# Three New $C_{21}$ Steroidal Glycosides from the Stems of *Marsdenia tenacissima*

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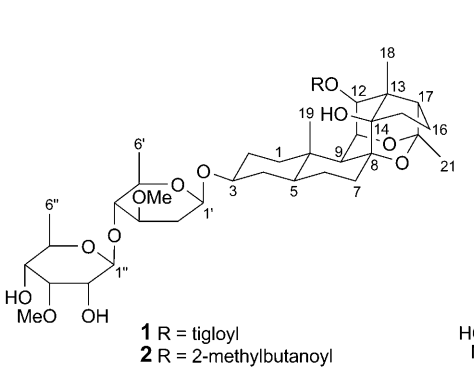
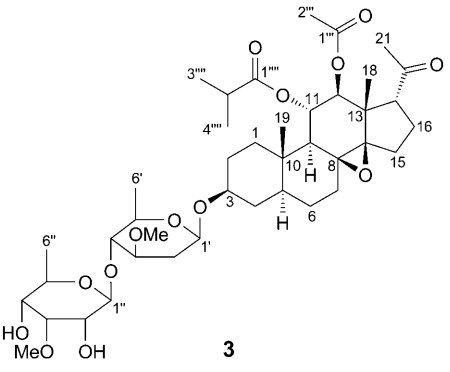
Three new glycosides, (3*β*,5*α*,8*α*,11*α*,12*β*,14*β*,17*α*,20*R*)-3-[(2,6-dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-*β*-D-allopyranosyl)-3-*O*-methyl-*β*-D-*arabino*-hexopyranosyl)oxy]-12-*O*-tigloyl-8,20:11,20-diepoxypregnane-12,14-diol (**1**), (3*β*,5*α*,8*α*,11*α*,12*β*,14*β*,17*α*,20*R*)-3-[(2,6-dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-*β*-D-allopyranosyl)-3-*O*-methyl-*β*-D-*arabino*-hexopyranosyl)oxy]-12-*O*-(2-methylbutanoyl)-8,20:11,20-diepoxypregnane-12,14-diol (**2**), and (3*β*,5*α*,11*α*,12*β*,14*β*,17*α*)-12-acetoxy-3-[(2,6-dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-*β*-D-allopyranosyl)-3-*O*-methyl-*β*-D-*arabino*-hexopyranosyl)oxy]-20-oxo-8,14-epoxypregnan-11-yl isobutyrate (**3**) were isolated from the stems of *Marsdenia tenacissima*. The structures of the new compounds were elucidated by means of spectral data, including HR-ESI-MS, and 1D- and 2D-NMR.

**Introduction.** – The stems of *Marsdenia tenacissima* (ROXB.) WIGHT et ARN. (Asclepiadaceae), a traditional Chinese medicine known as *'tongguanteng'*, is used for the treatment of many diseases, such as cancers and asthma [1]. Since 1990s, *Xiao'aiping* injection (an extract of Marsdenia tenacissima) has been produced and marketed by *Nanjing Sanhome Pharmaceutical Co., Ltd.* (Nanjing, Jiangsu, P. R. China), and clinically proved to be effective for esophageal, lung, and gastric cancer. Many steroidal glycosides have been isolated from this plant and reported [2–6]. The present investigation revealed three new $C_{21}$ steroidal glycosides, **1**–**3**, which were determined to be (3*β*,5*α*,8*α*,11*α*,12*β*,14*β*,17*α*,20*R*)-3-[(2,6-dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-*β*-D-allopyranosyl)-3-*O*-methyl-*β*-D-*arabino*-hexopyranosyl)oxy]-12-*O*-tigloyl-8,20:11,20-diepoxypregnane-12,14-diol (**1**), (3*β*,5*α*,8*α*,11*α*,12*β*,14*β*,17*α*,20*R*)-3-[(2,6-dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-*β*-D-allopyranosyl)-3-*O*-methyl-*β*-D-*arabino*-hexopyranosyl)oxy]-12-*O*-(2-methylbutanoyl)-8,20:11,20-diepoxypregnane-12,14-diol (**2**) and (3*β*,5*α*,11*α*,12*β*,14*β*,17*α*)-12-acetoxy-3-[(2,6-dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-*β*-D-allopyranosyl)-3-*O*-methyl-*β*-D-*arabino*-hexopyranosyl)oxy]-20-oxo-8,14-epoxypregnan-11-yl isobutyrate (**3**). The isolation and structure elucidation of these three new $C_{21}$ steroidal glycosides are described in this article.

