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TWO NEW PREGNANE OLIGOGLYCOSIDES FROM *DREGEA SINENSIS* VAR. *CORRUGATA*

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ABSTRACT.—Two new oligoglycosides designated as dregeosides B and C have been isolated from the dried rhizomes of *Dregea sinensis* var. *corrugata*. Spectroscopic and chemical evidence are consistent with the structure 12-β-*O*-isovaleryl-dihydrosarcostin-3-*O*-β-D-glucopyranosyl-(1↦4)-3-*O*-methyl-6-deoxy-β-D-allopyranosyl-(1↦4)-β-D-oleandropyranosyl-(1↦4)-D-cymaropyranoside [**1**] for dregeoside B and the structure 12-β-*O*-acetyl-20-*O*-benzoyl-tomentogenin-3-*O*-β-D-oleandropyranosyl-(1↦4)-β-D-cymaropyranosyl-(1↦4)-β-D-cymaropyranoside [**9**] for dregeoside C.

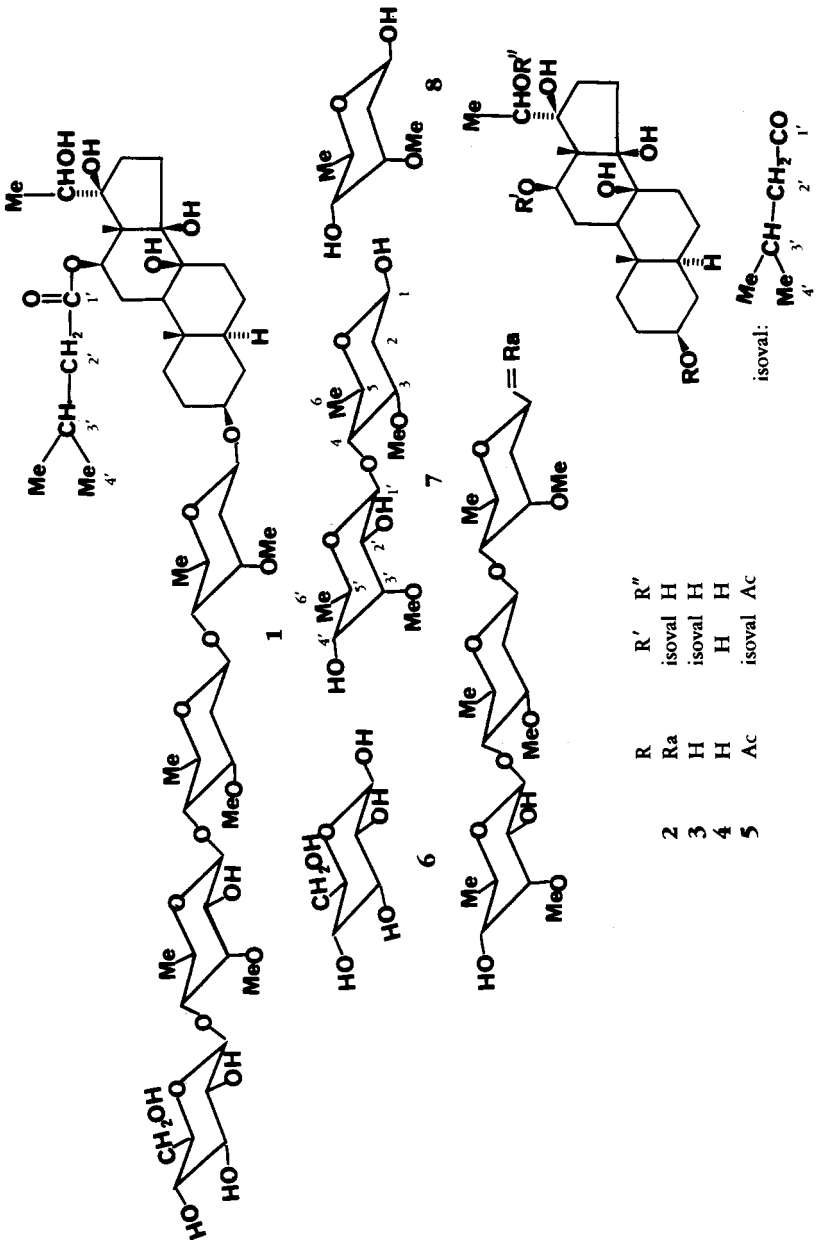
In a previous paper (1), we reported the isolation and structural elucidation of dregeoside A. As a continuation of our phytochemical investigation of *Dregea*, we are presenting here spectral and chemical evidence for the structures of two new pregnane oligoglycosides, designated as dregeosides B and C. Asclepiadaceae plants have shown significant physiological activities, and a pharmacological study shows that the crude glycoside from *Dregea sinensis* var. *corrugata* Schneid. has anticonvulsant and antihepatitis activity and therapeutic activity on chronic epilepsy (2). In order to obtain more medicinal compounds from plant sources, we initiated a study of this family of plants.

