Two New Polyoxypregnane Glycosides from *Marsdenia tenacissima*

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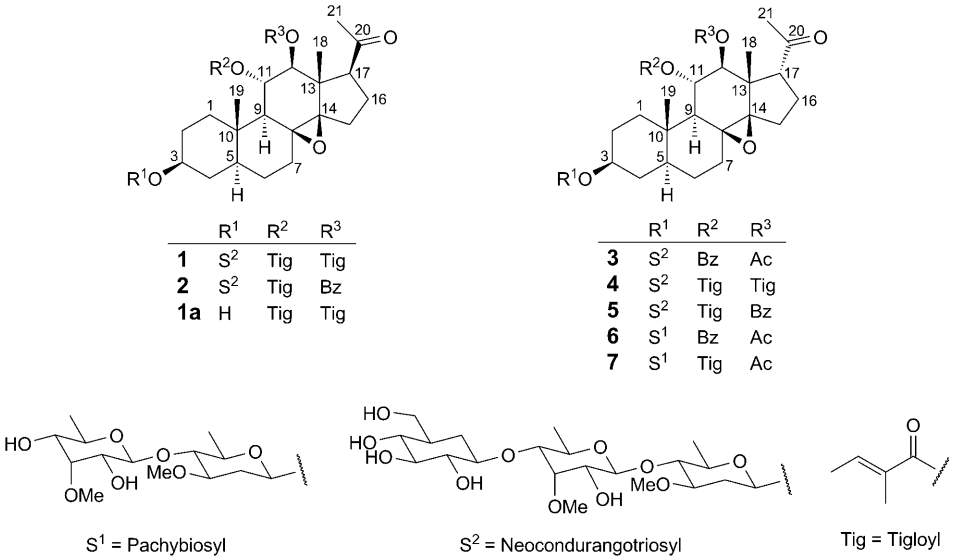
Two new polyoxypregnane glycosides, marsdenosides L and M (**1** and **2**, resp.), along with five known polyoxypregnane glycosides, **3**–**7**, were isolated from the stem of *Marsdenia tenacissima* (ROXB.) WIGHT ET ARN. (Asclepiadaceae). The structures and relative configurations of the new compounds were elucidated by spectroscopic methods, including mass spectrometry and NMR spectroscopy.

Introduction. – *Marsdenia tenacissima* (ROXB.) WIGHT ET ARN. (Asclepiadaceae), indigenous to the southwest of China, is used to treat asthma, inflammation, and cancer [1]. Previous chemical investigations on this plant showed the presence of pregnanes [2–16]. Some pregnanes can reverse multidrug resistance in P-glycoprotein-over-expressing multidrug-resistant cancer cells [2], and others showed cytotoxic activity against the KB-V1 cell line [3]. In this paper, we report the isolation and characterization of two new polyoxypregnane glycosides, marsdenosides L and M (**1** and **2**, resp.).

Results and Discussion. – Compounds **1**–**7** gave rise to positive *Liebermann–Burchard*, *Keller–Kiliani*, and xanthydrol reactions, indicating that they were all steroidal glycosides with 2-deoxy moieties [17].