**Results and Discussion.** – Compound **1** was obtained as a colorless, amorphous solid. The IR spectrum displayed absorption bands for OH (3440 $cm^{-1}$) and C=O (1707 $cm^{-1}$). Specific rotation, $[\alpha]_D^{25}$ ($c = 0.31$M, MeOH), was −5.3. The molecular formula was established as $C_{40}H_{62}O_{13}$ by HR-ESI-MS, showing the $[M+Na]^+$ ion peak at $m/z$ 773.4094 ($C_{40}H_{62}NaO_{13}^+$; calc. 773.4088).

The $^1$H-NMR spectroscopic data of the sugar moiety of **1** exhibited signals for two anomeric H-atoms at $\delta$(H) 4.58 (*dd*, $J$ = 10.0, 1.5, H−C(1′)) and 4.79 (*dd*, $J$ = 8.0, 2.0, H−C(1″)), with corresponding $^{13}$C-NMR signals at $\delta$(C) 97.2 and 99.1, suggesting the




presence of a disaccharide (*Table 1*). Both glycosidic linkages are $\beta$-oriented, as deduced from the coupling constants (10.0 and 8.0 Hz) of the two anomeric H-atoms. The $^{13}$C-NMR spectroscopic data ascribed to the sugar moiety of **1** (*Table 1*) were identical to those reported for pachybiose[1]) [6], which was confirmed by examination of the corresponding HMBC and NOESY spectra (*Fig. 1*). In addition, the $^{1}$H-NMR signals at $\delta$(H) 1.79 (*dd*, $J$ = 7.0, 1.0, 3 H), 1.86 (*s*, 3 H), and 6.85 (*dd*, $J$ = 7.0, 1.0, 1 H) suggested the presence of a tigloyl group, which was confirmed by the corresponding $^{13}$C-NMR and DEPT signals at $\delta$(C) 167.6 (C), 128.6 (C), 138.6 (CH), 12.1 (Me), 14.4 (Me), and HSQC, HMBC, and NOESY results (*Table 1* and *Fig. 1*). The configuration was identified to be *trans* by comparing the $^{1}$H-NMR spectroscopic data with the reference values [7].

For the aglycone moiety of **1**, 21 C-atoms were left, suggesting a $C_{21}$ steroid. This was supported by the three Me signals at $\delta$(H) 1.09 (*s*), 0.97 (*s*), and 1.20 (*s*) in the $^{1}$H-NMR spectrum (*Table 1*). The $^{1}$H- and $^{13}$C-NMR data of the aglycone were in good agreement with those of 3-*O*-pachybiosyltenacigenin A [6], except for the signals of C(11) and C(12), which were shifted by $\Delta\delta$(C) $-3.0$ and $+0.7$ ppm, respectively, due to the esterification of tigloyl. The linking position of tigloyl group and sugar moiety were deduced from the HMBC correlations H–C(12)/C(1‴) and H–C(1′)/C(3) (*Fig. 1*). Therefore, the structure of compound **1** was unequivocally assigned as (3$\beta$,5$\alpha$,11$\alpha$,12$\beta$,14$\beta$,17$\alpha$,20*R*)-3-*O*-$\beta$-allopyranosyl-(1 → 4)-$\beta$-oleandropyranoside-12-*O*-tigloyltenacigenin A[2]).

