Marstomentosides O-T, Polyoxypregnane Glycosides from *Marsdenia tomentosa*[1)]

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Received July 22, 1999; accepted September 10, 1999

Thirteen pregnane glycosides were isolated from fresh leaves of *Marsdenia tomentosa* collected in the Fukuyama district. Of these, six were glycosides previously obtained from the same plant collected in the Fukuoka district and one from another Asclepiadaceous plant. The structures of the six new glycosides were determined by spectrometric method.

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

In the preceding paper of this series, we described the isolation and identification of sixteen pregnane glycosides, marstomentosides A—N (**1**—**16**), including two known glycosides (**1**, **8**), from the leaves and caules of *M. tomentosa* Morren *et* Decaisne, collected in the Fukuoka district.[1)] This paper deals with the further isolation of six new glycosides from another collection.

The fresh leaves of *M. tomentosa*, collected in the Fukuyama district, were subjected to examination of the pregnane glycosides using the procedure described earlier[1)] to afford thirteen glycosides (**3**, **5**, **7**—**10**, **17**—**23**). Glycosides **17**—**23** were revealed to have new combinations of the known pregnanes and sugars, while six glycosides described as **3**, **5**, and **7**—**10**, were again isolated from this plant source. All component sugars in the glycosides from this plant were in the D-series, based on the optical rotation of each sugar from the hydrolysate of the pregnane glycoside mixture.[1)]

In the ^{1}H- and ^{13}C-NMR spectra, all signals due to the pregnane moiety of **17** coincided well with those of gagaminin glycosides.[1,2)] In the sugar moiety, three methoxy signals were observed along with four anomeric protons, one of which was suggested to be due to terminal D-glucose. The ^{13}C-NMR signals due to the sugar moiety were identical with those of the type **s-2** (β-D-glucosyl-(1→4)-β-D-thevetosyl-(1→4)-β-D-oleandrosyl-(1→4)-β-D-cymaroside) as already observed in the glycosides **3**, **5**, **7**, **12**, and **16**.[1)] Compound **17** was termed marstomentoside O.

Based on the high resolution (HR)-FAB-MS peak at *m/z* 1250.5742 ([M+Na]$^+$), the same molecular formula as **17**, $C_{63}H_{89}NO_{23}$, was suggested for **18**. Multiplicities of the ^{1}H- and ^{13}C-NMR signals were almost duplicates of those of **17**, except for the signals due to the olefinic linkage of (*E*)-cinnamic acid in **17**. The doublet signals were observed at δ 6.01 and 6.92 (J=13 Hz), suggesting the cinnamic acid in **18** to be in the (*Z*)-form. The locations of (*Z*)-cinnamic acid and nicotinic acid were confirmed to be 12-OH and 20-OH, respectively, based on the cross peaks between H-12α/C-1$_{(Z)\text{-Cin}}$, and H-20/C-7$_{\text{Nic}}$ in the heteronuclear multiple bond connectivity (HMBC) spectrum. Glycoside **18** was therefore assigned to be (*Z*)-derivative of **17** and was termed marstomentoside P.

In the NMR spectra of **19**—**21**, the common signals due to the pregnane moiety including the 17-acetyl side chain (C-20: δ 209.7 (s), C-21: δ 27.6 (q), H-21: δ 2.50 (s)) were observed along with (*E*)-cinnamoyl residue. The pregnane unit