Marsdenoside L (**1**) was obtained as a colorless amorphous powder. The molecular formula was established as $C_{51}H_{78}O_{19}$ by HR-ESI-MS peak at *m*/*z* 1017.5044 ([*M* + Na]$^+$, calc. 1017.5030). The ^{13}C-NMR spectrum of **1** indicated 51 C-atoms, 31 of which were assigned to the aglycone moiety, while 20 were assigned to the sugar moiety. TLC Acid hydrolysis of **1** gave oleandrose, glucose, and 6-deoxy-3-*O*-methylallose. The ^{1}H- and ^{13}C-NMR spectra of **1** (*Table 1*) showed the presence of three sugar units (three anomeric H-atom signals at δ(H) 4.36 (*d*, *J* = 6.0), 4.55 (*d*, *J* = 9.6), and 4.78 (*d*, *J* = 6.8), with the corresponding C-atom signals at δ(C) 104.3, 96.8, and 100.0, respectively). Meanwhile, the ^{1}H- and ^{13}C-NMR spectra showed two Me signals (δ(H) 1.26 (*d*, *J* = 5.6), 1.35 (*d*, *J* = 5.2) with the corresponding C-atom signals at δ(C) 18.0, 18.5), and two MeO groups (δ(H) 3.58 (*s*), 3.36 (*s*), and with the corresponding C-atom signals at δ(C) 61.1, 55.8, resp.). When **1** was exposed to β-glucosidase, enzymolysis yielded only one sugar fragment of glucose. This indicated that glucose was terminal sugar. The three glycosidic linkages were β-oriented, as deduced from the coupling constants (*J* = 6.0, 9.6, and 6.8) of the three anomeric signals. The sequence of the sugar units was deduced as β-D-glucopyranosyl-(1 → 4)-3-*O*-methyl-6-deoxy-β-D-allopyranosyl-(1 → 4)-β-D-oleandropyranose from the HMBC (*Fig. 1*) correlations (H–C(1)$_{Glc}$/C(4)$_{Allo}$,



H−C(1)$_{Allo}$/C(4)$_{Ole}$ and H−C(1)$_{Ole}$/C(3)$_{Steroid}$) (*Fig. 1*). Therefore, the sugar moiety of **1** was identified as neocondurangotriose, coincided exactly with those reported in the literature [9]. This was further confirmed by examination of the corresponding HMBC and NOESY spectra (*Figs. 1* and *2*).

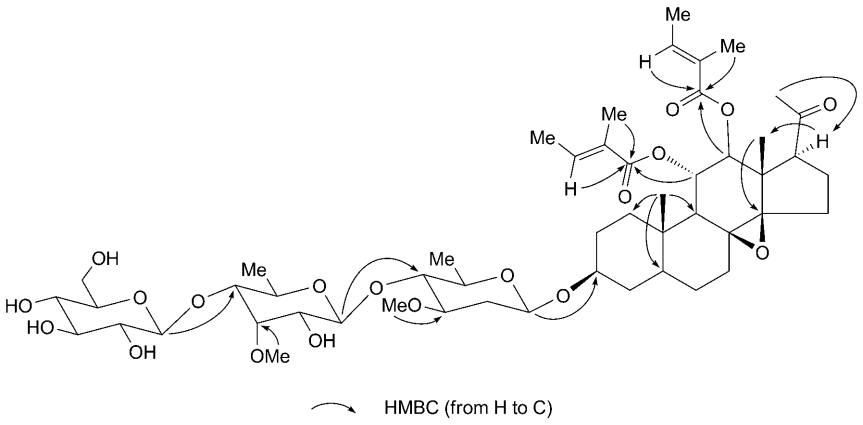


Fig. 1. *Key HMBC correlations of marsdenoside L* (**1**)

The ^{1}H- and ^{13}C-NMR spectroscopic data (*Table 2*) of the aglycone of **1** matched well with the one of 11α,12β-di-*O*-tigloyl-17β-tenacigenin B (**1a**) [3], except C(2), C(3), and C(4), which were shifted by δ(C) −2.3, +5.7, and −3.6 ppm, respectively. This suggested that the sugar moiety in **1** was linked at the 3-*O*-atom of the aglycone [18]. The deduction was confirmed by the cross peak between δ(H) 4.55 (H−C(1)$_{Ole}$) /

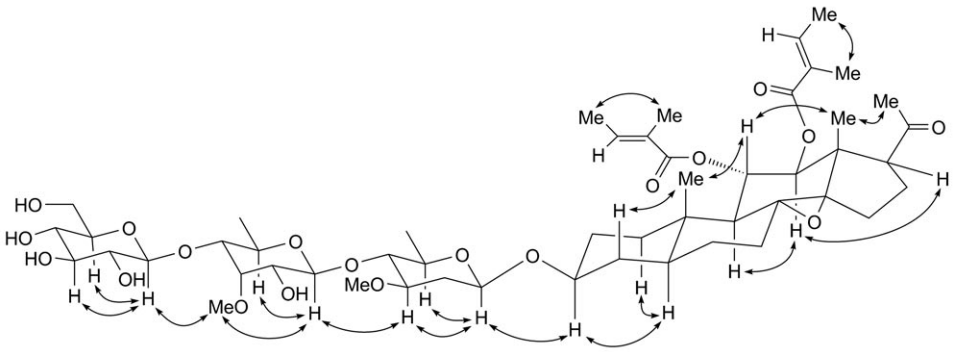


Fig. 2. *Key NOESY correlations of marsdenoside L* (**1**)