Compound **2** was obtained as a colorless, amorphous solid. The IR spectrum revealed the presence of OH (3439 cm$^{-1}$) and C=O (1707 cm$^{-1}$) groups. Specific rotation of **2**, $[\alpha]_D^{25}$ ($c$ = 0.28M, MeOH), was determined to be $-4.7$. The molecular formula was established by HR-ESI-MS as $C_{40}H_{64}O_{13}$ from the $[M+Na]^+$ ion peak at $m/z$ 775.4224 ($C_{40}H_{64}NaO_{13}^+$; calc. 775.4245). The $^{13}$C-NMR spectroscopic data were similar to those of **1** apart from the absence of the tigloyl group. Instead, the presence of 2-methylbutanoyl group was evident, which was confirmed by the $^{1}$H-NMR signals at $\delta$(H) 0.89 (*t*, $J$ = 7.5, 3 H) and 1.18 (*d*, $J$ = 7.0, 3 H), with corresponding $^{13}$C-NMR

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[1]) Pachybiose = 2,6-dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-$\beta$-D-allopyranosyl)-3-*O*-methyl-$\beta$-D-*arabino*-hexopyranose.

[2]) For systematic names, see the *Exper. Part.*

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

| | $\delta$(C)[a]) | $\delta$(H)[b]) | | $\delta$(C)[a]) | $\delta$(H)[b]) |
|---|---|---|---|---|---|
| $H_a$–C(1) | 38.5 | 1.58–1.63 (*m*) | Tigloyl: | | |
| $H_b$–C(1) | | 1.10–1.18 (*m*) | H–C(1‴) | 167.7 | |
| $H_a$–C(2) | 28.5 | 1.86–1.89 (*m*) | H–C(2‴) | 128.6 | |
| $H_b$–C(2) | | 1.45–1.47 (*m*) | H–C(3‴) | 138.6 | 6.85 (*dd*, *J* = 7.0, 1.0) |
| H–C(3) | 77.1 | 3.60–3.69 (*m*) | H–C(4‴) | 12.1 | 1.86 (*s*) |
| $H_a$–C(4) | 34.5 | 1.56–1.64 (*m*) | H–C(5‴) | 14.4 | 1.79 (*dd*, *J* = 7.0, 1.0) |
| $H_b$–C(4) | | 2.39–2.47 (*m*) | Oleandropyranose: | | |
| H–C(5) | 45.7 | 1.34–1.36 (*m*) | H–C(1′) | 97.2 | 4.58 (*dd*, *J* = 10.0, 1.5) |
| $H_a$–C(6) | 27.7 | 1.24–1.29 (*m*) | $H_a$–C(2′) | 36.1 | 1.45–1.52 (*m*) |
| $H_b$–C(6) | | 1.48–1.52 (*m*) | $H_b$–C(2′) | | 2.27–2.33 (*m*) |
| $H_a$–C(7) | 33.6 | 1.25–1.33 (*m*) | H–C(3′) | 78.9 | 3.36–3.38 (*m*) |
| $H_b$–C(7) | | 1.60–1.65 (*m*) | H–C(4′) | 79.4 | 3.30–3.34 (*m*) |
| C(8) | 77.8 | | H–C(5′) | 71.4 | 3.31–3.35 (*m*) |
| H–C(9) | 57.5 | 2.38–2.41 (*m*) | Me(6′) | 18.6 | 1.36 (*d*, *J* = 6.0) |
| C(10) | 35.4 | | MeO | 55.2 | 3.37 (*s*) |
| H–C(11) | 68.3 | 4.43–4.45 (*m*) | Allopyranose: | | |
| H–C(12) | 71.9 | 5.19 (*d*-like, *J* = 4.0) | H–C(1″) | 99.1 | 4.79 (*dd*, *J* = 8.0, 2.0) |
| C(13) | 44.3 | | H–C(2″) | 72.7 | 3.46–3.52 (*m*) |
| C(14) | 81.1 | | H–C(3″) | 81.1 | 3.77–3.80 (*m*) |
| $H_a$–C(15) | 34.2 | 1.29–1.36 (*m*) | H–C(4″) | 72.8 | 3.18 (*dd*, *J* = 9.5, 3.5) |
| $H_b$–C(15) | | 2.26–2.33 (*m*) | H–C(5″) | 71.4 | 3.52–3.57 (*m*) |
| $H_a$–C(16) | 23.0 | 1.43–1.48 (*m*) | Me(6″) | 17.8 | 1.25 (*d*, *J* = 6.0) |
| $H_b$–C(16) | | 1.84–1.89 (*m*) | MeO | 61.9 | 3.65 (*s*) |
| H–C(17) | 55.7 | 1.96–1.97 (*m*) | | | |
| H–C(18) | 16.5 | 1.09 (*s*) | | | |
| H–C(19) | 16.0 | 0.97 (*s*) | | | |
| C(20) | 99.7 | | | | |
| H–C(21) | 24.2 | 1.20 (*s*) | | | |

