[Chem. Pharm. Bull. 33(6)2287—2293(1985)]

# Studies on the Constituents of Asclepiadaceae Plants. LIX.[1] The Structures of Five New Glycosides from *Dregea volubilis* (L.) BENTH.

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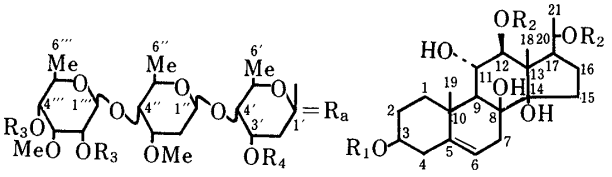
(Received September 17, 1984)

The glycosides of *Dregea volubilis* (L.) BENTH. were further investigated. Five new glycosides named dregeosides H (**1**), $D_{p1}$ (**2**), $D_{a1}$ (**3**), $G_{p1}$ (**4**), and $G_{a1}$ (**5**) were isolated and their structures were characterized on the basis of chemical and spectral evidence.

**Keywords**——dregeosides H, $D_{p1}$, $D_{a1}$, $G_{p1}$, $G_{a1}$; *Dregea volubilis* (L.); Asclepiadaceae; marsectohexol; drevogenin D; drebyssogenon G

We have already reported in a previous paper[2] the isolation of seven glycosides named dregeosides $A_{01}$, $A_{p1}$, $A_{11}$, $A_{a1}$, $C_{11}$, $K_{p1}$, and $K_{a1}$ from the stem of *Dregea volubilis* (L.) BENTH, which has been used as an antifebrile and emetic in South-east Asia. Among them, dregeosides $A_{p1}$ and $A_{01}$ showed antitumor activities against Ehrlich carcinoma (solid type) and the latter also showed activity against melanoma B-16. The present paper deals with the isolation and structural elucidation of five new glycosides named dregeosides H (**1**), $D_{p1}$,(**2**), $D_{a1}$ (**3**), $G_{p1}$ (**4**), and $G_{a1}$ (**5**).

The less polar portion of the crude glycosides of this plant was subjected to repeated silica gel and reversed phase gel column chromatography with various solvent systems to give **1**, **2**, **3**, **4**, and **5** (yields: 0.03, 0.02, 0.01, 0.03, and 0.01% from the dried crude drug, respectively) as amorphous white powders.



**1**: $R_1=R_a$, $R_2=R_3=R_4=H$
**6**: $R_1=R_2=H$
**10**: $R_1=R_a$, $R_2=R_3=Ac$, $R_4=H$
**11**: $R_1=R_a$, $R_2=R_3=R_4=Ac$

Chart 1

Dregeoside H (**1**) has the molecular formula $C_{41}H_{68}O_{16}$ on the basis of its elementary analysis. The field desorption mass spectrum (FD-MS) of **1** gave an ion peak at *m/z* 816 ($M^+$). On mild acidic hydrolysis (0.05 N $H_2SO_4$–75% MeOH, 70 °C, 30 min), **1** afforded the aglycone (**6**) and digitoxose (**7**) and asclepobiose (**8**) as sugars; the sugars were identified by thin-layer chromatography (TLC) comparison with authentic samples and from the molecular ion peaks in FD-MS (*m/z*: 148 ($M^+$) and 322 ($M^+$), respectively). High-resolution electron impact mass spectrometry (HR-EI-MS) of **6** showed the molecular ion peak at *m/z*: 382.2337 corresponding to $C_{21}H_{34}O_6$ (Calcd *m/z*: 382.2354). From the carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectrum, **6** has five quaternary carbons ($\delta$: 39.7, 54.4, 76.5, 85.4, and 142.0). The 500 MHz proton nuclear magnetic resonance ($^1$H-NMR) spectrum of **6** and spin-

TABLE I. $^{13}$C-NMR Chemical Shifts

| | Aglycone moiety | | | Sugar moiety |
|---|---|---|---|---|
| | **1** | **6** | | **1** |
| C-1 | 39.9 | 41.1 | C-1′ | 96.3 |
| C-2 | 30.3 (−2.3) | 32.6 | C-2′ | 38.9[b] |
| C-3 | 78.2[a] (+6.0) | 72.2 | C-3′ | 67.4 |
| C-4 | 40.8 (−3.2) | 44.0 | C-4′ | 83.8[d] |
| C-5 | 141.1 | 142.1 | C-5′ | 68.5[e] |
| C-6 | 118.3 | 117.8 | C-6′ | 18.5[f] |
| C-7 | 36.0[b] | 36.1 | C-1″ | 99.6 |
| C-8 | 76.4 | 76.5 | C-2″ | 36.6[b] |
| C-9 | 51.1 | 51.2 | C-3″ | 78.0[a] |
| C-10 | 39.6 | 39.7 | C-4″ | 83.3[d] |
| C-11 | 70.0[c] | 70.1[g] | C-5″ | 69.5[e] |
| C-12 | 82.1 | 82.3 | C-6″ | 18.5[f] |
| C-13 | 54.3 | 54.4 | 3″-OMe | 58.8 |
| C-14 | 85.3 | 85.4 | C-1‴ | 104.1* |
| C-15 | 35.9 | 35.9 | C-2‴ | 73.1* |
| C-16 | 27.4 | 27.5 | C-3‴ | 83.2* |
| C-17 | 56.7 | 56.8 | C-4‴ | 74.3* |
| C-18 | 12.0 | 12.1 | C-5‴ | 70.7* |
| C-19 | 17.8 | 18.0 | C-6‴ | 18.6[f] |
| C-20 | 69.6[c] | 69.6[g] | 3‴-OMe | 62.1 |
| C-21 | 23.2 | 23.3 | | |

