

## Two New C<sub>21</sub> Steroidal Glycosides from the Stems of *Marsdenia tenacissima*

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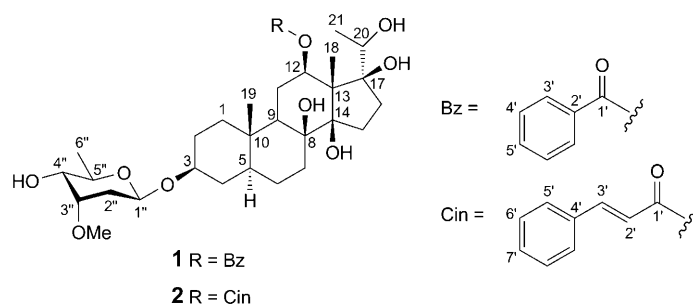
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Two new pregnane glycosides, (3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-3-( $\beta$ -cymaropyranosyloxy)-8,14,17,20-tetrahydroxypregnan-12-yl benzoate (**1**) and (3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-3-( $\beta$ -cymaropyranosyloxy)-8,14,17,20-tetrahydroxypregnan-12-yl cinnamate (**2**) were isolated from the stems of *Marsdenia tenacissima*. 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., commonly known as ‘tongguanteng’, is a traditional Chinese medicine distributed extensively in Yunnan Province of China. Acylated ployoxypregnane derivatives in the fraction of EtOH extract of the stems showed cytotoxic activity against the KB cell line [1]. Since 1990s, Xiaoaiping injection (an extract of *Marsdenia tenacissima*) has been produced and marketed by *Nanjing Sanhome Pharmaceutical Co., Ltd.* (Nanjing, Jiangsu, China), and clinically proved to be effective for esophageal cancer, gastric cancer, lung cancer, and hepatocellular carcinoma. Moreover, over forty C<sub>21</sub> steroidal glycosides have been isolated from the stems of *Marsdenia tenacissima* since 1980 [2–6]. Our investigation of seeking new C<sub>21</sub> steroidal glycosides from the stems of *Marsdenia tenacissima* has now led to the isolation of two new C<sub>21</sub> steroidal glycosides, (3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-3-( $\beta$ -cymaropyranosyloxy)-8,14,17,20-tetrahydroxypregnan-12-yl benzoate (**1**) and (3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-3-( $\beta$ -cymaropyranosyloxy)-8,14,17,20-tetrahydroxypregnan-12-yl cinnamate (**2**). The present report describes the detailed isolation and structural elucidation of these new C<sub>21</sub> steroidal glycosides.



**Results and Discussion.** – Compound **1** was obtained as a colorless, amorphous solid. The IR spectrum revealed the presence of OH ( $3442\text{ cm}^{-1}$ ), C=O ( $1710\text{ cm}^{-1}$ ), and an aromatic ring ( $1605, 1455\text{ cm}^{-1}$ ). Its specific rotation  $[\alpha]_{\text{D}}^{25}$  ( $c = 0.04, \text{MeOH}$ ) was  $+85.06$ . The molecular formula was established as  $\text{C}_{35}\text{H}_{52}\text{O}_{10}$  by HR-ESI-MS, showing the  $[M - \text{H}]^-$  ion peak of  $m/z$  631.3464 ( $\text{C}_{35}\text{H}_{51}\text{O}_{10}^-$ ; calc. 631.3482). Three Me groups at  $\delta(\text{H})$  0.98 (*s*, 3 H), 1.66 (*s*, 3 H) and 1.03 (*d*, 3 H) were observed in the  $^1\text{H}$ -NMR spectrum (Table 1), which, in combination with the  $^{13}\text{C}$ -NMR and the DEPT data, indicated a  $\text{C}_{21}$  steroidal skeleton for its aglycone moiety. Signals of aromatic H-atoms at  $\delta(\text{H})$  8.11–8.13 (*m*, 2 H), 7.46–7.49 (*m*, 2 H), and 7.59–7.61 (*m*, 1 H) in the  $^1\text{H}$ -NMR spectrum, a C=O signal at  $\delta(\text{C})$  167.80 in the  $^{13}\text{C}$ -NMR spectrum, and the HMBC interaction H–C(3')/C(1') suggested the presence of a benzoyl group (Bz) (Table 1, Fig. 1). The position of the ester moiety was confirmed by correlation between H–C(12) and C(1') as well as C=O in the HMBC spectra. The  $^1\text{H}, ^1\text{H}$ -COSY, HSQC, and HMBC spectra provided solid evidence to unambiguously assign all signals of the aglycone of **1** (Table 1). The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of the aglycone were in agreement with those of dresgenin isolated from *Marsdenia tenacissima* (except the data of C(2), C(3), and C(4)) [7]. Furthermore, the ROESY data showed correlations H–C(3)/H–C(5), H–C(5)/H–C(9), H–C(9)/H–C(12); in addition, the correlation H–C(12)/H–C(20) in ROESY confirmed that the side chain of C(17) was in  $\alpha$ -

