Pregnane Glycosides from *Marsdenia tomentosa*[1)]

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Sixteen glycosides of polyoxypregnanes, including two new pregnanes, isokidjoladinin and isotemontosin, were isolated from the leaves and caules of *Marsdenia tomentosa* collected in Fukuoka. The structures of fourteen new glycosides were elucidated and named marstomentosides A—N.

Key words polyoxypregnane glycoside; *Marsdenia tomentosa*; Asclepiadaceae; marstomentoside

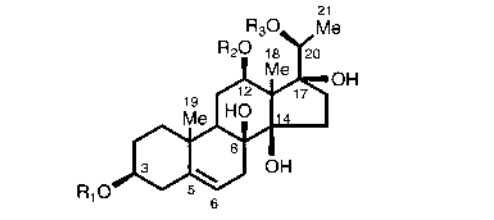
Marsdenia tomentosa Morren *et* Decaisne is grown in the warm districts in Japan and can be distinguished among Asclepiadaceous plants by its large leaves in the long caules. The pregnanes in this plant have been exhaustively studied and many (20*S*)-5α- and 5,6-didehydro-3β,8β,12β,14β,17β,20-hexahydroxy- or 3β,12β,14β,17β,20-pentahydroxypregnanes have been reported,[2)] although their glycosides remain undetermined.

During our investigation on the oviposition stimulating substances against *Parantica sita*, one of the danaid butterflies in Japan, we described the isolation and structural assignments of several cyclitols, including kijolanitol, a new cyclohexanepentol, and their glycosides from the H_2O-soluble polar fraction.[1)] In this paper, the structural determination of sixteen pregnane glycosides in the $CHCl_3$ soluble fractions from the leaves and the caules are described.

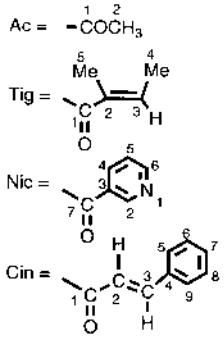
When the MeOH extract of the fresh leaves was partitioned with $CHCl_3/H_2O$, pregnane glycosides were observed in the $CHCl_3$ soluble fraction, which was subjected to silica gel and octadecylsilica (ODS) column chromatographies followed by HPLC to afford five glycosides (**1**—**5**). In the same manner, eleven glycosides (**6**—**16**), different from those in the leaves, were isolated from the $CHCl_3$ soluble fraction of the caules.

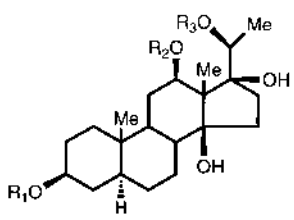
In order to identify the pregnanes and component sugars of the pregnane glycosides, pregnane rich fraction from the $CHCl_3$ extract of the aerial part was hydrolyzed under mild conditions. A mixture of the sugars was separated using a silica gel column to obtain five sugars along with two bioses, strophanthobiose and glucosyl-(1→4)-6-deoxy-3-*O*-methylallose. Each sugar was identified as D-cymarose (Cym), D-oleandrose (Ole), D-thevetose (Thv), 6-deoxy-3-*O*-methyl-D-allose (Alm) and D-glucose (Glc), respectively, by comparison with the authentic sample on TLC, ^{1}H-NMR and optical rotations. All glycosidic linkages of these sugars in the glycosides were assigned to be in the β-form based on the coupling constants of the anomeric protons in the ^{1}H-NMR spectra, as shown in Table 1.

A mixture of aglycones obtained by hydrolysis of the $CHCl_3$ extract, after separation of sugars, was subjected to column chromatography and two new pregnanes (**a-1**, **a-2**) were obtained along with five known pregnanes in this plant: kidjolanin,[2a)] penupogenin,[2a,3)] deacetylkidjoladinin,[2b)] gagaminin[2c,4)] and tomentomin.[2c)] The known pregnanes were



a-1: R_1=H, R_2=Ac, R_3=Tig
1[a)]: R_1=**s-1**, R_2=Cin, R_3=Nic
2 : R_1=**s-3**, R_2=Cin, R_3=Nic
3 : R_1=**s-2**, R_2=Cin, 20-one
6 : R_1=**s-1**, R_2=Cin, R_3=H
7 : R_1=**s-2**, R_2=Cin, R_3=H
8[a)]: R_1=**s-4**, R_2=Cin, R_3=H
9 : R_1=**s-5**, R_2=Cin, R_3=H
10 : R_1=**s-6**, R_2=Cin, R_3=H
11 : R_1=**s-7**, R_2=Cin, R_3=H
12 : R_1=**s-2**, R_2=Ac, R_3=Tig
13 : R_1=**s-6**, R_2=Tig, R_3=H
14 : R_1=**s-7**, R_2=Tig, R_3=H

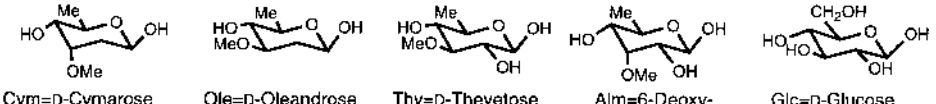




a-2 : R_1=H, R_2=Ac, R_3=Tig
4 : R_1=**s-1**, R_2=Cin, R_3=Nic
5 : R_1=**s-2**, R_2=Cin, R_3=Nic
15 : R_1=**s-1**, R_2=Ac, R_3=Tig
16 : R_1=**s-2**, R_2=Ac, R_3=Tig

a) Known compounds

s-1= ← Cym - Ole - Thv
s-2= ← Cym - Ole - Thv 4 Glc
s-3= ← Cym - Cym - Ole - Ole - Thv
s-4= ← Cym - Cym - Ole - Alm 4 Glc
s-5= ← Cym - Cym - Ole - Cym - Cym - Glc
s-6= ← Cym - Cym - Ole - Ole - Thv 4 Glc
s-7= ← Cym - Cym - Ole - Alm 4 Cym - Glc



Cym=D-Cymarose Ole=D-Oleandrose Thv=D-Thevetose Alm=6-Deoxy-3-*O*-Me-D-allose Glc=D-Glucose