Table 1. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$, 400 and 100 MHz, resp.) *of the Sugars of Marsdenosides L* (**1**) *and M* (**2**). δ in ppm, J in Hz. Trivial atom numbering.

	Marsdenoside L (**1**)		Marsdenoside M (**2**)	
	δ(C)	δ(H)	δ(C)	δ(H)
Ole:				
H–C(1)	96.8	4.55 (*d*, *J* = 9.6)	96.8	4.55 (*d*, *J* = 8.8)
CH_2(2)	36.1	2.24–2.28 (*m*), 1.46–1.51 (*m*)	36.1	2.26–2.31 (*m*), 1.48–1.52 (*m*)
H–C(3)	79.1	3.32–3.37 (*m*)	79.1	3.30–3.35 (*m*)
H–C(4)	82.2	3.28–3.34 (*m*)	82.2	3.25–3.30 (*m*)
H–C(5)	71.2	3.28–3.33 (*m*)	71.2	3.28–3.33 (*m*)
Me(6)	18.5	1.35 (*d*, *J* = 5.2)	18.4	1.32 (*d*, *J* = 5.6)
3-MeO	55.8	3.36 (*s*)	55.8	3.34 (*s*)
Allo:				
H–C(1)	100.0	4.78 (*d*, *J* = 6.8)	100.1	4.76 (*d*, *J* = 6.8)
H–C(2)	71.0	3.43–3.48 (*m*)	71.0	3.42–3.46 (*m*)
H–C(3)	80.4[a])	3.90–3.94 (*m*)	80.4[a])	3.88–3.93 (*m*)
H–C(4)	80.4[a])	3.27–3.32 (*m*)	80.4[a])	3.24–3.30 (*m*)
H–C(5)	69.2	3.83–3.90 (*m*)	69.2	3.82–3.93 (*m*)
Me(6)	18.0	1.26 (*d*, *J* = 5.6)	18.0	1.24 (*d*, *J* = 5.6)
3-MeO	61.1	3.58 (*s*)	61.0	3.55 (*s*)
Glc:				
H–C(1)	104.3	4.36 (*d*, *J* = 6.0)	104.3	4.32 (*d*, *J* = 6.0)
H–C(2)	73.8	3.32–3.40 (*m*)	73.5	3.31–3.39 (*m*)
H–C(3)	76.2	3.46–3.53 (*m*)	76.3	3.45–3.54 (*m*)
H–C(4)	69.6	3.50–3.56 (*m*)	69.6	3.49–3.56 (*m*)
H–C(5)	75.6	3.27–3.35 (*m*)	75.6	3.27–3.34 (*m*)
CH_2(6)	61.6	3.76–3.84 (*m*), 3.56–3.63 (*m*)	61.5	3.79–3.85 (*m*), 3.55–3.64 (*m*)

[a]) Overlapped signals.

δ(C) 76.2 (C(3)) in the HMBC spectrum of **1**. In the ^{1}H-NMR spectrum, there were signals for two tigloyl groups at δ(H) 1.67 (*s*, H–C(5′,5″)), 1.71, 1.72 (*d*, *J* = 8.0, H–C(4′,4″)), and 6.69 (*qq*, *J* = 6.8, 1.2, H–C(3′,3″)). The ^{13}C-NMR spectrum of **1**

Table 2. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$, 400 and 100 MHz, resp.) *of the Aglycone Part of Marsdenosides L* (**1**) *and M* (**2**). δ in ppm, J in Hz. Trivial atom numbering.