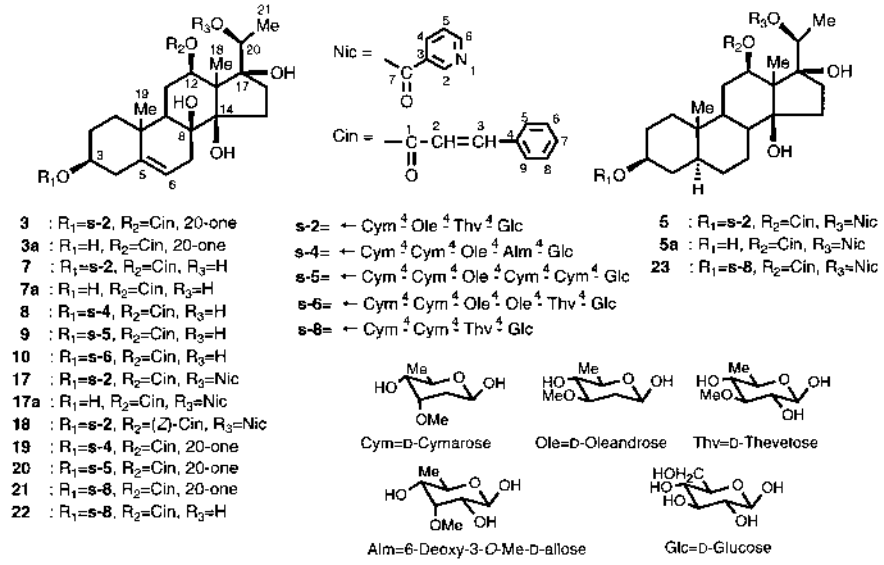

Chart 1

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Table 1. ^{13}C-NMR Spectral Data for the Aglycone Moieties of **17**—**23** [δ ppm in Pyridine-d_5]

C	**17**[a,b]	**18**[b,c]	**19**—**21**[a]	**22**[a]	**23**[a,b]
1	38.7	38.8	38.9	38.9	36.8
2	29.8	29.8	29.8	29.9	29.8
3	77.6	77.6	77.6	77.7	76.5
4	39.2	39.2	39.2	39.3	34.7
5	139.3	139.2	139.4	139.1	44.3
6	119.2	119.2	119.2	119.5	28.6
7	34.8	34.8	34.7	35.0	26.9
8	74.2	74.1	74.3	74.2	40.2
9	44.0	44.0	44.5	44.2	45.6
10	37.2	37.2	37.4	37.3	35.7
11	25.6	25.2	25.0	25.6	28.0
12	74.5	74.8	73.6	74.8	74.3
13	57.1	56.9	58.1	56.9	55.9
14	88.8	88.8	89.4	88.8	88.0
15	33.6[d]	33.6[d]	33.8[d]	32.9[d]	30.8[d]
16	34.0[d]	33.9[d]	33.0[d]	34.2[d]	34.4[d]
17	87.4	87.3	92.4	88.5	87.2
18	11.4	11.0	10.6	11.7	9.9
19	18.0	18.0	18.1	18.1	11.9
20	76.3	76.1	209.7	70.9	76.4
21	15.3	15.3	27.6	19.3	15.2

a) 12-*O*-(*E*)-Cinnamoyl residue: δ 166.5 (C-1), 120.2 (C-2), 143.9 (C-3), 135.0 (C-4), 128.4 (C-5,9), 129.1 (C-6,8), 130.1 (C-7). *b*) 20-*O*-Nicotinoyl residue: δ 151.3 (C-2), 126.9 (C-3), 137.2 (C-4), 123.0 (C-5), 153.7 (C-6), 164.6 (C-7). *c*) 12-*O*-(*Z*)-Cinnamoyl residue: δ 166.2 (C-1), 122.0 (C-2), 142.3 (C-3), 135.8 (C-4), 130.0 (C-5,9), 128.1 (C-6,8), 129.0 (C-7). *d*) Signal assignment may be interchangeable.

Table 2. ^{13}C-NMR Spectral Data for the Sugar Moieties of **17**—**23** [δ ppm in Pyridine-d_5]