$\delta$ ppm from internal TMS in $C_5D_5N$. *a—g*) In each column may be interchangeable. * The chemical shifts with asterisks have the longest dipole-dipole relaxation times as determined by PRFT measurements. ( ): Glycosidation shifts.

spin decoupling experiments showed five methine signals at $\delta$ 1.42 (1H, d, $J$=10 Hz, 9-CH), 1.94 (1H, m, 17-CH), 3.16 (1H, d, $J$=10 Hz, 12-CH$_\alpha$), 3.75 (1H, dq, $J$=8, 6 Hz, 20-CH), and 4.02 (1H, t, $J$=10 Hz, 11-CH$_\beta$). EI-MS, $^{13}$C- and $^1$H-NMR data suggested that **6** has a hydroxyl group at the C-8 position. Mitsuhashi *et al.* reported the $^{13}$C-NMR spectra of 20*R*- and 20*S*-hydroxy-C/D-*cis*-pregnane compounds.[3] They found remarkable differences in the carbon chemical shifts, especially in those assignable to C-16 and C-20. From the $^{13}$C-NMR chemical shifts of **6** at C-16 and C-20 (Table I), it has been established that **6** possesses 20*R* configuration. Consequently, **6** was deduced to be marsectohexol.[4] The $^1$H-NMR anomeric proton signals of **1** at $\delta$ 4.58 (1H, d, $J$=7.9 Hz), 4.82 (1H, dd, $J$=10, 2 Hz), 4.93 (1H, dd, $J$=10, 2 Hz) were consistent with a $\beta$-glycosyl linkage (from the coupling constants). The glycosidation shifts[5] of the aglycone carbons of **1** were observed at C-2 (−2.3 ppm), C-3 (+6.0), and C-4 (−3.2) (Table I), so that the sugar moiety was linked to the C-3 hydroxyl group of the aglycone. The glycosidation shifts[5] of the aglycone carbon for the other four glycosides described here were also observed at C-2, C-3, and C-4 (Tables II and III), and hence the sugar moiety was linked to the C-3 hydroxyl group of the aglycone in each case. The terminal 6-deoxy-3-*O*-methyl-allopyranosyl (**9**) signals of **1** were easily distinguished from other sugar signals by PRFT measurements.[6] The acetylation of **1** gave 12,20,2‴,4‴-tetra-*O*-acetate (**10**) and 12,20,3′,2‴,4‴-penta-*O*-acetate (**11**). From the results of $^1$H-NMR spin-spin decoupling experiments on **11**, the hydroxyl group at C-3′ of **1** was concluded to be acetylated. Thus, cymaropyranose (**12**) of **1** was linked to the hydroxyl group at C-4′ of the digitoxopyranosyl moiety. Therefore the structure of **1** was confirmed to be marsectohexol 3-*O*-6-deoxy-3-*O*-methyl-$\beta$-D-allopyranosyl-(1→4)-$\beta$-D-cymaropyranosyl-(1→4)-$\beta$-D-digitoxopyranoside.

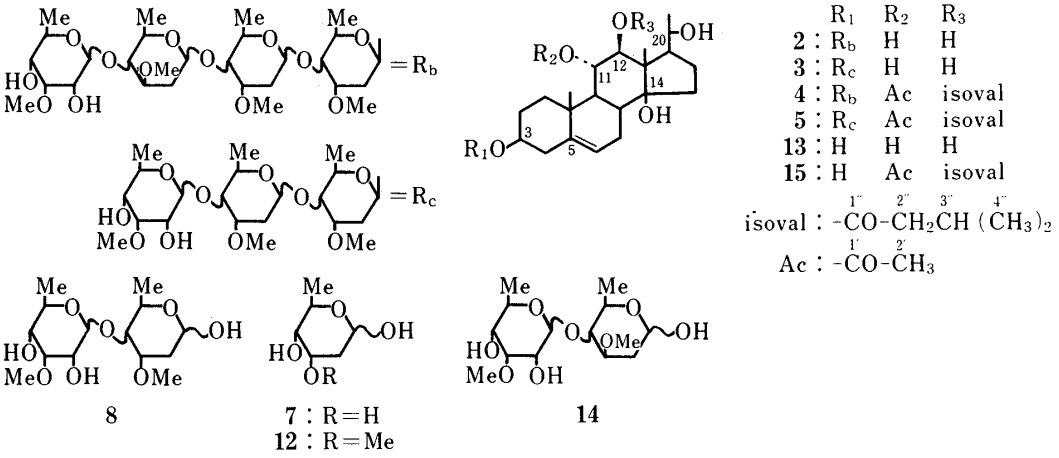



Chart 2

TABLE II. $^{13}$C-NMR Chemical Shifts for the Aglycone Moieties of **2**, **3**, **4**, and **5** and for **13** and **15**