Dregeoside B [**1**] showed positive Liebermann-Burchard and Keller-Kiliani reactions (3), which indicated the presence of a steroidal glycoside with a 2-deoxy sugar. Fabms of intact dregeoside B [**1**] produced a protonated molecular ion at *m/z* 1079 $[M+1]^+$ and ions at *m/z* 916 $[M+1-\text{glucose}]^+$, 755 $[M+1-\text{glucose}-3\text{-}O\text{-methyl-6-deoxyallose}]^+$, 610 $[M+1-\text{glucose}-3\text{-}O\text{-methyl-6-deoxyallose}-\text{oleandrose}]^+$, 465 $[M+1-\text{glucose}-3\text{-}O\text{-methyl-6-deoxyallose}-\text{oleandrose}-\text{cymarose}]^+$, and *m/z* 451, 433, 415, and 397 indicative of losses of one, two, three, and four molecules of H_2O, respectively, from the aglycone drevogenin **3** (mol wt 468). The ^{1}H-nmr spectrum of **1** at 400 MHz showed the methyl groups of the aglycone moiety at δ 0.97 (3H, s, Me-19), 1.06 (6H, d, $J=6.5$ Hz, Me-4′), 1.17 (3H, d, $J=6.5$ Hz, Me-21), 1.24 (3H, s, Me-18), and three secondary methyl groups and three methoxy groups at 1.23 (3H, d, $J=6$ Hz, Me), 1.26 (3H, d, $J=6$ Hz, Me), 1.35 (3H, d, $J=6$ Hz, Me), and 3.43 (3H, s, OMe), 3.46 (3H, s, OMe), and 3.47 (3H, s, OMe). The β linkages of the sugar were revealed by the coupling constants of four anomeric proton signals at δ 4.32 (1H, d, $J=7.3$ Hz), 4.56 (1H, d, $J=7.8$ Hz), 4.75 (1H, dd, $J=10$ and 2 Hz), and 4.83 (1H, dd, $J=10$ and 2 Hz).

Enzymatic hydrolysis of **1** with β-glucosidase (snail enzyme) afforded a triglycoside **2** and a sugar **6** that was identified as glucose by tlc comparison with an authentic sample, showing that glucopyranose is the terminal sugar. Acetylation of **2** afforded a triacetate. The fdms of this triacetate showed a prominent ion at *m/z* 245, corresponding to the diacetate of 3-*O*-methyl-6-deoxyallose. This indicates that 3-*O*-methyl-6-deoxyallose is the terminal sugar of **2**.

Mild acid hydrolysis of **2** afforded crystalline genin **3** and a mixture of two sugars. The separated sugar **7** was identified as pachybiose by mmp, ^{1}H nmr, [α]D, and comparison of its tlc with an authentic sample which was isolated from the same plant. The other sugar **8** was identified as cymarose by mmp, [α]D, and comparison of its tlc with an authentic sample (4).

The ability of the genin **3** to undergo methanolysis by the Zemplén method (5,6)


1
2 R Ra
3 H H
4 H H
5 Ac isoval Ac
6
7
8
R' R''
isoval H
isoval H
H H
isoval:

indicated the presence of an ester group. The mass spectrum of the methanolysis products contained prominent peaks at *m/z* 116, 85, and 57 assigned to methyl isovalerate, confirming the presence of an isovaleryl ester function in **3**. The hydrolysate afforded a crystalline product **4** identical with dihydrosarcostin (7). The ease of reaction of genin **3** with sodium periodate suggested that its C-20 hydroxy group was not esterified. The genin **3** was thus identified as 12-β-*O*-isovaleryl-dihydrosarcostin.