C	**17**, **18**	**19**	**20**	**21**—**23**	H[a]
Sug-1	Cym	Cym(1)	Cym(1)	Cym(1)	
1	96.3	96.4	96.3	96.4	
2	37.0	37.0	37.0[b]	37.0	
3	77.8	78.0	78.3[c]	78.0	
4	83.4	83.3	83.3[d]	83.3	H-1$_{Cym(2)}$
5	68.9	69.0	69.0[e]	69.2[b]	
6	18.5[b]	18.2[b]	18.5[f]	18.4[c]	
Sug-2	Ole	Cym(2)	Cym(2)	Cym(2)	
1	101.8	100.4	100.4	100.3	H-4$_{Cym(1)}$
2	37.6	37.2	37.2[b]	37.2	
3	79.2	77.7	78.0[c]	77.7	
4	83.1	83.1	83.1	83.1	H-1$_{Thv}$
5	71.9	68.8	68.8[e]	69.0[b]	
6	18.6[b]	18.4[c]	18.5[f]	18.5[c]	
Sug-3	Thv	Ole	Ole	Thv	
1	103.9	101.8	101.9	105.9	H-4$_{Cym(2)}$
2	74.9	37.5	37.7	74.8	
3	86.2	79.2	77.9[c]	85.8	
4	83.2	82.8	83.1[d]	83.0	H-1$_{Glc}$
5	72.0	72.0[b]	71.7	72.0[d]	
6	18.7[b]	18.8	18.6[f]	18.6[c]	
Sug-4	Glc	Alm	Cym(3)	Glc	
1	104.7	101.8	98.3	104.7	H-4$_{Thv}$
2	75.8	72.6	37.0[b]	75.8	
3	78.6	83.1	77.9[c]	78.6	
4	72.0	83.3	83.0[d]	71.9[d]	
5	77.9	69.5	69.2[e]	78.0	
6	63.1	18.5[b]	18.4[f]	63.1	
Sug-5		Glc	Cym(4)		
1		106.5	100.3		
2		75.4	36.7[b]		
3		78.3	77.7[c]		
4		71.9[c]	82.6		
5		78.3	69.3[e]		
6		63.0	18.3[f]		
Sug-6			Glc		
1			106.5		
2			75.4		
3			78.8[c]		
4			71.8		
5			78.4[c]		
6			63.0		
OMe	57.3	57.3	57.4	58.8	
	58.8	58.8 (×2)	58.6	58.9	
	60.5	61.6	58.8	60.5	
			58.9 (×2)		

a) Proton signals coupled *via* 3-bonds in HMBC spectrum of **21**. *b*—*f*) Signal assignments may be interchangeable in the same column.

in these glycosides was assignable as kidjolanin (**3a**).[3] The sugar moiety of **19** was identical with the type **s-4** (β-D-glucosyl-(1→4)-6-deoxy-3-*O*-methyl-β-D-allosyl-(1→4)-β-D-oleandrosyl-(1→4)-β-D-cymarosyl-(1→4)-β-D-cymaroside) which appeared in **8**.[1,4] Compound **19** was identical with compound **29** from *Leptadenia hastata* in Asclepiadaceae.[4]

The molecular formula of **20** was suggested to be $C_{71}H_{108}O_{27}$, based on a $[M+Na]^+$ peak at *m/z* 1415.6971. Signals due to the sugar moiety were consistent with those of the type **s-5** in **9**.[1] Glycoside **20** was therefore determined to be kidjolanin 3-O-β-D-glucosyl-(1→4)-β-D-cymarosyl-(1→4)-β-D-cymarosyl-(1→4)-β-D-oleandrosyl-(1→4)-β-D-cymarosyl-(1→4)-β-D-cymaroside (marstomentoside Q).

The sugar moiety of **21** seemed to be a tetraoside, based on four anomeric protons, two as broad doublet and two as doublet signals, showing a pattern similar to those of **17** and **18**. However, one of the anomeric protons at δ 4.69 (br d, J=10 Hz) due to oleandrose in **17** and **18** was not observed in **21**, instead, the presence of two cymaroses was suggested by signals with the same multiplicities of anomeric protons (δ 5.11, 5.28) as those of **19**. In the ^{13}C-NMR spectrum, the signals corresponding to the two cymaroses were in good agreement with those of **19**. Two sugars having anomeric protons with 8 Hz coupling constants were assignable to thevetose and glucose, when ^{1}H- and ^{13}C-NMR signals were compared with those of **17** and **18**. The sugar sequence was determined by the difference (DIF) of nuclear Overhauser effect (NOE) measurements. NOEs were observed between H-1$_{Cym(1)}$/H-3, H-1$_{Cym(2)}$/H-4$_{Cym(1)}$, H-1$_{Thv}$/H-4$_{Cym(2)}$, and H-1$_{Glc}$/H-4$_{Thv}$ by irradiation of each anomeric proton signal. The sugar sequence was further confirmed by HMBC as shown in Table 2. Thus, **21** was determined to be kidjolanin 3-*O*-β-D-glucosyl-(1→4)-β-D-thevetosyl-(1→4)-β-D-cymarosyl-(1→4)-β-D-cymaroside (type **s-8**), and was termed marstomentoside R.