Chart 1

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Table 1. ^{1}H-NMR Spectral Data for the Sugar Moieties (**s-1**—**s-7**) [δ ppm in Pyridine-d_5, J in Hz]

	s-1	**s-2**	**s-3**	**s-4**	**s-5**	**s-6**	**s-7**
H-3α	3.82—3.86[a)]	3.82—3.86[a)]	3.82—3.86[a)]	3.82—3.86[a)]	3.82—3.86[a)]	3.82—3.86[a)]	3.82—3.86[a)]
Sugar-1	Cym	Cym	Cym(1)	Cym(1)	Cym(1)	Cym(1)	Cym(1)
1	5.26 (dd, 9, 2)[a′)]	5.26 (dd, 10, 1)[a′)]	5.28 (br d, 9)[a′)]	5.28 (br d, 10)[a′)]	5.29 (br d, 10)[a′)]	5.29 (dd, 9, 2)[a′)]	5.28 (br d, 10)[a′)]
2	1.88, 2.30 (m)	1.88, 2.30 (m)	1.91, 2.36 (m)	1.90, 2.30 (m)	1.91, 2.32 (m)	1.91, 2.32 (m)	1.90, 2.30 (m)
3	4.07 (q, 3)	4.05 (q, 3)	4.10 (br s)	4.08 (q, 3)	4.09 (q, 3)	4.09 (q, 3)	4.08 (q, 3)
4	3.50 (dd, 9, 3)[b)]	3.48 (dd, 9, 3)[b)]	3.52 (dd, 9, 2)[b)]	3.50 (dd, 9, 3)[b)]	3.51 (dd, 9, 3)[b)]	3.52 (dd, 9, 3)[b)]	3.51 (dd, 9, 3)[b)]
5	4.25 (dq, 9, 6)	4.22 (dq, 9, 6)	4.23 (dq, 9, 6)	4.22 (dq, 9, 6)	4.22 (dq, 9, 6)	4.24 (dq, 9, 6)	4.22 (dq, 9, 6)
6	1.45 (d, 6)	1.42 (d, 6)	1.40 (d, 6)	1.38 (d, 6)	1.39 (d, 6)	1.40 (d, 6)	1.39 (d, 6)
Sugar-2	Ole	Ole	Cym(2)	Cym(2)	Cym(2)	Cym(2)	Cym(2)
1	4.71 (dd, 10, 2)[b′)]	4.69 (dd, 10, 1)[b′)]	5.13 (br d, 10)[b′)]	5.10 (br d, 10)[b′)]	5.11 (br d, 10)[b′)]	5.13 (dd, 9, 2)[b′)]	5.10 (dd, 10, 1)[b)]
2	1.79, 2.50 (m)	1.75, 2.48 (m)	1.85, 2.30 (m)	1.83, 2.30 (m)	1.80, 2.30 (m)	1.83, 2.32 (m)	1.80, 2.30 (m)
3	3.55—3.62	3.52—3.58	4.03 (br s)	3.98 (q, 3)	4.01 (q, 3)	4.03 (q, 3)	3.98 (q, 3)
4	3.66 (t, 9)[c)]	3.60 (t, 9)[c)]	3.47 (dd, 9, 2)[c)]	3.42 (dd, 9, 3)[c)]	3.46 (dd, 9, 3)[c)]	3.46 (dd, 9, 3)[c)]	3.41 (dd, 9, 3)[c)]
5	3.55—3.62	3.52—3.58	4.16 (dq, 9, 6)	4.14 (dq, 9, 6)	4.15 (dq, 9, 6)	4.18 (dq, 9, 6)	4.14 (dq, 9, 6)
6	1.70 (d, 6)	1.66 (d, 6)	1.39 (d, 6)	1.36 (d, 6)	1.38 (d, 6)	1.39 (d, 6)	1.37 (d, 6)
Sugar-3	Thv	Thv	Ole(1)	Ole	Ole	Ole(1)	Ole
1	4.94 (d, 8)[c′)]	4.86 (d, 8)[c′)]	4.69 (br d, 10)[c′)]	4.66 (br d, 10)[c′)]	4.68 (dd, 10, 1)[c′)]	4.69 (dd, 10, 1)[c′)]	4.66 (br d, 10)[c′)]
2	3.91 (dd, 8, 9)	3.87 (dd, 8, 9)	1.70, 2.48 (m)	1.80, 2.50 (m)	1.76, 2.50 (m)	1.75, 2.48 (m)	1.76, 2.50 (m)
3	3.58 (t, 9)	3.68 (t, 9)	3.50—3.65	3.52—3.62	3.50—3.65	3.50—3.65	3.52—3.60
4	3.62 (t, 9)	3.85 (t, 9)[d)]	3.50—3.65	3.55 (t, 9)[d)]	3.50—3.65	3.50—3.65	3.55 (t, 9)[d)]
5	3.72 (dq, 9, 6)	3.73 (dq, 9, 6)	3.50—3.65	3.52—3.62	3.50—3.65	3.50—3.65	3.52—3.60
6	1.59 (d, 6)	1.75 (d, 6)	1.44 (d, 6)	1.59 (d, 6)	1.42 (d, 6)	1.43 (d, 6)	1.60 (d, 6)
Sugar-4		Glc	Ole(2)	Alm	Cym(3)	Ole(2)	Alm
1		5.11 (d, 8)[d′)]	4.90 (br d, 10)	5.25 (d, 8)[d′)]	5.27 (dd, 10, 1)	4.88 (dd, 10, 2)	5.24 (d, 8)[d′)]
2		4.01 (t, 8)	1.75, 2.52 (m)	3.81 (dd, 8, 3)	1.80, 2.30 (m)	1.75, 2.50 (m)	3.82 (dd, 8, 3)
3		4.20 (t, 8)	3.50—3.65	4.46 (t, 3)	4.05 (q, 3)	3.50—3.65	4.34 (t, 3)
4		4.21 (t, 8)	3.59 (t, 9)[d)]	3.73 (dd, 9, 3)[e)]	3.44 (dd, 9, 3)[d)]	3.62 (t, 9)[d)]	3.48 (dd, 9, 3)[e)]
5		3.96 (m)	3.50—3.65	4.25 (dq, 9, 6)	4.18 (dd, 9, 6)	3.50—3.65	4.16 (dd, 9, 6)
6		4.33 (dd, 12, 5) 4.50 (dd, 12, 3)	1.72 (d, 6)	1.63 (d, 6)	1.35 (d, 6)	1.68 (d, 6)	1.35 (d, 6)
Sugar-5			Thv	Glc	Cym(4)	Thv	Cym(3)
1			4.95 (d, 8)[d′)]	4.96 (d, 8)[e′)]	5.08 (dd, 10, 1)[d′)]	4.87 (d, 8)[d′)]	5.12 (br d, 10)[e′)]
2			3.92 (dd, 8, 9)	4.01 (t, 8)	1.75, 2.25 (m)	3.89 (dd, 8, 9)	1.75, 2.26 (m)
3			3.59 (t, 9)	4.23 (t, 8)	4.10 (q, 3)	3.67 (t, 9)	4.12 (br s)
4			3.63 (t, 9)	4.18 (t, 8)	3.65 (dd, 9, 3)[e)]	3.85 (t, 9)[e)]	3.65 (dd, 9, 3)[f)]
5			3.73 (dq, 9, 6)	3.97 (m)	4.25 (dq, 9, 6)	3.73 (dq, 9, 6)	4.24 (dq, 9, 6)
6			1.59 (d, 6)	4.35 (dd, 12, 5) 4.52 (dd, 12, 2)	1.61 (d, 6)	1.75 (d, 6)	1.56 (d, 6)
Sugar-6					Glc	Glc	Glc
1					4.93 (d, 8)[e′)]	5.11 (d, 8)[e′)]	4.92 (d, 8)[f′)]
2					3.99 (dd, 8, 9)	4.01 (dd, 8, 9)	3.99 (dd, 8, 9)
3					4.23 (t, 9)	4.20 (t, 9)	4.22 (t, 9)
4					4.17 (t, 9)	4.20 (t, 9)	4.17 (t, 9)
5					3.97 (m)	3.94 (m)	3.98 (m)
6					4.38 (dd, 12, 5) 4.56 (dd, 12, 3)	4.33 (dd, 12, 5) 4.50 (dd, 12, 3)	4.38 (dd, 12, 6) 4.56 (dd, 12, 2)
OMe	3.53 (s) 3.61 (s) 3.88 (s)	3.50 (s) 3.58 (s) 3.93 (s)	3.49 (s) 3.55 (s) 3.58 (s) 3.63 (s) 3.88 (s)	3.51 (s) 3.54 (s) 3.62 (s) 3.63 (s)	3.52 (s) 3.53 (s) 3.57 (s) 3.61 (s) 3.63 (s)	3.48 (s) 3.52 (s) 3.58 (s) 3.63 (s) 3.93 (s)	3.53 (s) 3.54 (s) (×2) 3.62 (s) 3.86 (s)