	1a	Marsdenoside L (**1**)		Marsdenoside M (**2**)	
	δ(C)	δ(C)	δ(H)	δ(C)	δ(H)
H_α–C(1)	36.9	37.0	1.18–1.26 (*m*)	37.0	1.18–1.26 (*m*)
H_β–C(1)			1.41–1.46 (*m*)		1.42–1.50 (*m*)
H_α–C(2)	31.2	28.9	1.68–1.74 (*m*)	28.9	1.71–1.75 (*m*)
H_β–C(2)			1.23–1.28 (*m*)		1.23–1.28 (*m*)
H_α–C(3)	70.5	76.2	3.58–3.63 (*m*)	76.2	3.58–3.63 (*m*)
H_α–C(4)	38.0	34.4	1.66–1.71 (*m*)	34.4	1.66–1.71 (*m*)
H_β–C(4)			1.29–1.33 (*m*)		1.30–1.36 (*m*)
H_α–C(5)	44.4	44.2	1.30–1.35 (*m*)	44.2	1.33–1.37 (*m*)
H_α–C(6)	28.0	28.0	1.61–1.64 (*m*)	27.9	1.55–1.59 (*m*)
H_β–C(6)			1.79–1.83 (*m*)		1.82–1.86 (*m*)
H_α–C(7)	32.4	32.4	1.30–1.36 (*m*)	32.4	1.33–1.37 (*m*)
H_β–C(7)			2.03–2.10 (*m*)		2.00–2.05 (*m*)
C(8)	65.8	65.8	–	65.8	–
H_α–C(9)	52.6	52.6	1.94 (*d*, J = 9.6)	52.6	2.04 (*d*, J = 9.6)
C(10)	39.2	39.3	–	39.3	–
H_β–C(11)	67.8	67.8	5.36 (*t*, J = 10.0)	67.8	5.47 (*t*, J = 10.0)
H_α–C(12)	78.8	78.8	5.02 (*t*, J = 10.0)	79.5	5.20 (*t*, J = 10.0)
C(13)	47.2	47.2	–	47.2	–
C(14)	71.5	71.5	–	71.5	–
H_α–C(15)	26.8	26.9	1.43–1.48 (*m*)	26.9	1.38–1.45 (*m*)
H_β–C(15)			1.76–1.82 (*m*)		1.85–1.89 (*m*)
H_α–C(16)	26.1	26.0	1.78–1.82 (*m*)	26.0	1.65–1.71 (*m*)
H_β–C(16)			2.05–2.11 (*m*)		2.10–2.14 (*m*)
H_α–C(17)	61.0	61.0	2.91 (*q*, J = 10.4, 6.4)	61.0	3.00 (*q*, J = 10.4, 6.8)
H–C(18)	11.5	11.5	1.17 (*s*)	11.6	1.26 (*s*)
H–C(19)	12.8	12.6	1.06 (*s*)	12.7	1.09 (*s*)
C(20)	208.5	208.3	–	208.1	–
H–C(21)	31.2	31.4	2.01 (*s*)	31.4	1.96 (*s*)
Tig					
C(1′)	166.9	166.9	–	166.9	–
C(2′)	128.0	128.1	–	128.1	–
H–C(3′)	138.2	138.1	6.69 (*qq*, J = 6.8, 1.2)	138.4	6.50 (*qq*, J = 6.0, 1.2)
H–C(4′)	14.5	14.3	1.71 (*d*, J = 8.0)	14.1	1.46 (*d*, J = 8.0)
H–C(5′)	11.7	11.6	1.67 (*s*)	11.3	1.42 (*s*)
Tig or Bz					
C(1″)	167.4	167.4	–	166.3	–
C(2″)	128.3	128.4	–	129.6	–
H–C(3″)	138.6	138.5	6.69 (*qq*, J = 6.8, 1.2)	129.7	7.86 (*d*, J = 7.6)
H–C(4″)	14.5	14.3	1.72 (*d*, J = 8.0)	128.2	7.38 (*t*, J = 7.6)
H–C(5″)	11.7	11.7	1.67 (*s*)	133.1	7.51 (*t*, J = 7.6)
H–C(6″)	–	–	–	128.2	7.38 (*t*, J = 7.6)
H–C(7″)	–	–	–	129.7	7.86 (*d*, J = 7.6)