Acetylation of **3** with Ac_2O in pyridine yielded the di-*O*-acetyl derivative **5** also characterized from its ^1H nmr.

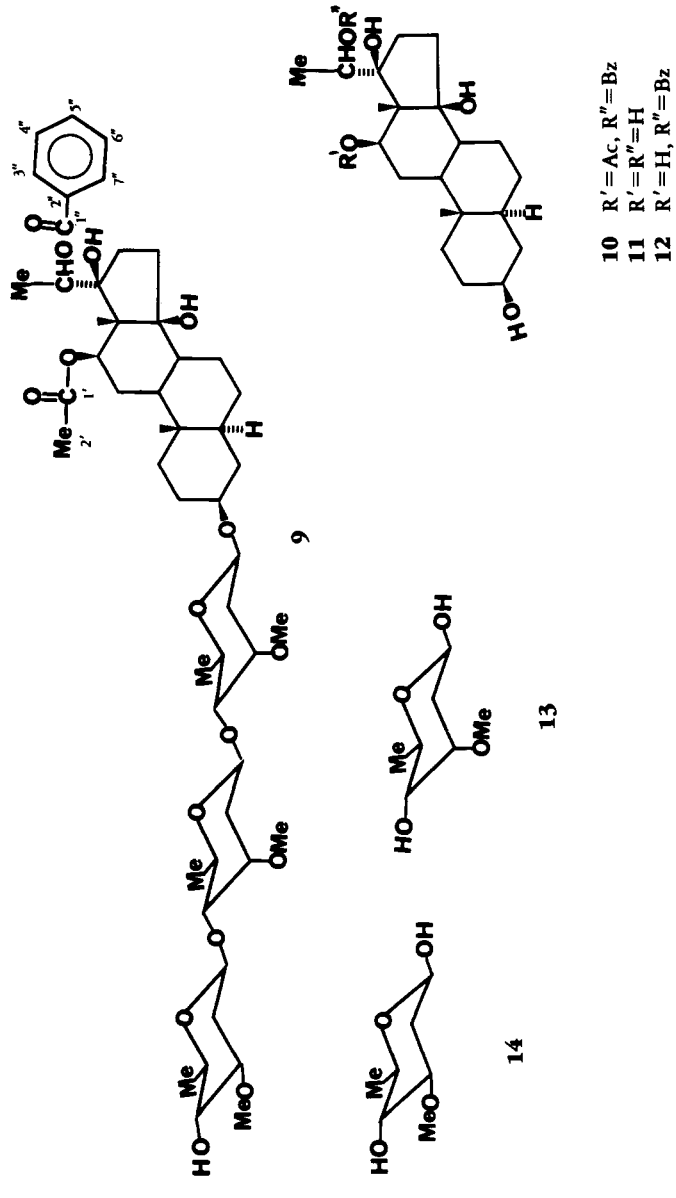
In light of the foregoing evidence, the structure of dregeoside B was established as 12-β-*O*-isovaleryl-dihydrosarcostin-3-*O*-β-D-glucopyranosyl-(1↦4)-3-*O*-methyl-6-deoxy-β-D-allopyranosyl-(1↦4)-β-D-oleandropyranosyl-(1↦4)-D-cymaropyranoside. Its ^{13}C-nmr spectrum is given in Table 1.

Dregeoside C [**9**] showed positive Liebermann-Burchard and Keller-Kiliani reactions. Fabms of intact dregeoside C [**9**] produced a protonated molecular ion at 947 $[M+1]^+$ and ions at *m/z* 802 $[M+1-\text{oleandrose}]^+$, 649 $[M+1-\text{oleandrose}-\text{cymarose}]^+$, and 514 $[M+1-\text{oleandrose}-\text{cymarose}-\text{cymarose}]^+$ and at

TABLE 1. ^{13}C-nmr Spectral Data for Dregeosides B [**1**] and C [**9**].[a]