Table 1.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Data of Compound **1**.  $\delta$  in ppm,  $J$  in Hz.

	$\delta(\text{C})^{\text{a}}$	$\delta(\text{H})^{\text{b}}$		$\delta(\text{C})^{\text{a}}$	$\delta(\text{H})^{\text{b}}$
$\text{H}_{\alpha}$ –C(1)	38.90 ( <i>t</i> )	1.01–1.05 ( <i>m</i> )	$\text{H}_{\beta}$ –C(16)	35.23 ( <i>t</i> )	1.60–1.64 ( <i>m</i> )
$\text{H}_{\beta}$ –C(1)		1.67–1.69 ( <i>m</i> )	C(17)	89.20 ( <i>s</i> )	
$\text{H}_{\alpha}$ –C(2)	33.49 ( <i>t</i> )	1.80–1.84 ( <i>m</i> )	Me(18)	11.81 ( <i>q</i> )	1.66 ( <i>s</i> )
$\text{H}_{\beta}$ –C(2)		1.80–1.84 ( <i>m</i> )	Me(19)	13.06 ( <i>q</i> )	0.98 ( <i>s</i> )
$\text{H}_{\alpha}$ –C(3)	78.60 ( <i>d</i> )	3.61–3.69 ( <i>m</i> )	H–C(20)	71.44 ( <i>d</i> )	3.57 ( <i>q</i> , $J = 6.3$ )
$\text{H}_{\alpha}$ –C(4)	25.81 ( <i>t</i> )	1.64–1.66 ( <i>m</i> )	Me(21)	18.94 ( <i>q</i> )	1.03 ( <i>d</i> , $J = 6.3$ )
$\text{H}_{\beta}$ –C(4)		1.15–1.17 ( <i>m</i> )	12-BzO:		
$\text{H}_{\alpha}$ –C(5)	46.23 ( <i>d</i> )	1.10–1.13 ( <i>m</i> )	C(1')	167.80 ( <i>s</i> )	
$\text{H}_{\alpha}$ –C(6)	34.86 ( <i>t</i> )	1.37–1.38 ( <i>m</i> )	C(2')	131.99 ( <i>s</i> )	
$\text{H}_{\beta}$ –C(6)		1.80–1.84 ( <i>m</i> )	H–C(3')	130.91 ( <i>d</i> )	8.11–8.13 ( <i>m</i> )
$\text{H}_{\alpha}$ –C(7)	34.01 ( <i>t</i> )	1.80–1.84 ( <i>m</i> )	H–C(4')	129.51 ( <i>d</i> )	7.46–7.49 ( <i>m</i> )
$\text{H}_{\beta}$ –C(7)		2.06–2.07 ( <i>m</i> )	H–C(5')	134.22 ( <i>d</i> )	7.59–7.61 ( <i>m</i> )
C(8)	76.81 ( <i>s</i> )		H–C(6')	129.51 ( <i>d</i> )	7.46–7.49 ( <i>m</i> )
$\text{H}_{\alpha}$ –C(9)	47.59 ( <i>d</i> )	1.26–1.31 ( <i>m</i> )	H–C(7')	130.91 ( <i>d</i> )	8.11–8.13 ( <i>m</i> )
C(10)	37.26 ( <i>s</i> )		Cym:		
$\text{H}_{\alpha}$ –C(11)	24.94 ( <i>t</i> )	1.76–1.79 ( <i>m</i> )	$\text{H}_{\alpha}$ –C(1'')	97.06 ( <i>d</i> )	4.87 ( <i>dd</i> , $J = 8.3, 4.7$ )
$\text{H}_{\beta}$ –C(11)		1.99–2.02 ( <i>m</i> )	$\text{H}_{\alpha}$ –C(2'')	35.97 ( <i>t</i> )	2.10–2.15 ( <i>m</i> )
$\text{H}_{\alpha}$ –C(12)	76.46 ( <i>d</i> )	4.84–4.86 ( <i>m</i> )	$\text{H}_{\beta}$ –C(2'')		1.47–1.53 ( <i>m</i> )
C(13)	58.13 ( <i>s</i> )		$\text{H}_{\beta}$ –C(3'')	79.22 ( <i>d</i> )	3.57–3.61 ( <i>m</i> )
C(14)	89.32 ( <i>s</i> )		$\text{H}_{\beta}$ –C(4'')	74.50 ( <i>d</i> )	3.16 ( <i>dd</i> , $J = 9.5, 3.3$ )
$\text{H}_{\alpha}$ –C(15)	29.91 ( <i>t</i> )	1.80–1.84 ( <i>m</i> )	$\text{H}_{\alpha}$ –C(5'')	71.44 ( <i>d</i> )	3.71–3.76 ( <i>m</i> )
$\text{H}_{\beta}$ –C(15)		1.47–1.51 ( <i>m</i> )	Me(6'')	18.68 ( <i>q</i> )	1.23 ( <i>d</i> , $J = 6.3$ )
$\text{H}_{\alpha}$ –C(16)	35.23 ( <i>t</i> )	1.25–1.28 ( <i>m</i> )	MeO	58.06 ( <i>q</i> )	3.43 ( <i>s</i> )