(*Table 2*) also displayed resonances due to two tigloyl groups. The HMBC correlations between δ(H) 5.36 (*d*, J = 10.0, H_β–C(11)) and δ(C) 166.9 ($C(1')_{Tig}$) , and between δ(H) 5.02 (*d*, J = 10.0, H_β–C(12)) and δ(C) 167.4 ($C(1'')_{Tig}$) suggested that the two

tigloyl groups were attached at C(11) and C(12), respectively. In the ^{1}H-NMR of **1**, the splitting pattern and coupling constants of the signal of H−C(17) suggested that the C(17) side chain was in β-orientation. This was supported by the correlations between δ(H) 1.17 (H−C(18) and δ(H) 2.01 (H−C(21) and between δ(H) 2.91 (H−C(17) and δ(H) 5.02 (H−C(12) in the NOESY spectrum of **1**.

Based on the above findings, the structure of marsdenoside L (**1**) was elucidated as 3-*O*-β-D-glucopyranosyl-(1 → 4)-3-*O*-methyl-6-deoxy-β-D-allopyranosyl-(1 → 4)-β-D-oleandropyranosyl-11α,12β-di-*O*-tigloyl-17β-tenacigenin B.

Marsdenoside M (**2**) was obtained as a colorless amorphous powder. The molecular formula of **2** was determined to be $C_{53}H_{76}O_{19}$ based on the HR-ESI-MS data (*m*/*z* 1039.4900 ($[M+Na]^+$, calc. 1039.4873)). The ^{13}C-NMR spectroscopic data due to the sugar moiety of **2** were in agreement with those of **1** (*Table 1*). Therefore, compound **2** should possess the same sugar moiety as **1**. This was further confirmed by the fact that the mild acidic hydrolysis of **2** gave only one sugar fragment (neocondurangotriose). The same glycosidation shifts were observed in compound **2** (*Table 1*). Accordingly, the oligosaccharide chain was attached to the 3-*O*-atom of the aglycone. It was corroborated by the HMBC correlation between δ(H) 4.55 (H−C(1)$_{Ole}$) and δ(C) 76.2 (C(3)).

The ^{1}H- and ^{13}C-NMR spectra of **2** (*Table 2*) were similar to those of **1**, except for the signals ascribed to respective diester groups. In the ^{1}H- and ^{13}C-NMR of **2**, signals for a tigloyl group (δ(H) 1.42 (*s*, H−C(5′)), 1.46 (*d*, *J* = 8.0, H−C(4′)), and 6.50 (*qq*, *J* = 6.0, 1.2, H−C(3′), and δ(C) 11.3 (C(5′)), 14.1 (C(4′)), and 138.4 (C(3′)), respectively), and signals for a benzoyl group (δ(H) 7.38 (*t*, *J* = 7.6, H−C(4″,6″)), 7.51 (*t*, *J* = 7.6, H−C(5″)), 7.86 (*d*, *J* = 7.6, H−C(3″,7″)), and δ(C) 128.2 (C(4″,6″)), 133.1 (C(5″)), 129.7 (C(3″,7″)), respectively) were observed. In the HMBC spectrum of **2**, correlations between δ(H) 5.47 (*d*, *J* = 10.0, H$_\beta$−C(11)) and δ(C) 166.9 (C(1′)$_{Tig}$), and between δ(H) 5.20 (*d*, *J* = 10.0, H$_\alpha$−C(12)) and δ(C) 166.3 (C(1″)$_{Bz}$) suggested that the tigloyl and benzoyl groups were at C(11) and C(12), respectively. Consequently, the structure of **2** was established as 3-*O*-β-D-glucopyranosyl-(1 → 4)-3-*O*-methyl-6-deoxy-β-D-allopyranosyl-(1 → 4)-β-D-oleandropyranosyl-11α-*O*-tigloyl-12β-*O*-benzoyl-17β-tenacigenin B.

Compounds **3**–**7** were identified as marsdenoside K [9], tenacissosides B [4], C [4], I [8], and A [4], respectively, by comparing their ORD, IR, ^{1}H- and ^{13}C-NMR, and MS data with literature values.