a—*f*) The signals *a*—*f*) showed response by irradiation of the corresponding *a*′—*f*′), respectively, in DIF-NOE.

identified by comparisons of their NMR data with those of the literature.[2)] HR-FAB-MS of **a-1** showed a $[M+Na]^+$ peak at *m/z* 529.2776, suggesting a molecular formula to be $C_{28}H_{42}O_8$, the same formula as kidjoladinin.[2b)] In the ^{13}C-NMR spectrum of **a-1**, chemical shifts of all signals in the steroid nucleus were almost identical to those of gagaminin,[4b)] showing two olefinic carbons and six carbinyl carbons. Among these, three were singlet and assignable to C-8, C-14 and C-17, while three other doublets were assigned to C-3, C-12 and C-20. Acyl substituents were identified as one acetyl and one tigloyl group, based on the ^{1}H- and ^{13}C-NMR spectra as presented in Tables 2 and 4. The locations of two acids were assigned to be 12-*O*-acetyl and 20-*O*-tigloyl by correlations of the carbinyl protons at H-12α and H-20 to the carbonyl carbons of acetic acid and tiglic acid, respectively, in the heteronuclear multiple bond connectivity (HMBC) spectrum (Table 2). The unsaturated linkage at C-5 was confirmed by the ^{1}H- and ^{13}C-NMR signals (H-6: δ 5.37, C-5: δ 140.1, C-6: δ 118.5). Therefore, **a-1** was assigned to be an isomer of kidjoladinin[2b)] with respect to the locations of acetyl and tigloyl substituents, and was thus named isokidjoladinin.

The ^{1}H- and ^{13}C-NMR spectra of **a-2** also suggested the presence of acetyl and tigloyl substituents as in **a-1**. In HR-FAB-MS, the molecular formula was suggested to be $C_{28}H_{44}O_7$. The ^{13}C-NMR spectrum showed five carbinyl but

Table 2. ^{1}H-NMR Spectral Data for the Aglycone Moieties of **1**—**16**, and **a-1**, **a-2** [δ ppm in Pyridine-d_5, J in Hz]

H	**1**, **2**	**3**	**4**, **5**	**6**—**11**	**12**	**a-1**	**13**, **14**	**15**, **16**	**a-2**
3	3.85 (m)	3.86 (m)	3.84 (m)	3.86 (m)	3.83 (m)	3.86 (m)	3.83 (m)	3.82 (m)	3.84 (m)
6	5.35 (m)	5.32 (m)		5.38 (m)	5.33 (m)	5.37 (m)	5.38 (m)		
12	5.32 (dd, 12, 5)	5.19 (dd, 12, 5)	5.14 (dd, 12, 5)	5.28 (dd, 11, 4)	5.12 (dd, 12, 5)	5.14 (dd, 12, 5)[a]	5.19 (dd, 12, 5)	4.95 (dd, 12, 4)	4.97 (dd, 12, 4)[c]
18	2.09 (s)	2.03 (s)	1.79 (s)	2.14 (s)	1.96 (s)	1.98 (s)	2.08 (s)	1.66 (s)	1.67 (s)
19	1.31 (s)	1.36 (s)	0.71 (s)	1.38 (s)	1.32 (s)	1.39 (s)	1.35 (s)	0.71 (s)	0.79 (s)
20	5.30 (q, 6)		5.26 (q, 6)	4.12 (q, 6)	5.04 (q, 6)	5.05 (q, 6)[b]	4.03 (q, 6)	4.99 (q, 6)	5.00 (q, 6)[d]
21	1.57 (d, 6)	2.50 (s)	1.60 (d, 6)	1.34 (d, 6)	1.46 (d, 6)	1.47 (d, 6)	1.31 (d, 6)	1.50 (d, 6)	1.50 (d, 6)
12-*O*-Acyl	Cin	Cin	Cin	Cin	Ac	Ac	Tig	Ac	Ac
2	6.54 (d, 16)	6.81 (d, 16)	6.52 (d, 16)	6.94 (d, 16)	2.20 (s)	2.21 (s)[a]		2.19	2.19[c]
3	7.83 (d, 16)	8.00 (d, 16)	7.80 (d, 16)	8.17 (d, 16)			7.31 (qd, 7, 1)		
4							1.59 (dd, 7, 1)		
5(9)	7.43 (m)	7.63 (m)	7.44 (m)	7.52 (m)			2.02 (t, 1)		
6(8)	7.34 (m)	7.35 (m)	7.35 (m)	7.30 (m)					
7	7.34 (m)	7.43 (br t, 7)	7.35 (m)	7.30 (m)					
20-*O*-Acyl	Nic		Nic		Tig	Tig		Tig	Tig
2	9.52 (dd, 2, 1)		9.58 (dd, 2, 1)						
3					7.04 (qd, 6, 1)	7.04 (qd, 6, 1)[b]		7.09 (qd, 7, 1)	7.10 (qd, 7, 1)[d]
4	8.30 (dt, 8, 2)		8.35 (dt, 8, 2)		1.64 (dd, 7, 1)	1.60 (dd, 7, 1)		1.64 (dd, 7, 1)	1.63 (dd, 7, 1)
5	7.18 (ddd, 8, 5, 1)		7.23 (ddd, 8, 5, 1)		1.90 (t, 1)	1.91 (t, 1)[b]		1.94 (t, 1)	1.94 (t, 1)[d]
6	8.81 (dd, 5, 2)		8.85 (dd, 5, 2)						

a—*d*) Coupled with a carbonyl carbon signal at *a*) δ 171.2, *b*) δ 167.1, *c*) δ 171.1, or *d*) δ 167.2, respectively, in the HMBC spectrum.

no olefinic carbons in the steroid nucleus. The hydroxy groups were located in C-3, C-12, C-14, C-17, and C-20 based on three doublet and two singlet carbinyl carbon signals in the ^{13}C-NMR spectrum, along with the multiplicities of carbinyl protons in the ^{1}H-NMR spectrum. Finally, the substituents were located at 12-*O*-acetyl and 20-*O*-tigloyl based on the HMBC measurement as in **a-1**. Thus, **a-2** was assigned to be an isomer of tomentosin[2d] and was named isotomentosin.