Dregeoside B [**1**]					Dregeoside C [**9**]			
Carbon	Aglycone	Sugar	Carbon	Moiety	Aglycone	Sugar	Carbon	Moiety
C-1	38.5	Cymarose	C-1	96.4	38.1	Cymarose	C-1	96.6
C-2	31.9		C-2	37.4	33.2		C-2	37.3
C-3	70.6		C-3	78.0	70.9		C-3	77.4
C-4	38.7		C-4	83.2	38.9		C-4	83.7
C-5	46.0		C-5	69.3	45.4		C-5	68.7
C-6	34.3		C-6	18.6	34.0		C-6	18.5
C-7	34.5		3-OMe	58.9	34.3		3-OMe	58.5
C-8	76.1	Oleandrose	C-1	101.6	40.0	Cymarose	C-1′	100.3
C-9	46.8		C-2	37.3	46.6		C-2′	38.0
C-10	38.7		C-3	79.3	38.2		C-3′	77.4
C-11	26.4		C-4	83.2	28.7		C-4′	83.1
C-12	77.6		C-5	72.1	74.8		C-5′	68.7
C-13	45.7		C-6	18.6	56.1		C-6′	18.6
C-14	87.6		3-OMe	57.1	83.3		3-OMe	58.4
C-15	33.4	Allose	C-1	103.7	34.1	Oleandrose	C-1	102.1
C-16	32.8		C-2	72.2	32.7		C-2	37.3
C-17	88.5		C-3	83.1	88.7		C-3	81.1
C-18	11.9		C-4	83.1	11.8		C-4	76.7
C-19	16.4		C-5	69.2	16.2		C-5	73.5
C-20	69.5		C-6	18.6	69.5		C-6	18.1
C-21	16.7		3-OMe	61.7	16.7		3-OMe	56.8
C-1′	172.6	Glucose	C-1	106.1	170.6			
C-2′	43.3		C-2	75.4	21.6			
C-3′	25.6		C-3	78.3				
C-4′	22.5		C-4	71.9				
C-1″			C-5	78.1	166.2			
C-2″			C-6	63.1	130.3			
C-3″					130.3			
C-4″					129.2			
C-5″					133.4			
C-6″					129.2			
C-7″					130.3			

[a]Obtained at 400 MHz in $CDCl_3$, δ TMS = 0 ppm.



10 R′=Ac, R″=Bz
11 R′=R″=H
12 R′=H, R″=Bz

m/z 497, 479, and 461, indicative of losses of one, two, and three molecules of H_2O, respectively, from dregeoside C [**9**] containing the aglycone, drevogenin C [**10**] (mol wt 514). The ^{1}H-nmr spectrum of **9** at 400 MHz showed the following signals: δ 1.23 (6H, d, J = 6 Hz, 2 × Me), 1.34 (3H, d, J = 6 Hz, Me), 3.38 (3H, s, OMe), 4.45 (6H, s, 2 × OMe), of which a methyl group could be assigned to C-3 and C-6 of a molecular deoxy sugar. The anomeric protons of the sugars gave signals at 4.47 (1H, dd, J = 10 and 2 Hz, H-1 of cymarose), 4.74 (1H, dd, J = 10 and 2 Hz, H-1 of cymarose), 4.82 (1H, dd, J = 10 and 2 Hz, H-1 of oleandrose), indicating the configuration of each sugar was the β-D form. Two signals at 4.60 (1H, dd, J = 10 and 5 Hz, H-12) and 4.70 (1H, dd, J = 6.5 Hz, H-20), revealed that ester groups are attached at the C-12 and C-20 positions (8).

Dregeoside C [**9**] was acetylated with Ac_2O/pyridine to give a monoacetate. Mild acid hydrolysis of the monoacetate with dilute H_2SO_4 yielded 4-*O*-acetyloleandrose, cymarose, and drevogenin C [**10**]. The sugar moieties cymarose [**13**] and oleandrose [**14**] were identical with authentic samples as determined by tlc and glc (trimethylsilyl derivative of sugar), which led to the conclusion that oleandrose is the terminal sugar.