<sup>a</sup>) Measured at 125 MHz in  $\text{CD}_3\text{OD}$ . <sup>b</sup>) Measured at 500 MHz in  $\text{CD}_3\text{OD}$ .

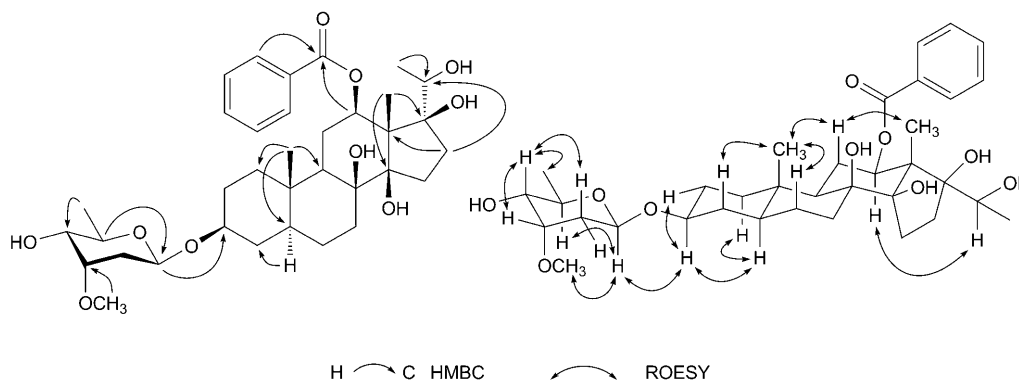


Fig. 1. Key HMBC (left) and Key ROESY (right) Correlations of **1**

position (Fig. 1). Therefore, the structure of the aglycone of **1** was determined as (3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-8,14,17,20-tetrahydroxypregnan-12-yl benzoate.