The aglycones of **1** and **2** seemed to have the same pregnane, having (*E*)-cinnamic acid and nicotinic acid. Since carbinyl carbons were observed as three each of doublet (δ 77.6, 74.5, 76.3) and singlet (δ 74.2, 88.8, 87.4) signals, along with the olefinic proton at H-6 (δ 5.35), the aglycone was suggested to be a hexahydroxypregn-5-ene, possibly, having hydroxy groups at 3β,8β,12β,14β,17β and 20, and the linkages of cinnamic acid and nicotinic acid were assigned to 12-OH and 20-OH, respectively, based on the HMBC measurement. Therefore, the aglycones in **1** and **2** were identified as gagaminin.[2c,4]

In **1**, three anomeric protons were observed as two doublet of doublets (δ 5.26, J=9,2 Hz: 4.71, J=10, 2 Hz) and one doublet (δ 4.94, J=8 Hz) signals, along with three 6-methyl proton signals (δ 1.45, 1.59, 1.70) and three methoxy proton signals (δ 3.53, 3.61, 3.88). Therefore, the sugar moiety was suggested to be composed of two moles of 2,6-dideoxy-3-*O*-methylhexose and one of 6-deoxy-3-*O*-methylhexose. In comparison of the chemical shifts of the anomeric protons with those obtained previously, Ole shows an anomeric proton signal in a higher field (δ 4.73—4.89) than Cym(δ 5.08—5.27) in pyridine-d_5.[5] Similarly, the anomeric proton of Thv is observed in the field higher than 5.00 ppm while that of Alm in a field lower than δ 5.00.[6] Therefore, one of the doublet of doublets signals observed at δ 4.71 was assignable to the anomeric proton of Ole and the others at δ 5.26 to that of Cym. The anomeric proton observed as a doublet signal at δ 4.94 was assignable to Thv.[6] The ^{1}H- and ^{13}C-signals in each sugar were assigned by normal NMR measurements, including ^{1}H–^{1}H correlation spectroscopy (COSY), and ^{1}H–^{13}C COSY. In difference (DIF) of nuclear Overhauser effect (NOE) measurements, the signals of H-3α, H-4$_{Cym}$, H-4$_{Ole}$ (weak) showed response by the irradiation of H-1$_{Cym}$, H-1$_{Ole}$, H-1$_{Thv}$, respectively. In the HMBC spectrum, 3-bond correlation between H-4$_{Cym}$/C-1$_{Ole}$, H-1$_{Thv}$/C-4$_{Ole}$ and H-4$_{Ole}$/C-1$_{Thv}$ was also observed. Therefore, the sugar sequence was determined to be Thv–Ole–Cym–(aglycone) (type **s-1**). Glycoside **1** was considered to be stephanoside G, previously obtained from *Stephanotis japonica* Makino.[4b] The NMR data of the two glycosides were identical with each other.

Glycoside **2** (marstomentoside A) appeared to be a pentaoside, based on five methoxy signals at δ 3.49—3.88, five 6-methyl signals at δ 1.39—1.72, and five anomeric protons at δ 4.69—5.28, four of which were observed as doublet of doublets, and one a doublet pattern. Since FAB-MS suggested a molecular formula of **2** to be $C_{71}H_{103}NO_{24}$, the sugar moiety was composed of four moles of 2,6-dideoxy-3-*O*-methylhexose and one 6-deoxy-3-*O*-methylhexose. The molar ratio of 2,6-dideoxy-3-*O*-methylhexose was determined to be two moles each of Cym(δ 5.13, 5.28) and Ole(δ 4.69, 4.90) based on the chemical shifts of the anomeric protons described above.[5] The 6-deoxy-3-*O*-methylhexose was assigned to be Thv by an anomeric proton signal at δ 4.95 and by large coupling constants of H-1—H-5. The sugar sequence was determined to be Thv–Ole–Ole–Cym–Cym–(aglycone) (type **s-3**) by NOEs between H-1$_{Thv}$/H-4$_{Ole(2)}$, H-1$_{Ole(2)}$/H-4$_{Ole(1)}$, H-1$_{Ole(1)}$/H-4$_{Cym(2)}$, H-1$_{Cym(2)}$/H-4$_{Cym(1)}$ in the DIF-NOE measurement.

Glycoside **3** (marstomentoside B), showing one carbonyl carbon signal at δ 209.7, was suggested to be a glycoside of kidjolanin, which was the only pregnane having a 17α-acetyl side chain, reported from this plant.[2a] All ^{13}C-NMR signals due to the aglycone moiety, including five carbinyl carbons assignable to C-3, C-8, C-12, C-14 and C-17, and a cin-

Table 3. ^{13}C-NMR Spectral Data for the Sugar Moieties (**s-1**—**s-7**) [δ ppm in Pyridine-d_5][a)]