Complete alkaline hydrolysis of **10** with 5% KOH/MeOH gave tomemtogenin C [**11**], benzoic acid, and HOAc, identical with authentic samples. Partial alkaline hydrolysis of **10** with 8% K_2CO_3/MeOH/H_2O gave a product C **12** which showed a molecular ion at *m/z* 472, consistent with a composition $C_{28}H_{40}O_6$. Ions at *m/z* 105 and 232 $[M - CH_3CHOCOC_6H_5]^+$ indicated the presence of a benzoyl group, as did its ^{1}H-nmr spectrum (signals at 7.46–8.05, but not at 2.10). The signal for H-12 was shifted from 4.60 ppm to 3.95 ppm, indicating that the benzoyl group is attached at C-20.

In light of the foregoing evidence, the structure of dregeoside C [**9**] was established as 12-β-*O*-acetyl-20-*O*-benzoyl-tomentogenin-3-*O*-β-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside. This structure is consistent with its ^{13}C-nmr spectrum (Table 1).

EXPERIMENTAL

Mp's were determined on a Kofler micromelting point apparatus and are uncorrected. All [α]D values were measured with a JASCO-20C polarimeter. Uv spectra were measured with a Shimadzu uv-210 spectrometer. Ir spectra were taken with a Perkin-Elmer 577. Glc analysis was carried out with Shimadzu GC-9A spectrometer. ^{1}H-nmr and ^{13}C-nmr spectra were recorded on AM-400 (Bruker) spectrometer; TMS was used as the internal standard and chemical shifts are recorded in δ (ppm) value. Mass spectra were recorded with a JEOL LMS-D-300 mass spectrometer. Tlc was performed using normal phase Si gel plates with $CHCl_3$-MeOH (95:5) and reversed-phase plates (RP-8-F_{254} S, Fertigplatten) with MeOH-H_2O (8:2).

PLANT MATERIAL.—The rhizomes of *D. sinensis* var. *corrugata* were collected in Li Qiang Yunnan province, China in October 1986 and identified by Prof. P.T. Li. A voucher specimen, Herbarium No. 1168281, is preserved at our institute.

PLANT EXTRACTION.—Shade-dried powdered rhizomes (5.0 kg) of *D. sinensis* var. *corrugata* were extracted with hot EtOAc. Aqueous concentrates were obtained by evaporation of EtOAc in vacuo. The aqueous concentrate was fractionated with different organic solvents to afford a petroleum ether extract (20 g) and a $CHCl_3$ extract (10.5 g). The $CHCl_3$ extract (i.e., crude glycoside) was subjected to cc on Si gel with $CHCl_3$-MeOH (95:5) and further on reversed-phase (RP-8) with MeOH-H_2O (7:3) to afford dregeosides B (100 mg) and C (130 mg).

Dregeoside B [**1**].—Amorphous powder: mp 135–138°, $[\alpha]^{20}D$ + 12.5° (c = 0.13, MeOH). It showed positive Liebermann-Burchard and Keller-Kiliani reactions and underwent $NaIO_4$ oxidation. Ir max (KBr) 3400, 1720, 2925, 1400, 1385, 1195, 1160, 1080, 1060 cm^{-1}; ^{1}H-nmr (400 MHz, $CDCl_3$) δ 4.32 (1H, d, J = 7.3 Hz, H-1′ of glucose), 4.56 (1H, d, J = 7.8 Hz, H-1′ of allose), 4.75 (1H, dd, J = 10 and 2 Hz, H-1′ of cymarose), 4.83 (1H, dd, J = 10 and 2 Hz, H-1′ of oleandrose), 4.70 (1H, d, J = 10 and 5 Hz, H-12), 3.67 (1H, m, D_2O exchange q, J = 6 Hz, H-20), 3.46 (3H, s, OMe), 3.43 (3H, s, OMe), and