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopic data of the sugar moiety of **1** (Table 1) showed a Me group ( $\delta(\text{H})$  1.23 (*d*,  $J = 6.3$ )), a MeO group ( $\delta(\text{H})$  3.43 (*s*, 3 H)), and a  $\text{CH}_2$  group ( $\delta(\text{C})$  35.97,  $\delta(\text{H}_\alpha)$  2.10–2.15,  $\delta(\text{H}_\beta)$  1.47–1.53), as well as an anomeric H-atom ( $\delta(\text{H})$  4.87 (*dd*,  $J = 8.3, 4.7, 1$  H)). The  $^1\text{H}$ ,  $^1\text{H}$ -COSY correlations H–C(1'')/H $_\alpha$ –C(2''), H–C(1'')/H $_\beta$ –C(2''), H $_\alpha$ –C(2'')/H–C(3''), H $_\beta$ –C(2'')/H–C(3''), H–C(5'')/H–C(6''), and the HMBC interaction MeO/C(3'') suggested the presence of a 2,6-dideoxy sugar (Fig. 1). Correlations of sugar moiety H–C(3'')/H–C(4''), H–C(4'')/H–C(6''), H–C(5'')/C(1'') in the ROESY experiment (Fig. 1) further confirmed the structure of the sugar moiety. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of the sugar moiety were in agreement with those of the terminal cymarose of cynaversicoside-D isolated from *Cynanchum versicolor* [8]. Therefore, from the ROESY correlations (Fig. 1) and the coupling constant (8.25 Hz) of the anomeric H-atom in the  $^1\text{H}$ -NMR spectrum, the sugar moiety was identified as  $\beta$ -cymaropyranose (Cym). Additionally, a long-range correlation was observed between H–C(1'') of the sugar and C(3) of the aglycone in the HMBC spectrum. Thus, the sugar was indicated to link at C(3) of the aglycone.

Finally, from the data described above, the structure of **1** was unequivocally determined as (3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-3-( $\beta$ -cymaropyranosyloxy)-8,14,17,20-tetrahydroxypregnan-12-yl benzoate.

Compound **2** was obtained as a colorless, amorphous solid. IR spectrum revealed the presence of OH ( $3429\text{ cm}^{-1}$ ) and C=O ( $1701\text{ cm}^{-1}$ ), there also were signals of a C=C bond ( $1635\text{ cm}^{-1}$ ) and an aromatic ring ( $1578, 1453\text{ cm}^{-1}$ ). The specific rotation  $[\alpha]_{\text{D}}^{25}$  of compound **2** ( $c = 0.11, \text{CHCl}_3$ ) was determined to be +27.27. The molecular formula was established by HR-ESI-MS as  $\text{C}_{37}\text{H}_{54}\text{O}_{10}$  from the  $[\text{M} - \text{H}]^-$  ion peak of  $m/z$  657.3634 ( $\text{C}_{37}\text{H}_{53}\text{O}_{10}^-$ ; calc. 657.3639). Compared with the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of compound **1**, the data of compound **2** (Table 2) indicated the presence of an additional C=C bond ( $\delta(\text{C})$  146.72 and 119.37). Correlations in HMBC C(1')/H–C(3') ( $\delta(\text{H})$  7.77 (*d*,  $J = 16.0, 1$  H)), C(1')/H–C(2') ( $\delta(\text{H})$  6.61 (*d*,  $J = 16.0, 1$  H)), H–C(2')/C(4'), H–C(3')/C(5'), suggested that the C=C bond is placed between a C=O group and a benzene ring, indicating that the acyl moiety of compound **2** is a cinnamate.

Table 2.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Data of Compound **2**.  $\delta$  in ppm,  $J$  in Hz.