| | **2** | **3** | **13** | **4** | **5** | **15** |
|---|---|---|---|---|---|---|
| C-1 | 39.8 | 39.7 | 40.0 | 38.8 | 38.7 | 39.0 |
| C-2 | 30.6 (−2.0) | 30.6 (−2.0) | 32.6 | 30.5 (−2.3) | 30.5 (−2.3) | 32.8 |
| C-3 | 78.0 (+6.5) | 78.0 (+6.5) | 71.5 | 77.2 (+6.3) | 78.0 (+7.1) | 70.9 |
| C-4 | 40.0 (−3.9) | 40.0 (−3.9) | 43.9 | 39.9 (−4.0) | 39.8 (−4.1) | 43.9 |
| C-5 | 140.7 | 140.7 | 141.3 | 139.7 | 139.8 | 140.6 |
| C-6 | 122.2 | 122.2 | 121.3 | 122.8 | 122.8 | 122.1 |
| C-7 | 28.2 | 28.2 | 28.1 | 28.3 | 28.3 | 28.3 |
| C-8 | 38.3 | 38.2 | 38.2 | 37.2 | 37.4 | 37.5 |
| C-9 | 50.0 | 50.0 | 49.8 | 48.3 | 48.3 | 48.1 |
| C-10 | 39.5 | 39.4 | 39.4 | 39.5 | 39.5 | 39.5 |
| C-11 | 71.6 | 71.6 | 71.5 | 72.2 | 72.2 | 72.3 |
| C-12 | 80.5 | 80.5 | 80.4 | 79.0 | 79.0 | 79.0 |
| C-13 | 54.0 | 54.0 | 54.0 | 54.1 | 54.0 | 54.1 |
| C-14 | 84.3 | 84.3 | 84.2 | 83.3 | 83.4 | 83.5 |
| C-15 | 34.1 | 34.1 | 34.0 | 33.7 | 33.6 | 33.7 |
| C-16 | 27.1 | 27.1 | 27.0 | 26.5 | 26.5 | 26.5 |
| C-17 | 54.7 | 54.7 | 54.6 | 52.5 | 52.5 | 52.5 |
| C-18 | 11.4 | 11.4 | 11.5 | 12.2 | 12.1 | 12.3 |
| C-19 | 18.9 | 18.9 | 19.1 | 19.3 | 19.3 | 19.5 |
| C-20 | 70.5 | 70.4 | 70.3 | 70.5 | 70.5 | 70.5 |
| C-21 | 23.6 | 23.5 | 23.6 | 23.7 | 23.8 | 23.8 |
| C-1′ | | | | 170.1 | 170.1 | 170.3 |
| C-2′ | | | | 21.7 | 21.7 | 21.4 |
| C-1″ | | | | 173.1 | 173.1 | 172.4 |
| C-2″ | | | | 43.7 | 43.6 | 43.7 |
| C-3″ | | | | 25.5 | 25.4 | 25.7 |
| C-4″ | | | | 22.6 | 22.6 | 22.5 |

$\delta$ ppm from internal TMS in $C_5D_5N$. ( . ): Glycosidation shifts.

Dregeosides $D_{p1}$ (**2**) and $D_{a1}$ (**3**) both have the same aglycone moiety. On mild acidic hydrolysis, **2** gave drevogenin D[7] (**13**), **12**, and pachybiose (**14**), which were identified by TLC comparison with authentic samples, while **3** gave **13**, **12**, and **8**. In the infrared (IR) and $^{13}$C-NMR spectra (Table II), **2** and **3** showed no carbonyl group signals. In the $^1$H-NMR spectra of **2** and **3**, the C-11 and C-12 proton signals appeared at $\delta$ 3.70 (1H, t, $J$=10 Hz) and 3.11

TABLE III. $^{13}$C-NMR Chemical Shifts for the Sugar Moieties of **2**, **3**, **4**, and **5**

| | | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Cym | C-1 | 96.3 | 96.3 | 96.4 | 96.4 |
| | C-2 | 37.1[a] | 36.9[a] | 37.5[a] | 36.9[a] |
| | C-3 | 77.8 | 78.1[b] | 77.8[b] | 78.0 |
| | C-4 | 83.4[b] | 83.8[c] | 82.8[c] | 83.8[b] |
| | C-5 | 68.9[c] | 69.0[d] | 68.9[d] | 69.0 |
| | C-6 | 18.6[d] | 18.5 | 18.5[e] | 18.6 |
| | 3-OMe | 58.8[e] | 58.8 | 58.8[f] | 58.8 |
| | C-1′ | 100.4 | 100.3 | 100.4 | 100.3 |
| | C-2′ | 37.3[a] | 36.9[a] | 37.5[a] | 37.3[a] |
| | C-3′ | 77.8 | 77.8[b] | 78.0[b] | 78.1 |
| | C-4′ | 83.2[b] | 83.3[c] | 83.1[c] | 83.5[b] |
| | C-5′ | 69.0[c] | 69.3[d] | 69.0[d] | 69.3 |
| | C-6′ | 18.6[d] | 18.5 | 18.6[e] | 18.6 |
| | 3′-OMe | 58.9[e] | 58.8 | 58.8[f] | 58.8 |
| Ole | C-1 | 101.8 | | 101.8 | |
| | C-2 | 37.5[a] | | 37.1[a] | |
| | C-3 | 79.2 | | 79.2 | |
| | C-4 | 82.7[b] | | 83.4[c] | |
| | C-5 | 72.0 | | 72.0 | |
| | C-6 | 18.5[d] | | 18.6[e] | |
| | 3-OMe | 57.1 | | 57.1 | |
| Allo | C-1 | 101.8* | 104.1* | 101.8* | 104.1* |
| | C-2 | 73.2* | 73.1* | 73.2* | 73.1* |
| | C-3 | 83.9* | 83.2* | 83.9* | 83.8* |
| | C-4 | 74.5* | 74.4* | 74.5* | 74.4* |
| | C-5 | 71.0* | 70.7* | 71.0* | 70.7* |
| | C-6 | 18.6[d] | 18.5 | 18.8[e] | 18.6 |
| | 3-OMe | 62.0 | 62.0 | 62.1 | 62.1 |

$\delta$ ppm from internal TMS in $C_5D_5N$. *a—f*) In each column may be interchangeable. * The chemical shifts with asterisks have the longest dipole-dipole relaxation times as determined by PRFT measurements. Cym: β-D-cymaropyranosyl. Ole: β-D-oleandropyranosyl. Allo: 6-deoxy-3-*O*-methyl-β-D-allopyranosyl.

(1H, d, $J$=10 Hz), respectively. The β-linkage of the sugars of **2** and **3** was indicated by the coupling constants of the anomeric proton signals at $\delta$ 4.48 (1H, dd, $J$=10, 2 Hz), 4.75 (1H, dd, $J$=10, 2 Hz), 4.80 (1H, d, $J$=8 Hz), and 4.85 (1H, dd, $J$=10, 2 Hz) for **2**, and at $\delta$ 4.59 (1H, d, $J$=8 Hz), 4.76 (1H, dd, $J$=10, 2 Hz), and 4.85 (1H, dd, $J$=10, 2 Hz) for **3**. The $^{13}$C-NMR signals (Tables II and III) of the aglycone moiety of **2** and **3** indicated the presence of **13**. In the sugar moiety, **2** has two **12**, one oleandropyranose and one **9**, and **3** has two **12** and one **9**. The PRFT measurements[6] of **2** and **3** indicated the terminal sugar to be **9**. Thus, the structures of **2** and **3** were established as drevogenin D 3-*O*-6-deoxy-3-*O*-methyl-β-D-allopyranosyl-(1→4)-β-D-oleandropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside and drevogenin D 3-*O*-6-deoxy-3-*O*-methyl-β-D-allopyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-β-D-cymaropyranoside, respectively.

Mild acidic hydrolysis and the $^{13}$C-NMR spectrum indicated that the aglycone moiety of dregeosides $G_{p1}$ (**4**) and $G_{a1}$ (**5**) is drebyssogenin G[8] (**15**). In the $^1$H-NMR spectra of **4** and **5**, the C-11 and C-12 proton signals were seen at $\delta$ 5.35 (1H, t, $J$=10 Hz) and 4.78 (1H, d, $J$=10 Hz), respectively. Since both the C-11 and C-12 proton signals of **4** and **5** were moved downfield in comparison with those of **2** and **3**, the hydroxyl groups at C-11 and C-12 of **4** and **5** were acylated. The $^{13}$C-NMR signals of the sugar moiety of **4** and **5** were compatible with

those of **2** and **3**, respectively (Table III). On hydrolysis, **4** gave **12** and **14**, while **5** gave **12** and **8**. On the basis of these data, the structures of dregeosides $G_{p1}$ (**4**) and $G_{a1}$ (**5**) were deduced to be drebyssogenin G 3-*O*-6-deoxy-3-*O*-methyl-*β*-D-allopyranosyl-(1→4)-*β*-D-oleandropyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside and drebyssogenin G 3-*O*-6-deoxy-3-*O*-methyl-*β*-D-allopyranosyl-(1→4)-*β*-D-cymaropyranosyl-(1→4)-*β*-D-cymaropyranoside, respectively.

Tests of the antitumor activities of these glycosides are in progress.

## Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter at room temperature. IR spectra were recorded on a JASCO A-102 spectrometer. $^1$H-NMR spectra were run on a JEOL GX-500 (500 MHz) spectrometer in $CDCl_3$ or in a mixture of $CDCl_3$–$CD_3OD$, and $^{13}$C-NMR spectra on a FX-200 (50 MHz) machine in $C_5D_5N$ solution with tetramethylsilane (TMS) as an internal standard. EI-MS were determined with a JEOL JMS-D-300 mass spectrometer and FD-MS with a JEOL JMS-01 SG-2. *Rf* values in TLC on silica gel (Kiesel gel 60 $F_{254}$, Merck) refer to the following solvent systems: $Rf_1$ $CHCl_3$–MeOH (9 : 1, v/v), $Rf_2$ acetone–benzene (3 : 5). Column chromatography was carried out on Wakogel C-200 (200 mesh), Wakogel C-100 (100 mesh), and Lobar column Lichroprep RP-8 (reversed phase).

**Isolation of Glycosides**——The crude glycosides mixture (100.2 g) was subjected to column chromatography on silica gel, with solvents of increasing polarity from $CHCl_3$ to $CHCl_3$–MeOH (1 : 1, v/v) to separate fraction 1 (28.6 g: a mixture of **4** and **5**) and fraction 2 (6.7 g: a mixture of **1**, **2**, and **3**). Fraction 1 was rechromatographed on silica gel with acetone–hexane (4 : 6) to separate fraction I (2.0 g: mainly **4**) and fraction II (0.5 g: mainly **5**). Fraction 2 was rechromatographed on silica gel with $CHCl_3$–MeOH (95 : 5, v/v) to separate fraction A (1.6 g: a mixtue of **1** and **3**) and fraction B (2.2 g: mainly **2**). Fraction A was rechromatographed on silica gel with acetone–hexane (1 : 1, v/v) to separate fraction III (157 mg: mainly **1**) and fraction IV (288 mg: mainly **3**). Fraction B was rechromatographed on silica gel with acetone–hexane (55 : 45, v/v) to separate fraction V (210 mg: mainly **2**). Fractions I, II, III, IV, and V were each rechromatographed on a reversed phase gel column (eluent: $H_2O$–MeOH (2 : 8)) to afford chromatographically pure **4** (219 mg), **5** (147 mg), **1** (86 mg), **3** (257 mg), and **2** (210 mg), respectively.

**Dregeoside H (1)**——An amorphous white powder, mp 147—150 °C, $[\alpha]_D^{20}$ +34.2° ($c$=1.01, MeOH). *Anal.* Calcd for $C_{41}H_{68}O_{16}\cdot 1/4H_2O$: C, 59.78; H, 8.41. Found: C, 59.88; H, 8.62. IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3400 (OH), 1160 (C–O–C). FD-MS *m/z*: 816 ($M^+$). $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 1.20 (3H, d, $J$=6.4 Hz, $CH_3$ of sugar moiety), 1.24 (3H, d, $J$=6.1 Hz, $CH_3$ of sugar moiety), 1.26 (3H, s, 19-$CH_3$), 1.27 (3H, d, $J$=5.8 Hz, 21-$CH_3$), 1.28 (3H, d, $J$=5.8 Hz, $CH_3$ of sugar moiety), 1.39 (3H, s, 18-$CH_3$), 1.43 (1H, d, $J$=10 Hz, 9-CH), 2.10 (1H, ddd, $J$=13, 4, 2 Hz, 2′- or 2″-CH), 2.14 (1H, ddd, $J$=13, 4, or 2 Hz, 2′- or 2″-CH), 2.28 (1H, m, 7-CH), 3.207 (1H, d, $J$=10 Hz, 12-$CH_\alpha$), 3.209 (1H, dd, $J$=8, 4 Hz, 4′- or 4″-CH), 3.23 (1H, dd, $J$=10, 3 Hz, 4‴-CH), 3.25 (1H, dd, $J$=10, 3 Hz, 4′- or 4″-CH), 3.77 (1H, t, $J$=3 Hz, 3‴-CH), 3.43 (3H, s, 3″-$OCH_3$), 3.66 (3H, s, 3‴-$OCH_3$), 3.95 (1H, dq, $J$=9.5, 6.1 Hz, 5′- or 5″- or 5‴-CH), 4.03 (1H, t, $J$=10 Hz, 11-$CH_\beta$), 4.24 (1H, m, 3′-CH), 4.58 (1H, d, $J$=7.9 Hz, 1‴-CH), 4.82 (1H, dd, $J$=10, 2 Hz, 1′- or 1″-CH), 4.93 (1H, dd, $J$=10, 2 Hz, 1′- or 1″-CH), 5.34 (1H, d, $J$=5.2 Hz, 6-CH). $^{13}$C-NMR (50 MHz, $C_5D_5N$): see Table I.