Experimental Part

General. Most of the solvents used were of anal. grade (*Changlian Chemical Plant*, Chengdu, P. R. China), except the mobile phase used for HPLC (HPLC grade (*Fisher*)). Anal. TLC: silica gel GF_{254} plates (0.4 mm; *Yantai Institute of Chemical Technology*) and anal. HPLC (*Shimadzu*), with ELSD detector (*SEDEX 75*). Column chromatography (CC): silica gel (SiO_2; 100–200 or 200–300 mesh; *Qingdao Marine Chemical Plant*, P. R. China), MPLC *RP-C$_{18}$* (*Büchi*) and *Sephadex LH-20* (*GE Healthcare*). Optical rotation: *Perkin-Elmer-241* polarimeter. IR Spectra: *Vector 22-FTIR* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra (^{1}H- and ^{13}C-NMR, ^{1}H,^{1}H-COSY, HMQC, and HMBC): *Bruker AV-400* spectrometer, at 400 (^{1}H) or 100 MHz (^{13}C); $CDCl_3$ solns.; in ppm rel. to Me_4Si (= 0 ppm, *J* in Hz). ESI-MS or HR-ESI-MS: *BrukerBioTOF-Q* mass spectrometers; in *m*/*z*.

Plant Material. The stems of *M. tenacissima* were collected from Yunnan province, P. R. China, in October 2006, and identified by Prof. *Shu Wang* (West China School of Pharmacy, Sichuan University,

Chengdu 610041, P. R. China). A voucher specimen (No. HX.Y061001) was deposited with the West China School of Pharmacy, Sichuan University, Chengdu 610041, P. R. China.

Extraction and Isolation. The air-dried, powdered stems of *M. tenacissima* (30 kg) were repeatedly percolated with 70% EtOH (600 l) at r.t., and yielded 3200 g of residue after evaporation of the solvent. The residue was suspended in H_2O (40 l) and successively partitioned by macroporous adsorptive resins to afford a H_2O fraction (1003 g), a 10% EtOH fraction (140 g), a 30% EtOH fraction (223 g), a 50% EtOH fraction (840 g), and a 70% EtOH fraction (221 g). The 70% EtOH fraction (80 g) was subjected to CC (SiO_2; cyclohexane/acetone 80:20 → 10:90) to give *Fractions A–I*. *Fr. E* (2.5 g) was subjected to CC (MPLC *RP-C_{18}*, 44% EtOH; *Sephadex LH-20*, 25% EtOH) to afford **1** (42 mg) and **2** (40 mg). *Fr. D* (3.0 g) was subjected to CC (MPLC *RP-C_{18}*, 42% EtOH; *Sephadex LH-20*, 20% EtOH) to afford **3** (60 mg), **4** (165 mg), and **5** (25 mg). *Fr. B* (3.5 g) was subjected to CC (MPLC *RP-C_{18}*, 38% EtOH; *Sephadex LH-20*, 20% EtOH) to afford **6** (82 mg). The 50% EtOH fraction (100 g) was subjected to CC (SiO_2; cyclohexane/acetone 70:30 → 0:100) to give *Fractions J–T*. *Fr. L* (0.8 g) was subjected to CC (*Sephadex LH-20*, 20% EtOH) to afford **7** (80 mg).