	$\delta(\text{C})^{\text{a}}$	$\delta(\text{H})^{\text{b}}$		$\delta(\text{C})^{\text{a}}$	$\delta(\text{H})^{\text{b}}$
$\text{H}_\alpha\text{-C}(1)$	38.90 ( <i>t</i> )	1.66–1.72 ( <i>m</i> )	$\text{C}(17)$	89.15 ( <i>s</i> )	
$\text{H}_\beta\text{-C}(1)$		0.98–1.07 ( <i>m</i> )	$\text{Me}(18)$	11.73 ( <i>q</i> )	1.58 ( <i>s</i> )
$\text{H}_\alpha\text{-C}(2)$	33.59 ( <i>t</i> )	2.00–2.18 ( <i>m</i> )	$\text{Me}(19)$	13.09 ( <i>q</i> )	0.98 ( <i>s</i> )
$\text{H}_\beta\text{-C}(2)$		1.78–1.84 ( <i>m</i> )	$\text{H-C}(20)$	71.60 ( <i>d</i> )	3.55 ( <i>q</i> , $J = 6.3$ )
$\text{H}_\alpha\text{-C}(3)$	78.59 ( <i>d</i> )	3.60–3.67 ( <i>m</i> )	$\text{Me}(21)$	18.79 ( <i>q</i> )	1.07 ( <i>d</i> , $J = 6.3$ )
$\text{H}_\alpha\text{-C}(4)$	25.80 ( <i>t</i> )	1.60–1.66 ( <i>m</i> )	12-Cinnamoyloxy:		
$\text{H}_\beta\text{-C}(4)$		1.12–1.18 ( <i>m</i> )	$\text{C}(1')$	168.40 ( <i>s</i> )	
$\text{H}_\alpha\text{-C}(5)$	46.22 ( <i>d</i> )	1.08–1.13 ( <i>m</i> )	$\text{H-C}(2')$	119.37 ( <i>d</i> )	6.61 ( <i>d</i> , $J = 16.0$ )
$\text{H}_\alpha\text{-C}(6)$	34.85 ( <i>t</i> )	1.78–1.84 ( <i>m</i> )	$\text{H-C}(3')$	146.72 ( <i>d</i> )	7.77 ( <i>d</i> , $J = 16.0$ )
$\text{H}_\beta\text{-C}(6)$		1.31–1.39 ( <i>m</i> )	$\text{C}(4')$	135.90 ( <i>s</i> )	
$\text{H}_\alpha\text{-C}(7)$	33.94 ( <i>t</i> )	1.78–1.84 ( <i>m</i> )	$\text{H-C}(5')$	129.38 ( <i>d</i> )	7.61–7.63 ( <i>m</i> )
$\text{H}_\beta\text{-C}(7)$		1.78–1.84 ( <i>m</i> )	$\text{H-C}(6')$	129.97 ( <i>d</i> )	7.39–7.41 ( <i>m</i> )
$\text{C}(8)$	76.80 ( <i>s</i> )		$\text{H-C}(7')$	131.49 ( <i>d</i> )	7.39–7.41 ( <i>m</i> )
$\text{H}_\alpha\text{-C}(9)$	47.67 ( <i>d</i> )	1.20–1.26 ( <i>m</i> )	$\text{H-C}(8')$	129.97 ( <i>d</i> )	7.39–7.41 ( <i>m</i> )
$\text{C}(10)$	37.25 ( <i>s</i> )		$\text{H-C}(9')$	129.38 ( <i>d</i> )	7.61–7.63 ( <i>m</i> )
$\text{H}_\alpha\text{-C}(11)$	24.95 ( <i>t</i> )	1.93–2.00 ( <i>m</i> )	Cym:		
$\text{H}_\beta\text{-C}(11)$		1.68–1.75 ( <i>m</i> )	$\text{H}_\alpha\text{-C}(1'')$	97.05 ( <i>d</i> )	4.86 ( <i>dd</i> , $J = 9.7, 2.0$ )
$\text{H}_\alpha\text{-C}(12)$	76.09 ( <i>d</i> )	4.70 ( <i>dd</i> , $J = 11.4, 4.4$ )	$\text{H}_\alpha\text{-C}(2'')$	35.96 ( <i>t</i> )	2.12–2.16 ( <i>m</i> )
$\text{C}(13)$	57.95 ( <i>q</i> )		$\text{H}_\beta\text{-C}(2'')$		1.48–1.55 ( <i>m</i> )
$\text{C}(14)$	89.30 ( <i>s</i> )		$\text{H}_\beta\text{-C}(3'')$	79.21 ( <i>d</i> )	3.53–3.57 ( <i>m</i> )
$\text{H}_\alpha\text{-C}(15)$	29.91 ( <i>t</i> )	1.78–1.84 ( <i>m</i> )	$\text{H}_\beta\text{-C}(4'')$	74.50 ( <i>d</i> )	3.16 ( <i>dd</i> , $J = 9.5, 3.3$ )
$\text{H}_\beta\text{-C}(15)$		1.48–1.53 ( <i>m</i> )	$\text{H}_\alpha\text{-C}(5'')$	71.44 ( <i>d</i> )	3.70–3.74 ( <i>m</i> )
$\text{H}_\alpha\text{-C}(16)$	35.22 ( <i>t</i> )	1.58–1.67 ( <i>m</i> )	$\text{Me}(6'')$	18.68 ( <i>q</i> )	1.23 ( <i>d</i> , $J = 6.3$ )
$\text{H}_\beta\text{-C}(16)$		1.24–1.28 ( <i>m</i> )	$\text{MeO}$	58.06 ( <i>s</i> )	3.42 ( <i>s</i> )