**Acidic Hydrolysis of 1**——A solution of **1** (71.4 mg) in MeOH (15 ml) was treated with 0.2 N $H_2SO_4$ (5 ml), and the mixture was allowed to stand at around 70 °C for 30 min. $H_2O$ (15 ml) was added and the whole mixture was concentrated to 20 ml. The solution was again warmed at around 70 °C for a further 30 min, then the solution was extracted with $Et_2O$ (50 ml). The aqueous layer was neutralized with 1% $Ba(OH)_2$. The precipitates were filtered off and the solution was evaporated to dryness. The mixure of **6**, **7**, and **8** (62.9 mg) which was obtained from the aqueous layer was separated by column chromatography on silica gel (eluent: $CHCl_3$–MeOH–$H_2O$ (10 : 2 : 1) lower layer) to afford **6** (15.3 mg), **7** (9.6 mg), and **8** (17.8 mg).

**Marsectohexol (6)**——An amorphous white powder, mp 243.5—244.5 °C. High-resolution EI-MS *m/z*: Calcd for $C_{21}H_{34}O_6$: 382.2354. Found: 382.2337. $^1$H-NMR (500 MHz, $CDCl_3$–$CD_3OD$ (9 : 1)) $\delta$: 1.18 (3H, d, $J$=6 Hz, 21-$CH_3$), 1.25 (3H, s, 19-$CH_3$), 1.39 (3H, s, 18-$CH_3$), 1.42 (1H, d, $J$=10 Hz, 9-CH), 1.94 (1H, m, 17-CH), 3.16 (1H, d, $J$=10 Hz, 12-$CH_\alpha$), 3.75 (1H, dq, $J$=8, 6 Hz, 20-CH), 4.02 (1H, t, $J$=10 Hz, 11-$CH_\beta$), 5.34 (1H, d, $J$=5.5 Hz, 6-CH). $^{13}$C-NMR (50 MHz, $C_5D_5N$): see Table I.

**Digitoxose (7)**——Colorless syrup, FD-MS *m/z*: 148 ($M^+$), $Rf_1$: 0.19 and $Rf_2$: 0.14.

**Asclepobiose (8)**——An amorphous white powder, FD-MS *m/z*: 322 ($M^+$). $Rf_1$: 0.33 and $Rf_2$: 0.22.

**Acetylation of 1**——A solution of **1** (11.9 mg) in pyridine (1 ml), was treated with acetic anhydride (0.5 ml) and stirred at room temperature overnight. Usual work-up of the reaction mixture and column chromatography on silica gel (eluent: $CHCl_3$–MeOH (99 : 1, v/v) gave **10** (4.5 mg) and **11** (6.9 mg).

**Compound 10**——An amorphous white powder. $^1$H-NMR ($CDCl_3$) $\delta$: 1.14 (3H, d, $J$=6.1 Hz, 21-$CH_3$), 1.17 (3H, d, $J$=6.1 Hz, 6‴-$CH_3$), 1.21 (3H, d, $J$=6 Hz, 6″-$CH_3$), 1.23 (3H, d, $J$=6.3 Hz, 6′-$CH_3$), 1.26 (3H, s, 19-$CH_3$),

1.34 (3H, s, 18-$CH_3$), 1.51 (1H, d, $J$=10 Hz, 9-CH), 1.94 (1H, m, 17-CH), 2.01, 2.08, 2.11, 2.20 (each 3H, s, CO-$CH_3$), 3.19 (1H, dd, $J$=10, 3.1 Hz, 4''-CH), 3.21 (1H, dd, $J$=9.5, 3 Hz, 4'-CH), 3.44, 3.48 (each 3H, s, 3''- or 3'''-$OCH_3$), 3.78 (2H, m, 3''- and 5'-CH), 3.91 (1H, dq, $J$=10, 6 Hz, 5''-CH), 3.95 (1H, t, $J$=2.7 Hz, 3'''-CH), 3.98 (1H, dq, $J$=10, 6.1 Hz, 5'''-CH), 4.13 (1H, dt, $J$=10, 6.7 Hz, 11-$CH_\beta$), 4.23 (1H, dt, $J$=4, 3 Hz, 3'-CH), 4.59 (1H, dd, $J$=10, 2.7 Hz, 4'''-CH), 4.71 (1H, d, $J$=10 Hz, 12-$CH_\alpha$), 4.72 (1H, dd, $J$=8.2, 2.7 Hz, 2'''-CH), 4.79 (1H, d, $J$=8.2 Hz, 1'''-CH), 4.82 (1H, dd, $J$=10, 2 Hz, 1'- or 1''-CH), 4.87 (1H, dq, $J$=9.2, 6.1 Hz, 20-CH), 4.92 (1H, dd, $J$=10, 2 Hz, 1'- or 1''-CH), 5.35 (1H, d, $J$=5.5 Hz, 6-CH).