In the aglycone of **22**, the 21-methyl signal was observed in a doublet pattern, similar to compounds **17** and **18**, suggesting C-20 to be a carbinol carbon. The presence and location of (*E*)-cinnamic acid was suggested at 12-OH by the lower shift of H-12α (δ 5.28, dd, J=11, 4 Hz), along with two doublet signals (δ 6.94, 8.17, J=16 Hz, H-2$_{Cin}$, H-3$_{Cin}$), while the C-20 carbinyl proton was observed at the normal chemical shift (δ 4.12, q, J=6 Hz). Therefore, the pregnane moiety was identified as penupogenin (**7a**).[1,3] The sugar moiety was identified as type **s-8**, by comparison of the ^{13}C-NMR signals with those of **21**. Thus, **22** was assigned to be penupogenin 3-*O*-β-D-glucosyl-(1→4)-β-D-thevetosyl-(1→4)-β-D-cymaro-

syl-(1→4)-β-D-cymaroside, and was termed marstomentoside S.

In the ^{1}H-NMR spectrum of **23**, no olefinic proton at H-6 was observed. The presence of cinnamic acid and nicotinic acid units with four moles of sugars was suggested by the molecular formula, $C_{63}H_{91}NO_{22}$, and proton signals in the aromatic region. The pregnane in **23** was therefore thought to be tomentomin (**5a**).[1,5] The sugar moiety was assigned to be type **s-8** by the NMR comparisons with those of **21** and **22**. Compound **23** was assigned to be tomentomin 3-*O*-β-D-glucosyl-(1→4)-β-D-thevetosyl-(1→4)-β-D-cymarosyl-(1→4)-β-D-cymaroside, and was termed marstomentoside T.

Glycosides of penupogenin and kidjolanin were major in this plant source, while the tomentomin glycosides were primary in the Fukuoka district sample.

Experimental

^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectra were recorded on a JNM-A500 spectrometer in pyridine-d_5. 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, br=broad. For TLC and column chromatography, the following solvent systems were used, 1: $CHCl_3$–MeOH–H_2O (10 : 1 : 1.2—7 : 3 : 1.6, bottom layer), 2: EtOAc–MeOH–H_2O (8 : 1 : 1.2—7 : 1 : 1.2, top layer), 3: CH_3CN–H_2O (1 : 4—4 : 1). Spray reagent for TLC: 10% H_2SO_4.

Extraction and Isolation Fresh leaves (1.7 kg) of *Marsdenia tomentosa* Morren *et* Decaisne, collected in August, 1996 in Fukuyama, Hiroshima prefecture, were homogenized in MeOH and the mixture was filtered. The MeOH solution was evaporated *in vacuo* and the concentrated solution was partitioned with $CHCl_3$. The $CHCl_3$ extract (27.3 g) was chromatographed on a silica gel column (solvents 1, 2) and an octadecyl silica (ODS) column (solvent 3). Finally, a mixture of glycosides was purified by HPLC (ODS column with solvent 3) to give 13 glycosides; **3**: 34 mg, **5**: 12 mg, **7**: 16 mg, **8**: 80 mg, **9**: 9 mg, **10**: 13 mg, **17**: 26 mg, **18**: 14 mg, **19**: 15 mg, **20**: 15 mg, **21**: 25 mg, **22**: 32 mg, **23**: 5 mg.