Marsdenoside L (*= (3β,5α,11α,12β,14β,17β)-12-(Tigloyloxy)-3-[(β-*D*-glucopyranosyl-(1 → 4)-3-*O*-methyl-6-deoxy-β-*D*-allopyranosyl-(1 → 4)-2,6-dideoxy-3-*C*-methyl-β-*D*-arabino-hexopyranosyl)oxy]-20-oxo-8,14-epoxypregnan-11-yl Tigloate = (2*S*,4a*S*,4b*S*,5*S*,6*S*,6a*S*,7*S*,9a*R*,10a*S*,12a*S*)-7-Acetyl-2-{[(2*S*,2′*R*,3*S*,4*S*,4′*R*,5*R*,6*R*,6′*R*)-3-hydroxy-4,4′-dimethoxy-2′,6-dimethyl-5-{[(1*R*,2*R*,3*S*,4*R*,5*R*)-2,3,4-trihydroxy-5-(hydroxymethyl)cyclohexyl]oxy}octahydro-2*H*,2′*H*-2,3′-bipyran-6′-yl]oxy}-4a,6a-dimethyltetradecahydro-2*H*-cyclopenta[1,2]phenanthro[1,10a-b]oxirene-5,6-diyl (2*E*,2′*E*)-Bis(2-methylbut-2-enoate)*; **1**). Colorless amorphous powder. $[\alpha]_D^{20} = +21.9$ ($c = 0.365$, MeOH). IR (KBr): 3424, 2934, 1721, 1650, 1452, 1383, 1276, 1160, 1072, 711. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. The key correlations of HMBC and NOESY are presented in *Figs. 1* and *2*. HR-ESI-MS: 1017.5044 ($[M+Na]^+$, $C_{51}H_{78}NaO_{19}^+$; calc. 1017.5030).

Marsdenoside M (*= (3β,5α,11α,12β,14β,17β)-12-(Benzoyloxy)-3-[(β-*D*-glucopyranosyl-(1 → 4)-3-*O*-methyl-6-deoxy-β-*D*-allopyranosyl-(1 → 4)-2,6-dideoxy-3-*C*-methyl-β-*D*-arabino-hexopyranosyl)oxy]-20-oxo-8,14-epoxypregnan-11-yl Tigloate = (2*S*,4a*S*,4b*S*,5*S*,6*S*,6a*S*,7*S*,9a*R*,10a*S*,12a*S*)-7-Acetyl-2-{[(2*S*,2′*R*,3*S*,4*S*,4′*R*,5*R*,6*R*,6′*R*)-3-hydroxy-4,4′-dimethoxy-2′,6-dimethyl-5-{[(1*R*,2*R*,3*S*,4*R*,5*R*)-2,3,4-trihydroxy-5-(hydroxymethyl)cyclohexyl]oxy}octahydro-2*H*,2′*H*-2,3′-bipyran-6′-yl]oxy}-4a,6a-dimethyl-5-{[(2*E*)-2-methylbut-2-enoyl]oxy}tetradecahydro-2*H*-cyclopenta[1,2]phenanthro[1,10a-b]oxiren-6-yl Benzoate*; **2**). $[\alpha]_D^{20} = +40.3$ ($c = 0.31$, MeOH). IR (KBr): 3424, 2933, 1716, 1650, 1450, 1383, 1272, 1160, 1075, 731. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. HR-ESI-MS: 1039.4900 ($[M+Na]^+$, $C_{53}H_{76}NaO_{19}^+$; calc. 1039.4873).

Acid Hydrolysis of **1**. A soln. of **1** (5 mg) in MeOH (2 ml) and 0.2M H_2SO_4 (2 ml) was kept for 1 h at 90°. After that, oleandrose, glucose, and 6-deoxy-3-*O*-methylallose were detected by TLC ($CHCl_3$/MeOH 8:1) by comparison with authentic samples.

Mild Acid Hydrolysis. A soln. of **1** and **2** (5 mg) in MeOH (3 ml) and 0.1M H_2SO_4 (1 ml) was kept for 30 min at 60°, then H_2O (3 ml) was added and the whole was concentrated to 4 ml. The soln. was heated for further 30 min at 60° and neutralized with aq. $Ba(OH)_2$ soln. The precipitate was filtered off and the filtrate was evaporated to dryness to give a mixture of hydrolyzate of **1** or **2**. Both hydrolyzates contained one sugar fragment identified as neocondurangotriose by TLC ($CHCl_3$/MeOH 15:1) comparison with an authentic sample.

Enzymatic Hydrolysis of **1**. A soln. of 0.1M AcOH/AcONa (pH 4.6) buffer (1 ml) and β-glucosidase (30 µl; 250 U/ml; *Sigma*) was added to **1** (2 mg). The mixture was incubated for 30 min at 60°, and then extracted with $CHCl_3$ (3 × 5 ml). The aq. layer contained only one monosaccharide identified as glucose by TLC ($CHCl_3$/MeOH 5:1).

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