<sup>a</sup>) Measured at 125 MHz in  $\text{CD}_3\text{OD}$ . <sup>b</sup>) Measured at 500 MHz in  $\text{CD}_3\text{OD}$ .

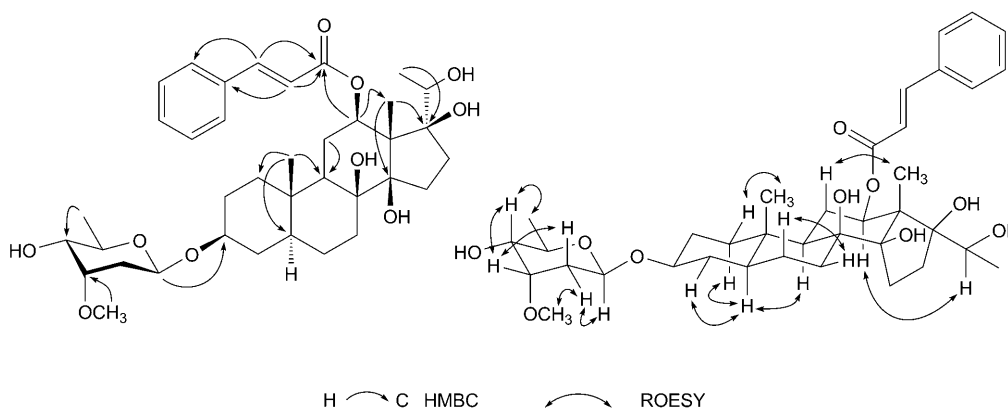


Fig. 2. Key HMBC (left) and Key ROESY (right) Correlations of **2**

Furthermore, the correlation in HMBC between  $\text{H-C}(12)$  and  $\text{C}(1')$  confirmed that the cinnamate group is linked to  $\text{C}(12)$  of the aglycone. Taking the spectra of HMBC and ROESY together shown in Fig. 2, the structure of **2** was assigned as

(3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-3-( $\beta$ -cymaropyranosyloxy)-8,14,17,20-tetrahydroxypregnan-12-yl cinnamate.