Marstomentoside O (**17**): Solid. $[\alpha]_D^{20}$ +93.8° (c=1.17, MeOH). HR-FAB-MS *m/z*: 1250.5728 (Calcd for $C_{63}H_{89}NO_{23}$+Na: 1250.5724). ^{1}H-NMR δ: aglycone moiety (agl.) 1.31 (3H, s, H-19), 1.57 (3H, d, J=6 Hz, H-21), 2.08 (3H, s, H-18), 3.84 (1H, m, H-3), 5.30 (1H, q, J=6 Hz, H-20), 5.32 (1H, dd, J=12, 4 Hz, H-12), 5.35 (1H, m, H-6), 6.54, 7.83 (1H each, d, J=16 Hz, H-2, 3_{Cin}), 7.18 (1H, ddd, J=8, 5, 1 Hz, H-5_{Nic}), 8.30 (1H, dt, J=8, 2 Hz, H-4_{Nic}), 8.81 (1H, dd, J=5, 2 Hz, H-6_{Nic}), 9.52 (1H, dd, J=2, 1 Hz, H-2_{Nic}); sugar moiety (sug.) 1.42 (3H, d, J=6 Hz, H-6_{Cym}), 1.66 (3H, d, J=6 Hz, H-6_{Ole}), 1.75 (3H, d, J=6 Hz, H-6_{Thv}), 3.50, 3.58, 3.93 (3H each, s, 3-OMe), 4.69 (1H, br d, J=10 Hz, H-1_{Ole}), 4.87 (1H, d, J=8 Hz, H-1_{Thv}), 5.12 (1H, d, J=8 Hz, H-1_{Glc}), 5.27 (1H, dd, J=10, 1 Hz, H-1_{Cym}).

Marstomentoside P (**18**): Solid. $[\alpha]_D^{26}$ +43.6° (c=0.70, MeOH). HR-FAB-MS *m/z*: 1250.5742 (Calcd for $C_{63}H_{89}NO_{23}$+Na: 1250.5724). ^{1}H-NMR δ: (agl.) 1.36 (3H, s, H-19), 1.56 (3H, d, J=6 Hz, H-21), 1.79 (3H, s, H-18), 3.83 (1H, m, H-3), 5.18 (1H, dd, J=12, 4 Hz, H-12), 5.22 (1H, q, J=6 Hz, H-20), 5.33 (1H, m, H-6), 6.01, 6.92 (1H each, d, J=13 Hz, H-2, $3_{(Z)\text{-}Cin}$), 7.34 (1H, dd, J=8, 5 Hz, H-5_{Nic}), 8.43 (1H, dt, J=8, 2 Hz, H-4_{Nic}), 8.89 (1H, dd, J=5, 2 Hz, H-6_{Nic}), 9.60 (1H, d, J=2 Hz, H-2_{Nic}); (sug.) 1.42 (3H, d, J=6 Hz, H-6_{Cym}), 1.66 (3H, d, J=6 Hz, H-6_{Ole}), 1.75 (3H, d, J=6 Hz, H-6_{Thv}), 3.50, 3.58, 3.93 (3H each, s, 3-OMe), 4.69 (1H, br d, J=10 Hz, H-1_{Ole}), 4.87 (1H, d, J=8 Hz, H-1_{Thv}), 5.12 (1H, d, J=8 Hz, H-1_{Glc}), 5.27 (1H, dd, J=10, 1 Hz, H-1_{Cym}).