3.47 (3H, s, OMe), 1.06 (6H, d, J = 6.5 Hz, 4′-Me), 1.17 (3H, d, J = 6.5 Hz, 21-Me), 1.22 (3H, d, J = 6 Hz, Me), 1.26 (3H, d, J = 6 Hz, Me), 1.35 (3H, d, J = 6 Hz, Me), 1.24 (3H, s, Me-18), 0.97 (3H, s, Me-19); ^{13}C-nmr see Table 1; fabms *m/z* (rel. int.) $[M+1]^+$ 1079 (65), $[M+1-$tetrasaccharide$]^+$ 468 (64), $[468-H_2O]^+$ 450 (25), $[468-2H_2O]^+$ 432 (20), $[468-(Me)_2CH\text{-}CH_2\text{-}COOH]^+$ 366 (25), $[468-(Me)_2CH\text{-}CH_2\text{-}COCH-H_2O]^+$ 330 (13), $[(Me)_2\text{-}CH\text{-}CH_2C\equiv O]^+$ 85 (100), $[(Me)_2\text{-}CH\text{-}CH_2\text{-}]^+$ 57 (65); sugar fragments [tetrasaccharide]$^+$ 610 (20), $[610-3MeOH]^+$ 514 (18), [610 − pachybiose]$^+$ 288 (13), [3-*O*-methyl-6-deoxyallose]$^+$ 178 (13), [oleandrose or cymarose]$^+$ 162 (4.5), $[162-MeOH]^+$ 130 (7.5). *Anal.* calcd for $C_{53}H_{90}O_{22}$, C 58.99, H 8.35; found C 58.85, H 8.25%.

ENZYMATIC HYDROLYSIS OF **1** WITH β-GLUCOSIDASE (SNAIL ENZYME).—A suspension of **1** (30 mg) in 0.3 M NaOAc buffer adjusted to pH 5.5 was treated with a suspension of β-glucosidase prepared from a snail (*Fruticila grainesil*). The mixture was allowed to stand at 37° for 1 week, then extracted with MeOH. The insoluble precipitate was filtered off, and the filtrate was evaporated to dryness. The residue was subjected to cc on Si gel [increasing polarity of solvent from $CHCl_3$-MeOH (95:5)] to separate **2** and **6**. Compound **6** was identified as glucose by comparison with an authentic sample ([α]D, tlc, mmp).

MILD ACID HYDROLYSIS OF **2**.—To solution of **2** (40 mg) in 50% MeOH (20 ml) was added 0.05 M H_2SO_4 (5 ml). The mixture was then concentrated under reduced pressure to remove the MeOH. The aqueous portion was repeatedly extracted with $CHCl_3$-MeOH (99:1), and the organic layer was washed in sequence with H_2O, 2 N Na_2CO_3, and again with H_2O, dried over Na_2SO_4, and evaporated to afford genin **3** which crytallized from Me_2CO/hexane as colorless needles (15 mg) mp 165–168°. It underwent $NaIO_4$ oxidation and identified as 12-*O*-isovaleryl-dihydrosarcotin. ^{1}H-nmr (400 MHz, $CDCl_3$) δ 0.907 (3H, s, Me-19), 1.06 (6H, d, J = 6.5 Hz, Me-4′), 1.17 (3H, s, J = 6.5 Hz, Me-21), 1.24 (3H, s, Me-18), 3.65 (1H, q, J = 6.5 Hz, H-20), 4.70 (1H, dd, J = 10 and 5 Hz, H-12). The aqueous hydrolysate was neutralized with freshly prepared $BaCO_3$, filtered, and concentrated under reduced pressure to afford a mixture of sugars which were isolated through cc affording **7** (2.5 mg): $[\alpha]^{20}D$ −8.5 (c = 0.32, H_2O) and **8** (3.0 mg), $[\alpha]^{20}D$ +49.5° (c = 0.12, H_2O); ^{1}H-nmr (400 MHz, $CDCl_3$) δ 1.27, 1.34 (each 3H, d, J = 6 Hz, Me-6 of -6′), 1.59 (1H, ddd, J = 13, 10.5, and 4 Hz, 2-CH_β), 2.21 (1H, ddd, J = 13, 4, and 2 Hz, 2-CH_α), 3.41, 3.64 (each 3H, s, 3- or 3′-OMe), 4.76 (1H, d, J = 8 Hz, 1′-H_α), 5.25 (1H, dd, J = 4 and 2 Hz, 1-CH_β). Compound **8**: δ 1.26 (H, d, J = 6.4 Hz, Me-6), 1.55 (1H, ddd, J = 14, 4, and 2 Hz, 2-CH_β), 3.31 (1H, dd, J = 10 and 3 Hz, 4-CH), 3.52 (3H, s, 3-OMe), 3.75 (1H, ddd, J = 4, 3, and 2 Hz, 3-CH), 4.21 (1H, dq, J = 10 and 6.4 Hz, 5-CH), 5.05 (1H, dd, J = 10 and 2 Hz, 1-CH_α).