**Compound 11**——An amorphous white powder. $^1$H-NMR ($CDCl_3$) $\delta$: 1.14 (3H, d, $J$=6 Hz, 21-$CH_3$), 1.170, 1.174, and 1.258 (each 3H, d, $J$=6 Hz, respectively, 6'- or 6''- or 6'''-$CH_3$), 1.259 (3H, s, 19-$CH_3$), 1.34 (3H, s, 18-$CH_3$), 1.51 (1H, d, $J$=10 Hz, 9-CH), 1.94 (1H, m, 17-CH), 2.02, 2.07, 2.09, 2.10, 2.20 (each 3H, s, CO-$CH_3$), 3.17 (1H, dd, $J$=9, 3 Hz, 4''-CH), 3.30 (1H, dd, $J$=9, 3Hz, 4'-CH), 3.42, 3.47 (each 3H, s, 3''- or 3'''-$OCH_3$), 3.75 (1H, dt, $J$=4, 3 Hz, 3''-CH), 3.81 (1H, dq, $J$=9, 6 Hz, 5''-CH), 3.84 (1H, dq, $J$=9, 6 Hz, 5'-CH), 3.93 (1H, t, $J$=3 Hz, 3'''-CH), 3.96 (1H, dq, $J$=10, 6 Hz, 5'''-CH), 4.14 (1H, dt, $J$=10, 8 Hz, 11-$CH_\beta$), 4.58 (1H, dd, $J$=10, 3 Hz, 4'''-CH), 4.708 (1H, dd, $J$=8, 3 Hz, 2'''-CH), 4.710 (1H, d, $J$=10 Hz, 12-$CH_\alpha$), 4.768, 4.78 (each 1H, dd, $J$=10, 2 Hz, 1'- or 1''-CH), 4.772 (1H, d, $J$=8 Hz, 1'''-CH), 4.87 (1H, dq, $J$=8, 6 Hz, 20-CH), 5.36 (1H, d, $J$=5.5 Hz, 6-CH), 5.37 (1H, dt, $J$=4, 3 Hz, 3'-CH).

**Dregeoside $D_{p1}$ (2)**——An amorphous white powder, mp 136.5—139 °C, $[\alpha]_D^{20}$ +0.78° ($c$=1.02, MeOH). *Anal.* Calcd for $C_{49}H_{82}O_{18}\cdot H_2O$: C, 60.22; H, 8.67. Found: C, 60.11; H, 8.82. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3400 (OH), 1160 (C–O–C). $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 1.13 (3H, s, 19-$CH_3$), 1.15 (3H, s, 18-$CH_3$), 1.21, 1.22, 1.26, and 1.35 (each 3H, d, $J$=5, 5, 6, and 6 Hz, respectively, $CH_3$ of sugar moiety), 1.23 (3H, d, $J$=6 Hz, 21-$CH_3$), 3.11 (1H, d, $J$=10 Hz, 12-$CH_\alpha$), 3.39, 3.44, 3.44, 3.66 (each 3H, s, –$OCH_3$ of sugar moiety), 3.70 (1H, t, $J$=10 Hz, 11-$CH_\beta$), 4.48 (1H, dd, $J$=10, 2 Hz, anomeric H), 4.75 (1H, dd, $J$=10, 2 Hz, anomeric H), 4.80 (1H, d, $J$=8 Hz, anomeric H), 4.85 (1H, dd, $J$=10, 2 Hz, anomeric H), 5.45 (1H, d, $J$=4.6 Hz, 6-CH). $^{13}$C-NMR (50 MHz, $C_5D_5N$): see Tables II and III.

**Dregeoside $D_{a1}$ (3)**——An amorphous white powder, mp 139.5—143 °C, $[\alpha]_D^{20}$ +2.13° ($c$=1.03, MeOH). *Anal.* Calcd for $C_{42}H_{70}O_{15}\cdot 1/2H_2O$: C, 61.22; H, 8.69. Found: C, 61.38; H, 8.94. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3400 (OH), 1160 (C–O–C). $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 1.13 (3H, s, 19-$CH_3$), 1.17 (3H, s, 18-$CH_3$), 1.21, 1.23, 1.28 (each 3H, d, $J$=6.4 Hz, respectively, $CH_3$ of sugar moiety), 1.27 (3H, d, $J$=6.4 Hz, 21-$CH_3$), 2.11, 2.13 (each 1H, ddd, $J$=13, 4, 2 Hz, 2-$CH_\beta$ of cymaropyranosyl moiety), 3.11 (1H, d, $J$=10 Hz, 12-$CH_\alpha$), 3.22, 3.27 (each 1H, dd, $J$=9.5, 3 Hz, 4-$CH_\beta$ of sugar moiety), 3.42, 3.44, 3.66 (each 3H, s, –$OCH_3$ of sugar moiety), 3.70 (1H, t, $J$=10 Hz, 11-$CH_\beta$), 3.77 (1H, t, $J$=3 Hz, 3-CH or 6-deoxy-3-*O*-methyl-allopyranosyl moiety), 3.84, 3.91 (each 1H, dq, $J$=9.6, 6.4 Hz, 5-CH of sugar moiety), 4.59 (1H, d, $J$=7.9 Hz, anomeric H), 4.76, 4.85 (each 1H, dd, $J$=10, 2 Hz, anomeric H), 5.46 (1H, d, $J$=5.2 Hz, 6-CH). $^{13}$C-NMR (50 MHz, $C_5D_5N$): see Tables II and III.