Compound **19**: Solid. $[\alpha]_D^{26}$ +44.7° (c=0.60, MeOH). HR-FAB-MS *m/z*: 1287.6134 (Calcd for $C_{64}H_{96}O_{25}$+Na: 1287.6138). ^{1}H-NMR δ: (sug.) 1.37 (3H, d, J=6 Hz, H-$6_{Cym(2)}$), 1.39 (3H, d, J=6 Hz, H-$6_{Cym(1)}$), 1.60 (3H, d, J=6 Hz, H-6_{Ole}), 1.64 (3H, d, J=6 Hz, H-6_{Alm}), 3.51, 3.55, 3.62, 3.83 (3H each, s, 3-OMe), 4.66 (1H, br d, J=10 Hz, H-1_{Ole}), 4.97 (1H, d, J=8 Hz, H-1_{Glc}), 5.10 (1H, br d, J=10 Hz, H-$1_{Cym(2)}$), 5.25 (1H, d, J=8 Hz, H-1_{Alm}), 5.27 (1H, dd, J=10, 1 Hz, H-$1_{Cym(1)}$).

Marstomentoside Q (**20**): Solid. $[\alpha]_D^{25}$ +42.8° (c=0.60, MeOH). HR-FAB-MS *m/z*: 1415.6971 (Calcd for $C_{71}H_{108}O_{27}$+Na: 1415.6975). ^{1}H-NMR δ: (agl.) 1.35 (3H, s, H-19), 2.03 (3H, s, H-18), 2.50 (3H, s, H-21), 3.84 (1H, m, H-3), 5.19 (1H, dd, J=12, 4 Hz, H-12), 5.30 (1H, m, H-6), 6.81, 8.00 (1H each, d, J=16 Hz, H-2, 3_{Cin}); (sug.) 1.34 (3H, d, J=6 Hz, H-$6_{Cym(3)}$), 1.38 (3H, d, J=6 Hz, H-$6_{Cym(2)}$), 1.40 (3H, d, J=6 Hz, H-$6_{Cym(1)}$),1.43 (3H, d, J=6 Hz, H-6_{Ole}), 1.62 (3H, d, J=6 Hz, H-$6_{Cym(4)}$), 3.53 (×2), 3.57, 3.61, 3.62 (3H each, s, 3-OMe), 4.68 (1H, br d, J=10 Hz, H-1_{Ole}), 4.93 (1H, d, J=8 Hz, H-1_{Glc}), 5.08 (1H, br d, J=10 Hz, H-$1_{Cym(4)}$), 5.11 (1H, br d, J=10 Hz, H-$1_{Cym(2)}$), 5.27 (1H, br d, J=10 Hz, H-$1_{Cym(3)}$), 5.28 (1H, br d, J=10 Hz, H-$1_{Cym(1)}$).

Marstomentoside R (**21**): Solid. $[\alpha]_D^{25}$ +30.7° (c=1.00, MeOH). HR-FAB-MS *m/z*: 1143.5349 (Calcd for $C_{57}H_{84}O_{22}$+Na: 1143.5352). ^{1}H-NMR δ: (agl.) 1.35 (3H, s, H-19), 2.03 (3H, s, H-18), 2.50 (3H, s, H-21), 3.86 (1H, m, H-3), 5.19 (1H, dd, J=12, 4 Hz, H-12), 5.31 (1H, m, H-6), 6.80, 7.99 (1H each, d, J=16 Hz, H-2, 3_{Cin}); (sug.) 1.38 (3H, d, J=6 Hz, H-$6_{Cym(1)}$), 1.56 (3H, d, J=6 Hz, H-$6_{Cym(2)}$), 1.74 (3H, d, J=6 Hz, H-6_{Thv}), 3.48 (1H, dd, J=9, 3 Hz, H-$4_{Cym(1)}$), 3.51 (1H, dd, J=9, 3 Hz, H-$4_{Cym(2)}$), 3.57, 3.61, 3.93 (3H each, s, 3-OMe), 3.69 (1H, dd, J=9, 8 Hz, H-3_{Thv}), 3.76 (1H, m, H-5_{Thv}), 3.84 (1H, t, J=9 Hz, H-4_{Thv}), 3.88 (1H, t, J=8 Hz, H-2_{Thv}), 3.96 (1H, m, H-5_{Glc}), 4.01 (1H, dd, J=9, 8 Hz, H-2_{Glc}), 4.02 (1H, br q, J=3 Hz, H-$3_{Cym(2)}$), 4.06 (1H, br q, J=3 Hz, H-$3_{Cym(1)}$), 3.84 (1H, t, J=9 Hz, H-4_{Thv}), 4.19 (1H, t, J=9 Hz, H-4_{Glc}), 4.22 (1H, t, J=9 Hz, H-3_{Glc}), 4.33 (1H, dd, J=11, 5 Hz, H-$6a_{Glc}$), 4.50 (1H, dd, J=11, 1 Hz, H-$6b_{Glc}$), 4.69 (1H, d, J=8 Hz, H-1_{Thv}), 5.11 (1H, br d, J=10 Hz, H-$1_{Cym(2)}$), 5.12 (1H, d, J=8 Hz, H-1_{Glc}), 5.28 (1H, br d, J=10 Hz, H-$1_{Cym(1)}$).

