner gave monoacetyl neoprazerigenin A, which was recrystallized from MeOH as colorless needles: mp 148–150° [lit. (6) mp 149–151°]; ^1H nmr ($CDCl_3$, 80 MHz) δ 0.93 (3H, s, Me-18), 1.01 (3H, d, J = 7.7 Hz, Me-21), 1.05 (3H, s, Me-19), 1.08 (3H, d, J = 4.9 Hz, Me-27), 2.02 (3H, s, OAc), 3.29 (1H, br d, J = 11.4 Hz, H-26α), 3.95 (1H, dd, J = 11.4, 2 Hz, H-26β), 4.63 (1H, q, J = 6.3 Hz, H-16), 5.39 (1H, br d, J = 2.5 Hz, H-6); ms (30 eV) *m/z* (rel. int.) $[M]^+$ 472 (0.2), 454 (0.2), 439 (0.2), 413 (0.8), $[M - (HOAc + H_2O)]^+$ 394 (100.0), 379 (5.9), 139 (33.4).

DEGRADATION OF **4**.—Compound **4** (70 mg) was degraded in the same manner as described above. The degraded product was chromatographed on Si gel with hexane-EtOAc (8:5) to afford **8** as colorless needles from MeOH: mp 147–149°; $[\alpha]^{25}D$ −87.8° (c = 0.1, $CHCl_3$); ir ν max (KBr) 3400, 985, 920, 892, 870, 860, 830, 813 [intensity 920<892, 25 (*R*)-spiroketal]; ^1H nmr ($CDCl_3$, 300 MHz) δ 0.82 (3H, d, J = 6.6 Hz, Me-27), 0.97 (3H, d, J = 7.2 Hz, Me-21), 0.99 (3H, s, Me-18), 1.05 (3H, s, Me-19), 3.25 (1H, t, J = 11.1 Hz, H-26α), 3.4–3.6 (3H, m, H-3, -23, -26β), 4.71 (1H, q, J = 7.0 Hz, H-16), 5.38 (1H, d, J = 5.0 Hz, H-6); ^1H nmr (pyridine-d_5, 300 MHz) δ 0.71 (3H, d, J = 6.1 Hz, Me-27), 1.07 (3H, s, Me-18), 1.25 (3H, d, J = 7.0 Hz, Me-21), 1.29 (3H, s, Me-19); ^{13}C nmr see Table 2; ms (30 eV) *m/z* (rel. int.) $[M]^+$ 446 (4.4), $[M - Me]^+$ 431 (1.0), $[M - H_2O]^+$ 428 (86.6), $[M - (H_2O + Me)]^+$ 413 (2.8), $[M - 2H_2O]^+$ 410 (25.3), $[M - (2H_2O + Me)]^+$ 395 (50.7), $[M - 3H_2O]^+$ 392 (3.3),

$[M-(3H_2O+Me)]^+$ 377 (20.9), 361 (53.1), $[361-H_2O]^+$ 343 (30.9), $[361-2H_2O]^+$ 325 (34.5), 301 (1.0), 287 (4.2), $[301-H_2O]^+$ 283 (43.2), $[287-H_2O]^+$ 269 (46.7), $[301-2H_2O]^+$ 265 (14.5), $[287-2H_2O]^+$ 251 (100.0), 176 (34.5), 158 (61.7), 155 (24.5), 131 (27.7).

ACETYLATION OF **8**.—Compound **8** (10 mg) was acetylated as above to give diacetyl sibiricogenin [**9**], which was crystallized from MeOH as colorless needles: mp 192–193°; $[\alpha]^{26}D$ −73.6° ($c=0.1$, $CHCl_3$); ^1H nmr ($CDCl_3$, 80 MHz) δ 0.82 (3H, d, $J=6.0$ Hz, Me-27), 0.96 (3H, d, $J=7.0$ Hz, Me-21), 0.97 (3H, s, Me-18), 1.05 (3H, s, Me-19), 2.02 (6H, s, 2 × OAc), 3.36 (2H, m, H-26), 4.67 (1H, q, $J=7.0$ Hz, H-16), 4.82 (1H, dd, $J=11$, 5 Hz, H-23), 5.38 (1H, m, H-6); ms (30 eV) *m/z* (rel. int.) $[M]^+$ 530 (1.0), $[M-HOAc]^+$ 470 (0.3), $[M-(Me+HOAc)]^+$ 455 (0.8), $[M-(H_2O+HOAc)]^+$ 452 (100.0), $[M-(H_2O+HOAc+Me)]^+$ 437 (1.2), $[M-2HOAc]^+$ 410 (0.8), $[M-(2HOAc+H_2O)]^+$ 392 (9.3), $[M-(2HOAc+H_2O+Me)]^+$ 377 (5.0), 343 (0.8), $[343-H_2O]^+$ 325 (4.4), $[343-(HOAc+H_2O)]^+$ 265 (1.5), 251 (6.3), 235 (4.7), 197 (2.1), 173 (2.2), 158 (22.5), 145 (11.9), 85 (20.0).

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