	s-1	**s-2**	**s-3**	**s-4**	**s-5**	**s-6**	**s-7**
Sugar-1	Cym	Cym	Cym(1)	Cym(1)	Cym(1)	Cym(1)	Cym(1)
1	95.9	96.4	96.3	96.3	96.3	96.4	96.3
2	37.3	37.2	37.2	37.0	37.0[b)]	37.2	37.2
3	77.9	77.8	78.0	78.0	78.3	78.0[b)]	78.0
4	83.5	83.4 (Ole-1)	83.2	83.3	83.3[c)]	83.4[c)]	83.3[b)]
5	68.9	68.9	69.0	69.0	68.8[d)]	68.8	68.8
6	18.6	18.5[b)]	18.4[b)]	18.4[b)]	18.5	18.5[d)]	18.5
Sugar-2	Ole	Ole	Cym(2)	Cym(1)	Cym(2)	Cym(2)	Cym(2)
1	101.8 (Cym-4)	101.8 (Cym-4)	100.4	100.4	100.4	100.4 (Cym(1)-4)	100.4 (Cym(1)-4)
2	37.6	37.6	36.9	37.2	37.0[b)]	37.0	37.0
3	79.2	79.2	77.7	77.7	78.0[e)]	77.7[b)]	77.7
4	83.0 (Thv-1)	83.1 (Thv-1)	83.3	83.1	83.1[c)]	83.3[c)]	82.9[b)]
5	72.0	71.9	68.8	68.8	69.0[d)]	69.0	69.0
6	18.8	18.6[b)]	18.4[b)]	18.2[b)]	18.6	18.4[d)]	18.4
Sugar-3	Thv	Thv	Ole(1)	Ole	Ole	Ole(1)	Ole
1	104.0 (Ole-4)	103.9 (Ole-4)	101.9	101.8	101.8	101.9 (Cym(2)-4)	101.7 (Cym(2)-4)
2	75.2	74.8	37.5	37.5	37.6	37.5	37.5
3	88.1	86.2	78.9	79.2	78.8	78.9[b)]	79.3
4	75.9	83.2 (Glc-1)	82.7	82.8	83.1[c)]	83.2[c)]	83.0[b)] (Alm-1)
5	72.8	72.0	71.6	71.9	71.7	72.0	71.8[c)]
6	18.4	18.7[b)]	18.6[b)]	18.8	18.6	18.6[d)]	18.8
Sugar-4		Glc	Ole(2)	Alm	Cym(3)	Ole(2)	Alm
1		104.7 (Thv-4)	100.0	101.8	98.3	99.9 (Ole(1)-4)	101.8
2		75.8	37.6	72.6	37.2[b)]	37.6	72.5
3		78.6	79.4	83.1	77.9[e)]	79.5[b)]	83.1[b)]
4		72.0	83.1	83.3	83.0[c)]	83.1[c)]	83.2
5		77.9	72.1	69.4	69.2[d)]	72.0	69.4
6		63.1	18.8[b)]	18.5[b)]	18.4	18.6[d)]	18.5
Sugar-5			Thv	Glc	Cym(4)	Thv	Cym(3)
1			104.0	106.5	100.3	103.9 (Ole(2)-4)	100.4 (Alm-4)
2			75.2	75.4	36.7[b)]	74.9	36.8
3			88.1	78.3	78.3	86.3	78.0
4			75.9	71.9	82.6	82.6	83.0[b)] (Glc-1)
5			72.8	78.3	69.3[d)]	72.0	69.0
6			18.5[b)]	63.0	18.3	18.8[d)]	18.0
Sugar-6					Glc	Glc	Glc
1					106.5	104.7 (Thv-4)	106.5 (Cym(3)-4)
2					75.4	75.8	75.4
3					78.8	78.6[b)]	78.3
4					71.8	71.6	71.9[c)]
5					78.3[e)]	77.9[b)]	78.4
6					63.0	63.1	63.0
OMe	57.2	57.3	57.2 (×2)	57.3	57.4	57.2	57.3
	58.8	58.8	58.8 (×2)	58.8 (×2)	58.6	57.3	58.7
	60.8	60.5	60.8	61.6	58.7	58.7	58.8 (×2)
					58.9 (×2)	58.8	61.6
						60.5	

a) Proton signals coupled *via* 3-bonds are shown in parentheses. *b*—*e*) Signal assignments may be interchangeable.

namoyl residue at the 12β-hydroxy group, coincided well with those of kidjolanin,[7)] except for C-3 and its neighboring carbons. The NMR signals due to the sugar moiety showed resemblance to **s-1** except for the glycosylation shift of the C-4 of Thv and additional signals due to terminal Glc. The H-4 signal of Thv showed a response by irradiating H-1$_{Glc}$ in the DIF-NOE measurement and a cross peak to C-1$_{Glc}$ in the HMBC spectrum (Tables 1, 3). The sugar sequence was thus determined to be Glc–(1→4)–Thv–Ole–Cym–(aglycone) (type **s-2**).

Both **4** (marstomentoside C) and **5** (marstomentoside D) were suggested to be glycosides containing a nicotinic acid substituent, possibly at the C-20 hydroxy group, based on their strong dextrorotatory values, ([α]$_D$ +159.2°, 98.9°, respectively), and they were assigned as glycosides of tomentomin ((20*S*)-12-*O*-cinnamoyl-20-*O*-nicotinoyl-5α-pregnane-3β,12β,14β,17β,20-pentol).[2c)] The locations of two substituents at C-12 and C-20 were confirmed by HMBC. The sugar moieties linking to 3β-OH in **4** and **5** were identical with **s-1** and **s-2**, respectively.

Based on the NMR spectra, **6**—**11** seemed to be composed of the same pregnane, having one cinnamic acid. Three secondary and three tertiary carbinyl carbons in the pregnane moiety were assignable to C-3, C-8, C-12, C-14, C-17 and C-20. Since an acylation shift was observed at H-12 (δ 5.28), cinnamic acid was located in the 12-hydroxy group, and the pregnane moiety was assigned to be penupogenin.[2a,3)] Sugar moieties of **6** (marstomentoside E) and **7** (marstomentoside F) were assignable as **s-1** and **s-2**, respectively, based on the ^{1}H- and ^{13}C-NMR considerations.

Sugar moieties of **8**—**11** were assigned to be a pentaose in **8** or hexaoses in **9**—**11**, based on the numbers of anomeric

Table 4. ^{13}C-NMR Spectral Data for the Aglycone Moieties of **1**—**16**, and **a-1**, **a-2** [δ ppm in Pyridine-d_5]

C	**1**, **2**	**3**	**4**, **5**	**6**—**11**	**12**	**a-1**	**13**, **14**	**15**, **16**	**a-2**
1	38.7	38.9	36.8	38.9	38.7	39.0	38.8	36.9	37.1
2	29.8	29.8	29.9	29.9	29.8	32.0	29.8	29.9	32.2
3	77.6	77.6	76.5	77.7	77.6	71.5	77.6	76.5	70.4
4	39.2	39.2	34.7	39.3	39.2	43.3	39.2	34.7	39.0
5	139.3	139.3	44.3	139.1	139.2	140.1	139.1	44.3	44.8
6	119.2	119.1	28.7	119.5	119.3	118.5	119.5	28.7	28.8
7	34.8	34.7	26.9	35.0	34.8	34.8	35.0	26.9	26.9
8	74.2	74.2	40.2	74.2	74.3	74.3	74.2	40.2	40.3
9	44.0	44.5	45.6	44.2	44.0	44.0	44.0	45.6	45.7
10	37.2	37.4	35.7	37.3	37.2	37.2	37.2	35.7	35.7
11	25.6	25.0	27.8	25.6	25.5	25.6	25.5	27.7	27.8
12	74.5	73.6	74.4	74.8	74.4	74.5	74.4	75.0	75.0[a]
13	57.1	58.1	55.9	56.9	56.8	56.8	57.0	55.6	55.6
14	88.8	89.4	88.0	88.8	88.7	88.7	88.7	87.8	87.9
15	33.6[a]	33.8[a]	30.8[a]	32.9[a]	33.7[a]	33.7[a]	32.8[a]	30.8[a]	30.8[b]
16	34.0[a]	33.0[a]	34.4[a]	34.2[a]	34.8[a]	34.8[a]	34.1[a]	34.1[a]	34.2[b]
17	87.4	92.3	87.2	88.5	87.6	87.6	88.5	87.4	87.4
18	11.4	10.6	9.9	11.7	11.1	11.1	11.5	9.6	9.6
19	18.0	18.1	11.9	18.1	18.0	18.2	18.1	12.0	12.1
20	76.3	209.7	76.4	70.9	74.9	74.9	70.7	74.9	74.3[a]
21	15.3	27.6	15.2	19.3	15.3	15.3	19.4	15.3	15.3
12-*O*-Acyl									
	Cin	Cin	Cin	Cin	Ac	Ac	Tig	Ac	Ac
1	166.6	165.7	166.5	166.9	171.2	171.2	167.7	171.0	171.1
2	120.2	119.2	120.2	119.6	22.0	22.0	129.7	22.1	22.1
3	143.9	144.8	143.9	145.2			137.8		
4	134.8	135.0	134.8	135.0			14.2		
5	128.4	128.5	128.4	128.5			12.2		
6	129.2	129.2	129.2	129.1					
7	130.4	130.5	130.4	130.4					
8	129.2	129.2	129.2	129.1					
9	128.4	128.5	128.4	128.5					
20-*O*-Acyl									
	Nic		Nic		Tig	Tig		Tig	Tig
1					167.1	167.1		167.2	167.2
2	151.3		151.3		129.4	129.4		129.5	129.5
3	126.9		127.0		137.6	137.6		137.5	137.5
4	137.2		137.3		14.1	14.1		14.1	14.2
5	123.2		123.0		12.1	12.1		12.1	12.1
6	153.7		153.7						
7	164.6		164.7						