DI-*O*-ACETYL-ISOVALERYL-DIHYDROSARCOSTIN [**5**].—Crystalline **3** (5 mg) dissolved in anhydrous C_5H_5N (0.4 ml) was mixed with Ac_2O (0.5 ml), and the mixture was kept for 48 h at room temperature. After the usual workup of the reaction mixture, it afforded the acetylated product **5** (2.5 mg) which crystallized from Me_2CO/hexane: mp 146–149°; ^{1}H-nmr (400 MHz) δ 1.53 (3H, s, OAc), 1.98 (3H, s, OAc), 4.83–4.42 (3H, m, H-3, H-12, and H-20). *Anal.* calcd for $C_{30}H_{48}O_9$, C 65.22, H 8.69; found C 65.10, H 8.54%.

HYDROLYSIS OF **3** BY THE ZEMPLÉN METHOD.—To a solution of **3** (4 mg) in absolute MeOH (2 ml) was added NaOMe (4 ml), and the mixture was kept at room temperature. When the reaction was complete (tlc) it was neutralized with IR 120H resin and filtered. MeOH was removed under reduced pressure yielding a viscous product (3 mg), which gave ions at *m/z* 116, 85, and 57 in the lower mass region of its ms. The chromatographic separation of the hydrolysate afforded product **4**. The mmp, tlc, and [α]D comparison with the authentic material confirmed it as dihydrosarcostin (7) mp 269–271°, [α]D +63°.

DREGEOSIDE C [**9**].—Amorphous powder, mp 143–146°; $[\alpha]^{20}D$ +37.5° (c = 0.92, MeOH). *Anal.* calcd for $C_{51}H_{78}O_{16}$, C 64.69, H 8.25; found C 64.53, H 8.07%. It showed positive Liebermann-Burchard and Keller-Kiliani reactions. Uv λ max (MeOH) nm (log ε) 231 (4.23), 274 (3.12), 282 (3.05); ir max (KBr) 3420 (OH), 1715, 1730, 2925, 1440, 1195, 1160, 1080, 1050 cm^{-1}; ^{1}H nmr (400 MHz, $CDCl_3$) δ 7.49 (2H, t, J = 7.9 Hz, 4″-, 6″-CH), 7.62 (1H, tt, J = 7.9 and 1.2 Hz, 5″-CH), 8.05 (2H, dd, J = 7.9 and 1.2 Hz, 3″-, 7″-CH), 4.47 (1H, dd, J = 10 and 2 Hz, H-1 of cymarose), 4.74 (1H, dd, J = 10 and 2 Hz, H-1 of cymarose), 4.82 (1H, dd, J = 10 and 2 Hz, H-1 of oleandrose), 4.60 (1H, dd, J = 10 and 5 Hz, H-12), 4.70 (1H, q, J = 6.5 Hz, H-20), 3.39 (3H, s, OMe), 3.44 (3H, s, 2 × OMe), 2.10 (3H, s, Me-2′), 1.34 (3H, d, J = 6 Hz, Me), 1.25 (6H, d, J = 6 Hz, 2 × Me), 1.24 (3H, s, 18-Me), 0.97 (3H, s, Me-19); ^{13}C nmr see Table 1; fabms *m/z* (rel. int.) $[M+1]^+$ 947 (85), $[M+1-$trisaccharide$]^+$ 514 (75), $[514-H_2O]^+$ 496 (18), $[514-2H_2O]^+$ 478 (15), $[514-Ac]^+$ 471 (25), $[514-HOAc]^+$ 454 (32), $[514-BzOH]^+$ 392 (70), $[514-CH_3CHOCOC_6H_5]^+$ 365 (75), $[514-C_6H_5\text{-}C\equiv C]^+$ 309 (100); sugar fragments *m/z* [dicymarose and oleandrose]$^+$ 450 (15), $[450-3MeOH]^+$ 354 (25), [rearranged disaccharide fragment]$^+$ 290 (100), [cymarose or oleandrose]$^+$ 162 (32), $[162-MeOH]^+$ 130 (21).