**Dregeoside $G_{p1}$ (4)**——An amorphous white powder, mp 105—108 °C, $[\alpha]_D^{20}$ +23.3° ($c$=1.00, MeOH). *Anal.* Calcd for $C_{56}H_{92}O_{20}\cdot H_2O$: C, 60.96; H, 8.59. Found: C, 60.79; H, 8.41. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3400 (OH), 1735 (C=O), 1705 (C=O), 1160 (C–O–C). $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 0.96, 0.97 (each 3H, d, $J$=6.7 Hz, 4''-$CH_3$), 1.12 (3H, s, 19-$CH_3$), 1.20, 1.22, 1.26, and 1.35 (each 3H, d, $J$=6.1, 6.1, 6.5, and 5.5 Hz, respectively, $CH_3$ of sugar moiety), 1.25 (3H, d, $J$=7.0 Hz, 21-$CH_3$), 1.28 (3H, s, 18-$CH_3$), 1.95 (3H, s, 2'-$CH_3$), 3.39, 3.438, 3.441, 3.66 (each 3H, s, –$OCH_3$ of sugar moiety), 3.80 (1H, t, $J$=3 Hz, 3-CH of 6-dexoy-3-*O*-methyl-allopyranosyl), 4.48, 4.75, 4.83 (each 1H, dd, $J$=10, 2 Hz, anomeric H), 4.78 (1H, d, $J$=10 Hz, 12-$CH_\alpha$), 4.79 (1H, d, $J$=7.9 Hz, anomeric H), 5.35 (1H, t, $J$=10 Hz, 11-$CH_\beta$), 5.47 (1H, d, $J$=6 Hz, 6-CH). $^{13}$C-NMR (50 MHz, $C_5D_5N$): see Tables II and III.

**Dregeoside $G_{a1}$ (5)**——An amorphous white powder, mp 126.5—129 °C, $[\alpha]_D^{20}$ +25.3° ($c$=1.03, MeOH). *Anal.* Calcd for $C_{49}H_{80}O_{17}5/4\cdot H_2O$: C, 61.07; H, 8.63. Found: C, 60.93; H, 8.37. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3400 (OH), 1730 (C=O), 1705 (C=O), 1160 (C–O–C). $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 0.965, 0.971 (each 3H, d, $J$=6 Hz, 4''-$CH_3$), 1.20 (3H, s, 19-$CH_3$), 1.21, 1.27, 1.28 (each 3H, d, $J$=6.7 Hz, $CH_3$ of sugar moiety), 1.23 (3H, d, $J$=6.7 Hz, 21-$CH_3$), 1.29 (3H, s, 18-$CH_3$), 1.95 (3H, s, 2'-$CH_3$), 3.21, 3.23, 3.27 (each 1H, dd, $J$=9.5, 3 Hz, 4-CH of sugar moiety), 3.42, 3.44, 3.66 (each 3H, s, –$OCH_3$ of sugar moiety), 3.77 (1H, t, $J$=3 Hz, 3-CH of 6-deoxy-3-*O*-methyl-allopyranosyl), 3.91 (1H, dq, $J$=9.5, 6.7 Hz, 5-CH of sugar moiety), 4.59 (1H, d, $J$=7.9 Hz, anomeric H), 4.76, 4.83 (each 1H, dd, $J$=10, 2 Hz, anomeric H), 4.78 (1H, d, $J$=10 Hz, 12-$CH_\alpha$), 5.35 (1H, t, $J$=10 Hz, 11-$CH_\beta$), 5.47 (1H, d, $J$=5.5 Hz, 6-CH). $^{13}$C-NMR (50 MHz, $C_5D_5N$): see Tables II and III.

**Acidic Hydrolysis of 2—5**——A solution of one of the four glycosides (1 mg) in MeOH (7.5 ml) was treated with 0.2 N $H_2SO_4$ (2.5 ml) and the mixture was allowed to stand at around 50 °C for 15 min. $H_2O$ (5 ml) was added and the mixture was concentrated to 10 ml. The solution was warmed at around 50 °C for a further 30 min, then neutralized with 1% $Ba(OH)_2$ and the precipitates were filtered off. The filtrate was evaporated to dryness, and the products were analyzed by TLC. When **2** was hydrolyzed, **13**, **12**, and **14** were identified by comparison with authentic samples. When **3** was hydrolyzed, **13**, **12**, and **8** were identified; when **4** was hydrolyzed, **15**, **12**, and **14** were identified; when **5** was hydrolyzed, **15**, **12**, and **8** were identified, all by comparison with authentic samples. *Rf* values: **8** ($Rf_1$: 0.33, $Rf_2$: 0.22), **12** ($Rf_1$: 0.34, $Rf_2$: 0.37), **13** ($Rf_1$: 0.20, $Rf_2$: 0.14), **14** ($Rf_1$: 0.34, $Rf_2$: 0.26), **15** ($Rf_1$: 0.41, $Rf_2$: 0.47).

**Acknowledgement** The authors wish to thank Mr. K. Watanabe of this university for FD-MS measurement and Mr. M. Ikura for the 500 MHz $^1$H-NMR studies.

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