a, *b*) Signal assignment may be interchangeable.

protons, and on 3-*O*-methyl and 6-methyl proton signals in the sugar moieties in the ^{1}H-NMR spectra. In **8**, the sugars were composed of Glc, Ole, Alm and two moles of Cym. The sugar sequence of **8** was established to be Glc–(1→4)–Alm–Ole–Cym–Cym–(aglycone) (type **s-4**) by NOEs between H-1 in each sugar and H-4 of the connecting sugar or H-3α of penupogenin (Table 1). The same glycoside corresponding to **8** was reported from *Leptadenia hastata*.[8] A molecular formula of **9** (marstomentoside G) ($C_{71}H_{110}O_{27}$) and the NMR considerations suggested that the sugar moiety was composed of five moles of 2,6-dideoxy-3-*O*-methylhexose and Glc. The molar ratio of 2,6-dideoxy-3-*O*-methylhexose was determined to be four moles of Cym(δ 5.29, 5.27, 5.11, 5.08) and Ole(δ 4.68), based on the chemical shifts of the anomeric protons described above.[5] The sugar moiety in **9** was assigned as Glc–Cym–Cym–Ole–Cym–Cym–(aglycone) (type **s-5**) based on the response of each H-4$_{Cym}$ by irradiation of the anomeric protons, although the response of H-4$_{Ole}$ was ambiguous. In a similar procedure, the sugar moiety of **10** (marstomentoside H) was assigned as Glc–(1→4)–Thv–Ole–Ole–Cym–Cym–(aglycone) (type **s-6**). In the case of **10**, cross peaks were observed between H-4$_{Thv}$/C-1$_{Glc}$, H-4$_{Ole(2)}$/C-1$_{Thv}$, H-4$_{Ole(1)}$/C-1$_{Ole(2)}$, H-4$_{Cym(2)}$/C-1$_{Ole(1)}$ and H-4$_{Cym(1)}$/C-1$_{Cym(2)}$ in the HMBC spectrum.

The sugar moiety of **11** (marstomentoside I) was composed of one mole each of Ole, Alm and three moles of Cym, along with terminal Glc. The sequence was established as Glc–Cym–(1→4)–Alm–Ole–Cym–Cym–(aglycone) (type **s-7**) based on DIF-NOE and the 3-bond correlation in the HMBC spectrum (H-4$_{Cym(3)}$/C-1$_{Glc}$, H-1$_{Glc}$/C-4$_{Cym(3)}$, H-4$_{Alm}$/C-1$_{Cym(3)}$, H-1$_{Alm}$/C-4$_{Ole}$, H-4$_{Cym(2)}$/C-1$_{Ole}$ and H-4$_{Cym(1)}$/C-1$_{Cym(2)}$). In order to confirm the unusual sequence in which 6-deoxy-3-*O*-methylhexose such as Alm was located between two 2,6-dideoxyhexoses, **11** was hydrolyzed under mild conditions to obtain strophanthobiose along with other sugars. The direct linkage of the terminal glucose to Cym but not to Alm, and consequently, the location of Alm between Cym and Ole, was thus established.

In **12** (marstomentoside J), the presence of one acetyl and one tigloyl residue in 20(*S*)-3β,8β,12β,14β,17β,20-hexahydroxypregn-5-ene was suggested in the ^{1}H- and ^{13}C-NMR spectra. The assignment of 12-*O*-acetyl and 20-*O*-tigloyl

linkages was obtained from the HMBC spectrum. The aglycone was therefore considered to be **a**-**1**. The sugar moiety in **12** was identified as **s**-**2** by comparison of the NMR signals with those of **3**.

HR-FAB-MS of **13** (marstomentoside K) and **14** (marstomentoside L) suggested that two glycosides have the same molecular formula, $C_{67}H_{110}O_{28}$. The H-12 signal appeared at a lower field (δ 5.19) in comparison with H-20 (δ 4.03), suggesting that the 12-hydroxy group was acylated. The acyl residue was assignable as tiglic acid, and the aglycone of the two glycosides was determined to be deacetylkidjoladinin.[2b] The sugar moieties of **13** and **14** were assigned to be **s**-**6** and **s**-**7**, respectively, based on the ^{1}H- and ^{13}C-NMR spectra and by comparison of the signals due to the sugar moieties with those of **10** and **11**.

Both **15** (marstomentoside M) and **16** (marstomentoside N) showed the presence of tigloyl and acetyl residues in the saturated pentahydroxypregnane structure, and were composed of the same pregnane by comparisons of the ^{1}H- and ^{13}C-NMR signals due to the aglycone moieties. The acetyl group was assigned to be attached to the 12β-hydroxy group of (20*S*)-3β,12β,14β,17β,20-pentahydroxy-5α-pregnane based on the correlation of the corresponding ^{1}H (δ 4.95, dd, J=12,4 Hz) and ^{13}C signals (δ 171.0($\underline{C}OCH_3$)) in the HMBC spectrum. Similarly, a correlation was observed between H-20 (δ 4.99, q, J=6 Hz) and the carbonyl carbon of tiglic acid (δ 167.2). Therefore, aglycones of **15** and **16** were assignable as isotomentosin (**a**-**2**). Sugar moieties were determined to be **s**-**1** and **s**-**2**, respectively, by comparison of the NMR data with those of **1** and **3**.