### Experimental Part

*General.* Column chromatography (CC): Silica gel (SiO<sub>2</sub>, 200–300 mesh) was from *Qingdao Marine Chemical Plant*, Qingdao, P. R. China. *Sephadex LH-20* was purchased from *GE Healthcare Bio-Sciences AB*. *YMC\*GEL® ODS-A* was obtained from *YMC Co., Ltd.* TLC precoated silica gel *G* plates were from *Qingdao Marine Chemical Plant*, Qingdao, P. R. China. Optical Rotations: *RUDOLPH Automatic Polarimeter*. UV Spectra: *Agilent 8453 Spectrometer*,  $\lambda_{\max}$  (log  $\epsilon$ ) in nm. IR Spectra (KBr): *Bruker v33 Spectrometer*; in cm<sup>-1</sup>. <sup>1</sup>H-, <sup>13</sup>C-, and 2D-NMR Spectra: *Bruker-AV-500 spectrometer*;  $\delta$  in ppm rel. to Me<sub>4</sub>Si, *J* in Hz. MS: *Agilent-1100-JC/MSD-Trap* (ESI-MS) and *Micro-Q-TOF* (HR-ESI-MS) spectrometer; in *m/z*.

*Plant Material.* The stems of *Marsdenia tenacissima* were purchased from *Anhui Fengyuan Pharmaceutical Co., Ltd.*, P. R. China, in June 2006, and identified by Prof. *De-Kang Wu* (Nanjing University of Traditional Chinese Medicine). A voucher specimen has been deposited with the Herbarium of China Pharmaceutical University, Nanjing, P. R. China (reference number: No. 20060628).

*Extraction and Isolation.* The dried stems of *Marsdenia tenacissima* (30 kg) were extracted with 95% EtOH (720 l) at r.t. for 2 h for 3 times. The filtered soln. was concentrated *in vacuo* to yield an extract (17 kg), which was further extracted with AcOEt (50 l). After concentrating the AcOEt extract *in vacuo* to afford a residue (408.5 g), the residue was separated by CC (SiO<sub>2</sub>; petroleum ether (PE)/acetone 15:1  $\rightarrow$  acetone) to afford 154 fractions (*Fr. 1*). *Fr. 1* (79–82) was further chromatogramed by CC (SiO<sub>2</sub>; CHCl<sub>3</sub>/MeOH/PE 40:1:40) to yield 113 fractions (*Fr. 2*). *Fr. 2* (54–55) was subjected to additional CC (*Sephadex LH-20*; CH<sub>2</sub>Cl<sub>2</sub>/MeOH 1:1), and final CC (*ODS-A*; MeOH/H<sub>2</sub>O 73:27) to afford compounds **1** (8 mg) and **2** (13 mg).

(3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-3-( $\beta$ -Cymaropyranosyloxy)-8,14,17,20-tetrahydroxypregnan-12-yl Benzoate (**1**). Colorless, amorphous solid.  $[\alpha]_D^{25} = +85.06$  ( $c = 0.04$ , MeOH). UV (MeOH): 230 (3.54). IR (KBr): 3442, 2943, 1710, 1605, 1455. <sup>1</sup>H- and <sup>13</sup>C-NMR: *Table 1*. The key correlations of HMBC and ROESY are presented in *Fig. 1*. ESI-MS (pos.): 655 (6,  $[M + Na]^+$ ). HR-ESI-MS (neg.): 631.3464 ( $[M - H]^-$ , C<sub>35</sub>H<sub>51</sub>O<sub>10</sub><sup>-</sup>; calc. 631.3482).

(3 $\beta$ ,5 $\alpha$ ,12 $\beta$ ,14 $\beta$ ,17 $\alpha$ )-3-( $\beta$ -Cymaropyranosyloxy)-8,14,17,20-tetrahydroxypregnan-12-yl Cinnamate (**2**). Colorless, amorphous solid.  $[\alpha]_D^{25} = +27.27$  ( $c = 0.11$ , CHCl<sub>3</sub>). UV (MeOH): 280 (3.73). IR (KBr): 3429, 2943, 1701, 1635, 1578, 1453. <sup>1</sup>H- and <sup>13</sup>C-NMR: *Table 2*. The key correlations of HMBC and ROESY are presented in *Fig. 2*. ESI-MS (pos.): 681 (16,  $[M + Na]^+$ ). HR-ESI-MS (neg.): 657.3634 ( $[M - H]^-$ , C<sub>37</sub>H<sub>53</sub>O<sub>10</sub><sup>-</sup>; calc. 657.3639).

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