MILD ACID HYDROLYSIS OF DREGEOSIDE C [**9**].—To a solution of **9** (20 mg) in MeOH (10 ml) was added 0.05 M H_2SO_4 (2 ml), and the mixture was warmed for 30 min at 50° and concentrated under re-

duced pressure to remove MeOH. The aqueous concentrate was repeatedly extracted with $CHCl_3$, and the organic layer was washed in turn with H_2O, 1 M Na_2CO_3, and H_2O, dried over Na_2SO_4, and evaporated to afford the aglycone **10** (12 mg), mp 235–238°, $[\alpha]^{20}D$ +36.5 (c = 0.52, MeOH). *Anal.* calcd for $C_{30}H_{42}O_7$, C 70.03, H 8.17; found C 69.88, H 8.01%; ms *m/z* 514 $[M]^+$; ^{1}H-nmr (400 MHz, $CDCl_3$) δ 0.97 (3H, s, Me-19), 1.45 (3H, s, Me-18), 1.19 (3H, d, J = 6.5 Hz, Me-21), 2.10 (3H, s, Me-2′), 2.57, 3.35 (each H, br s, 3 × OH, D_2O exchange), 3.65 (1H, m, H-3), 4.60 (1H, dd, J = 10 and 5 Hz, H-12), 7.49–8.05 (5H, m, aromatic). The aqueous hydrolysate was neutralized with freshly precipitated $BaCO_3$, filtered, and concentrated under reduced pressure to yield a syrupy solution which gave a positive Keller-Kiliani reaction and which was identical with an authentic samples by tlc and gc comparison: tlc cymarose R_f 0.45 and oleandrose R_f 0.26 and gc column SE-54, 30 m, column temperature 160°, N_2 flow 20 ml/min, trimethylsilyl sugar relative retention time (min): 0.44 cymarose, 0.37 oleandrose.

COMPLETE ALKALINE HYDROLYSIS OF **10**.—Compound **10** (15 mg) was dissolved in 5% methanolic KOH (4 ml) and refluxed for 2 h. After adding H_2O (2 ml), MeOH was removed under reduced pressure. The aqueous concentrate was extracted with $CHCl_3$-MeOH (9:1), dried over Na_2SO_4, filtered, and evaporated to dryness, yielding tomentogenin [**3**] (3.5 mg) which crystallized from Me_2CO, mp 247–249, $[\alpha]^{20}D$ +36.5 (c = 0.45, MeOH). It was identified as tomentogenin (9) by comparison with an authentic sample (tlc, ir, mmp): ^{1}H-nmr ($CDCl_3$) 4.46 (1H, q, J = 6.5 Hz, H-20), 3.95 (1H, dd, J = 10 and 5 Hz, H-12), 3.84 (1H, m, C_3-H), 1.80 (3H, s, Me-18), 1.51 (3H, d, J = 6.5 Hz, Me-21), 1.28 (3H, s, Me-19).

PARTIAL ALKALINE HYDROLYSIS OF **10**.—Compound **10** (10 mg) was dissolved in 8% K_2CO_3/MeOH/H_2O (5 ml). MeOH was removed under reduced pressure. The aqueous concentrate was extracted with EtOAc, dried over Na_2SO_4, filtered, and evaporated to dryness yielding **12**, which chromatographed on Si gel with $CHCl_3$-MeOH (96:4): mp 213–215°, $[\alpha]^{20}D$ +17.8 (c = 0.35, MeOH), *m/z* $[M]^+$ 472 (80), $[M-H_2O]^+$ 450 (35), $[M-2H_2O]^+$ 436 (25), $[M-BzOH]^+$ 350 (35), $[M-CH_3CHCCOC_6H_5]^+$ 323 (60), $[C_6H_5C\equiv O]^+$ 105 (100), $[C_6H_5\text{-}]^+$ 77 (75); ir max (KBr) cm^{-1} 1715 (C=O); ^{1}H-nmr ($CDCl_3$) δ 1.30 (3H, s, Me-19), 1.85 (3H, s, Me-18), 1.25 (3H, d, J = 6.5 Hz, Me-21), 3.95 (1H, dd, J = 10 and 5 Hz, H-12), 3.65 (1H, m, C_3-H), 5.20 (1H, q, J = 6.5 Hz, H-20), 7.49–8.05 (5H, m, aromatic).

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