In this study, sixteen pregnane glycosides composed of seven pregnanes were isolated, and their structures were elucidated. The glycosides from the leaves and the caules did not duplicate each other. These glycosides were composed of seven pregnanes, two from the leaves and five from the caules, out of seventeen pregnanes already described in this plant.[2] Among these seven pregnanes, isokidjoladinin and isotomentosin have not been reported so far. Glycoside **11** has an unusual sugar sequence in which 6-deoxy-3-*O*-methylallose is located in the position between two 2,6-dideoxy-3-*O*-methylhexoses, and only one glycoside with a similar sugar sequence has been identified from the Asclepiadaceae plant.[9]

Experimental

^{1}H- and ^{13}C-NMR spectra were recorded on a JNM-A500 spectrometer in pyridine-d_5 unless otherwise noted. Chemical shifts are given in δ values, relative to internal tetramethylsilane, and the following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=doublet of doublets, br=broad. FAB-MS were recorded on a JEOL HX-110 spectrometer. Optical rotations were measured on a JASCO-DIP 360 polarimeter. The following solvent systems were used for column chromatography and TLC, 1: $CHCl_3$–MeOH–H_2O (7 : 1 : 1, 7 : 2 : 1 or 7 : 3 : 1, bottom layer), 2: benzene–acetone (8 : 1—3 : 1), 3: CH_3CN–H_2O (2 : 3—3 : 2). Spray reagent for TLC: 10% H_2SO_4.

Extraction and Isolation Fresh leaves of *Marsdenia tomentosa* Morren *et* Decaisne (1.65 kg), collected in May, 1996 in the suburbs of Fukuoka, were homogenized with MeOH, and the mixture was filtered. The residue was further eluted with MeOH. The whole MeOH solution was combined and evaporated *in vacuo.* The concentrated solution was partitioned with $CHCl_3$, and the $CHCl_3$ soluble fraction (ext. 37.9 g) was chromatographed on a silica gel column with solvent 1, and the fractions containing pregnane glycosides were further chromatographed on an ODS column with CH_3CN/H_2O. The glycosides thus obtained were finally purified by HPLC (Capcell Pack C_{18}) with solvent 3 to afford five glycosides, **1**: 19 mg, **2**: 8 mg, **3**: 11 mg, **4**: 6 mg, **5**: 24 mg. The caules, after removing the leaves, were air-dried (1.15 kg) and powdered. After elution with MeOH, the MeOH extract was treated in procedure similar to that of the leaves. From the $CHCl_3$ extract (34.4 g), 11 pregnane glycosides were isolated, all as solids. **6**: 40 mg, **7**: 16 mg, **8**: 30 mg, **9**: 20 mg, **10**: 23 mg, **11**: 25 mg, **12**: 21 mg, **13**: 25 mg, **14**: 10 mg, **15**: 24 mg, **16**: 22 mg.

Hydrolysis of the $CHCl_3$ Extract from the Leaves and Caules The fraction containing pregnane glycosides (6 g), prepared in the same manner from the leaves and caules collected in 1994 in the same place, was heated at 95 °C with 100 ml of 0.05 N HCl–50% dioxane for 2 h, and dioxane was evaporated *in vacuo.* The residue was partitioned with $CHCl_3/H_2O$, and the H_2O layer was deacidified with IR-410. The H_2O layer was then concentrated and passed through a silica gel column. The column was eluted with solv. 1 to afford five sugars, cymarose, oleandrose, thevetose, 6-deoxy-3-*O*-methylallose and glucose and two bioses, strophanthobiose and β-D-glucosyl-(1→4)-6-deoxy-3-*O*-methylallose. Each sugar was confirmed by comparison with the authentic sample on TLC and by ^{1}H-NMR consideration. Optical rotation was obtained after dissolving the sugars in H_2O and allowing them to stand for 24 h; cymarose: $[\alpha]_D^{27}$ +56° (c=2.92), oleandrose: $[\alpha]_D^{27}$ −12° (c=2.01), thevetose: $[\alpha]_D^{27}$ +35° (c=0.80), 6-deoxy-3-*O*-methylallose: $[\alpha]_D^{27}$ +10° (c=0.80), glucose: $[\alpha]_D^{27}$ +48° (c=1.56). Strophanthobiose: ^{1}H-NMR δ: 5.58 (1H, dd, J=9, 2 Hz, H-1$_{Cym}$), 4.93 (1H, d, J=8 Hz, H-1$_{Glc}$), 4.54 (1H, dd, J=12, 2 Hz, H-6a$_{Glc}$), 4.37 (1H, dd, J=12, 5 Hz, H-6b$_{Glc}$), 4.35 (1H, m, H-5$_{Cym}$), 4.22, 4.16 (1H each, t, J=9 Hz, H-3, 4$_{Glc}$), 4.17 (1H, q, J=3 Hz, H-3$_{Cym}$), 3.98 (1H, dd, J=9, 8 Hz, H-2$_{Glc}$), 3.94 (1H, m, H-5$_{Glc}$), 3.74 (1H, dd, J=9, 3 Hz, H-4$_{Cym}$), 3.51 (3H, s, OCH_3), 2.38 (1H, dq, J=14, 2 Hz, H-2a$_{Cym}$), 1.90 (1H, ddd, J=14, 10, 2 Hz, H-2b$_{Cym}$), 1.65 (3H, d, J=6 Hz, H-6$_{Cym}$). β-D-Glucosyl-(1→4)-6-deoxy-3-*O*-methylallose: ^{1}H-NMR δ: 5.54 (1H, d, J=8 Hz, H-1$_{Alm}$), 4.98 (1H, d, J=8 Hz, H-1$_{Glc}$), 4.54 (1H, t, J=3 Hz, H-3$_{Alm}$), 4.52 (1H, dd, J=12, 2 Hz, H-6a$_{Glc}$), 4.37 (1H, dd, J=12, 5 Hz, H-6b$_{Glc}$), 4.35 (1H, dq, J=10, 6 Hz, H-5$_{Alm}$), 4.20, 4.23 (1H each, t, J=9 Hz, H-3, 4$_{Glc}$), 4.02 (1H, dd, J=8, 9 Hz, H-2$_{Glc}$), 3.97 (1H, m, H-5$_{Glc}$), 3.95 (1H, dd, J=8, 3 Hz, H-2$_{Alm}$), 3.88 (3H, s, OCH_3), 3.82 (1H, dd, J=10, 3 Hz, H-4$_{Alm}$), 1.67 (3H, d, J=6 Hz, H-6$_{Alm}$). The $CHCl_3$ layer, after evaporation of the solvent, was subjected to column chromatography on a silica gel column with solvent 1 and 2 to afford the following pregnanes, **a**-**1** (16 mg), **a**-**2** (25 mg), kidjolanin (9 mg), penupogenin (25 mg), deacetylkidjoladinin (7 mg), gagaminin (3 mg) and tomentomin (10 mg).

Isokidjoladinin (**a**-**1**): Solid, $[\alpha]_D^{18}$ +10.4° (c=0.72, $CHCl_3$), HR-FAB-MS *m/z*: 529.2776 (Calcd for $C_{28}H_{42}O_8$+Na: 529.2778).