Marstomentoside S (**22**): Solid. $[\alpha]_D^{25}$ +36.0° (c=1.28, MeOH). HR-FAB-MS *m/z*: 1145.5504 (Calcd for $C_{57}H_{86}O_{22}$+Na: 1145.5508). ^{1}H-NMR δ: (agl.) 1.34 (3H, d, J=6 Hz, H-21), 1.37 (3H, s, H-19), 2.14 (3H, s, H-18), 3.86 (1H, m, H-3), 4.12 (1H, q, J=6 Hz, H-20), 5.28 (1H, dd, J=12, 4 Hz, H-12), 5.38 (1H, m, H-6), 6.94, 8.17 (1H each, d, J=16 Hz, H-2, 3_{Cin}); (sug.) 1.38 (3H, d, J=6 Hz, H-$6_{Cym(1)}$), 1.56 (3H, d, J=6 Hz, H-$6_{Cym(2)}$), 1.73 (3H, d, J=6 Hz, H-6_{Thv}), 3.57, 3.61, 3.93 (3H each, s, 3-OMe), 4.69 (1H, d, J=8 Hz, H-1_{Thv}), 5.11 (1H, br d, J=10 Hz, H-$1_{Cym(2)}$), 5.12 (1H, d, J=8 Hz, H-1_{Glc}), 5.28 (1H, br d, J=10 Hz, H-$1_{Cym(1)}$).

Marstomentoside T (**23**): Solid. $[\alpha]_D^{22}$ +107.5° (c=0.20, MeOH). HR-FAB-MS *m/z*: 1236.5931 (Calcd for $C_{63}H_{91}NO_{22}$+Na: 1236.5930). ^{1}H-NMR δ: (agl.) 0.70 (3H, s, H-19), 1.60 (3H, d, J=6 Hz, H-21), 1.78 (3H, s, H-18), 3.82 (1H, m, H-3), 5.14 (1H, dd, J=12, 4 Hz, H-12), 5.25 (1H, q, J=6 Hz, H-20), 6.52, 7.80 (1H each, d, J=16 Hz, H-2, 3_{Cin}), 7.22 (1H, ddd, J=8, 5, 1 Hz, H-5_{Nic}), 8.34 (1H, dt, J=8, 5 Hz, H-4_{Nic}), 8.84 (1H, dd, J=5, 2 Hz, H-6_{Nic}), 9.68 (1H, dd, J=2, 1 Hz, H-2_{Nic}); (sug.) 1.40 (3H, d, J=6 Hz, H-$6_{Cym(1)}$), 1.56 (3H, d, J=6 Hz, H-$6_{Cym(2)}$), 1.74 (3H, d, J=6 Hz, H-6_{Thv}), 3.57, 3.63, 3.94 (3H each, s, 3-OMe), 4.69 (1H, d, J=8 Hz, H-1_{Thv}), 5.11 (1H, br d, J=10 Hz, H-$1_{Cym(2)}$), 5.12 (1H, d, J=8 Hz, H-1_{Glc}), 5.28 (1H, br d, J=10 Hz, H-$1_{Cym(1)}$).

Acknowledgements We thank Ms. Y. Iwase and Mr. H. Hanazono for NMR and MS operations.

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