Isotomentosin (**a**-**2**): Solid, $[\alpha]_D^{19}$ −2.8° (c=1.12, $CHCl_3$), HR-FAB-MS *m/z*: 515.2990 (Calcd for $C_{28}H_{44}O_7$+Na: 515.2985).

Glycosides from the Leaves Glycoside **1** (Stephanoside G)[5]: Solid, $[\alpha]_D^{26}$ +153.3° (c=0.76, MeOH), HR-FAB-MS *m/z*: 1088.5203. (Calcd for $C_{57}H_{79}NO_{18}$+Na: 1088.5195).

Marstomentoside A (**2**): Solid, $[\alpha]_D^{30}$ +74.1° (c=0.32, MeOH), HR-FAB-MS *m/z*: 1376.6763 (Calcd for $C_{71}H_{103}NO_{24}$+Na: 1376.6768).

Marstomentoside B (**3**): Solid, $[\alpha]_D^{30}$ +37.0° (c=0.44, MeOH), HR-FAB-MS *m/z*: 1143.5348 (Calcd for $C_{57}H_{84}O_{22}$+Na: 1143.5352).

Marstomentoside C (**4**): Solid, $[\alpha]_D^{26}$ +159.2° (c=0.24, MeOH), HR-FAB-MS *m/z*: 1074.5402 (Calcd for $C_{57}H_{81}NO_{17}$+Na: 1074.5403).

Marstomentoside D (**5**): Solid, $[\alpha]_D^{30}$ +98.9° (c=0.96, MeOH), HR-FAB-MS *m/z*: 1236.5929 (Calcd for $C_{63}H_{91}NO_{22}$+Na: 1236.5930).

Glycosides from the Caules Marstomentoside E (**6**): Solid, $[\alpha]_D^{30}$ +30.4° (c=1.04, MeOH), HR-FAB-MS *m/z*: 983.4987 (Calcd for $C_{51}H_{76}O_{17}$+Na: 983.4980).

Marstomentoside F (**7**): Solid, $[\alpha]_D^{30}$ +69.7° (c=0.64, MeOH), HR-FAB-MS *m/z*: 1145.5527 (Calcd for $C_{57}H_{86}O_{22}$+Na: 1145.5508).

Glycoside **8**[8]: Solid, $[\alpha]_D^{26}$ +27.5° (c=1.20, MeOH), HR-FAB-MS *m/z*: 1289.6299 (Calcd for $C_{64}H_{98}O_{25}$+Na: 1289.6295).

Marstomentoside G (**9**): Solid, $[\alpha]_D^{26}$ +51.1° (c=0.80, MeOH), HR-FAB-MS *m/z*: 1417.7133 (Calcd for $C_{71}H_{110}O_{27}$+Na: 1417.7133).

Marstomentoside H (**10**): Solid, $[\alpha]_D^{27}$ +31.4° (c=0.92, MeOH), HR-FAB-MS *m/z*: 1433.7079 (Calcd for $C_{71}H_{110}O_{28}$+Na: 1433.7081).

Marstomentoside I (**11**): Solid, $[\alpha]_D^{30}$ +42.3° (c=1.00, MeOH), HR-FAB-MS *m/z*: 1433.7079 (Calcd for $C_{71}H_{110}O_{28}$+Na: 1433.7081).

Glycoside **11** (2 mg) was heated at 95 °C with 0.05 N HCl–50% dioxane (0.5 ml) for 0.5 h. The mixture was diluted with MeOH and deacidified with IRA-410. The solution was concentrated *in vacuo* and the residue was suspended in $CHCl_3$ and partitioned with H_2O. From the $CHCl_3$ layer, penupogenin was detected on TLC. In the H_2O layer, cymarose, oleandrose, 6-deoxy-3-*O*-methylallose and strophanthobiose were identified on TLC (solvent 1).

Marstomentoside J (**12**): Solid, $[\alpha]_D^{27}$ +23.9° (c=0.84, MeOH), HR-FAB-

MS *m/z*: 1139.5591 (Calcd for $C_{55}H_{88}O_{23}$+Na: 1139.5614).

Marstomentoside K (**13**): Solid, $[\alpha]_D^{26}$ +18.6° (*c*=1.0, MeOH), HR-FAB-MS *m/z*: 1385.7087 (Calcd for $C_{67}H_{110}O_{28}$+Na: 1385.7082).

Marstomentoside L (**14**): Solid, $[\alpha]_D^{26}$ +21.0° (*c*=0.45, MeOH), HR-FAB-MS *m/z*: 1385.7072 (Calcd for $C_{67}H_{110}O_{28}$+Na: 1385.7082).

Marstomentoside M (**15**): Solid, $[\alpha]_D^{20}$ +6.1° (*c*=0.96, MeOH), HR-FAB-MS *m/z*: 963.5298 (Calcd for $C_{49}H_{80}O_{17}$+Na: 963.5293).

Marstomentoside N (**16**): Solid, $[\alpha]_D^{30}$ +8.2° (*c*=0.88, MeOH), HR-FAB-MS *m/z*: 1125.5815 (Calcd for $C_{55}H_{90}O_{22}$+Na: 1125.5821).

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References

1) Abe F., Yamauchi T., Honda K., Hayashi N., *Phytochemistry*, **47**, 1297—1301 (1998).
2) *a*) Sasaki T., Hayashi K., Mitsuhashi H., *Chem. Pharm. Bull*., **20**, 628—629 (1972); *b*) Seto H., Sasaki T., Hayashi K., Mitsuhashi H., *ibid*., **24**, 2185—2190 (1976); *c*) Seto H., Hayashi K., Mitsuhashi H., *ibid*., **25**, 876—878 (1977); *d*) *Idem, ibid*., **23**, 1552—1554 (1975).
3) Mitsuhashi H., Shimizu Y., *Chem. Pharm. Bull*., **8**, 565—566 (1960).
4) *a*) Yamagishi T., Hayashi K., Mitsuhashi H., *Chem. Pharm. Bull*., **20**, 2289—2291 (1972); *b*) Yoshikawa K., Okada N., Kann Y., Arihara S., *ibid*., **44**, 1790—1796 (1996).
5) Abe F., Mori Y., Okabe H., Yamauchi T., *Chem. Pharm. Bull*., **42**, 1777—1783 (1994).
6) Yoshikawa K., Matsuchika K., Arihara S., Chang H.-C., Wang J.-D., *Chem. Pharm. Bull*., **46**, 1239—1243 (1998).
7) Tsukamoto S., Hayashi K., Mitsuhashi H., *Chem. Pharm. Bull*., **33**, 2294—2304 (1985).
8) Aquino R., Peluso G., De Tommasi N., De Simone F., Pizza C., *J. Nat. Prod*., **59**, 555—564 (1996).
9) Deepak D., Srivastava S., Khare A., *Phytochemistry*, **44**, 145—151 (1997).