[a]) Recorded at 125 MHz in $CDCl_3$. [b]) Recorded at 500 MHz in $CDCl_3$.

and DEPT signals at $\delta$(C) 176.3 (C), 41.6 (CH), 26.3 ($CH_2$), 17.6 (Me), and 11.9 (Me) (*Table 2*). The linking position of the 2-methylbutanoyl group was confirmed by the HMBC relationship H–C(12)/C(1‴) (*Fig. 2*). Thus, the structure of compound **2** was identified as (3$\beta$,5$\alpha$,11$\alpha$,12$\beta$,14$\beta$,17$\alpha$,20*R*)-3-*O*-$\beta$-allopyranosyl-(1 → 4)-$\beta$-oleandropyranoside-12-*O*-(2-methylbutanoyl)tenacigenin A[2]).

Compound **3** was obtained as a colorless, amorphous solid. The IR spectrum displayed absorption bands for OH (3433 $cm^{-1}$) and C=O (1736 $cm^{-1}$). Specific rotation, $[\alpha]_D^{25}$ ($c$ = 0.23M, MeOH), was +26.3. The molecular formula was established as $C_{41}H_{64}O_{14}$ by HR-ESI-MS, showing the $[M+Na]^+$ ion peak at $m/z$ 803.4202 ($C_{41}H_{64}NaO_{14}^+$; calc. 803.4194).

The $^{13}$C-NMR and DEPT data of compound **3** were in good agreement with those of marsdenoside F [8], except that the signal at $\delta$(C) 20.6, belonging to Me of the Ac group of marsdenoside F, is replaced with the signals at $\delta$(C) 34.5 (CH), 18.9 (Me), and 18.6 (Me) in **3** (*Table 3*). The corresponding $^1$H-NMR spectroscopic data, $\delta$(H) 2.39 (*qq*, *J* = 7.0, 7.0, 1 H), 1.07 (*d*, *J* = 7.0, 3 H), and 1.08 (*d*, *J* = 7.0, 3 H), suggested the

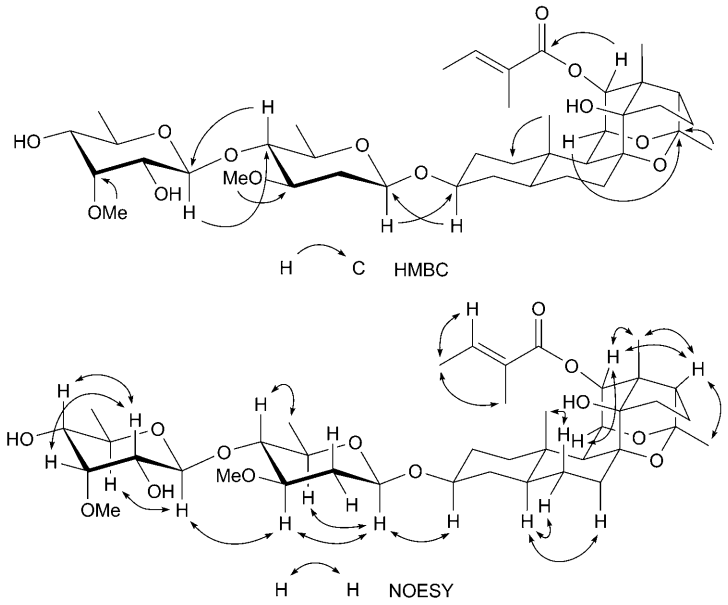


Fig. 1. *Key HMBC and NOESY correlations of* **1**

presence of an isobutyryl group. The linking position of the isobutyryl group was deduced from the HMBC H–C(11)/C(1‴) (*Fig. 3*). Accordingly, the structure of compound **3** was elucidated as (3$\beta$,5$\alpha$,11$\alpha$,12$\beta$,14$\beta$,17$\alpha$)-3-*O*-6-deoxy-3-*O*-methyl-$\beta$-D-

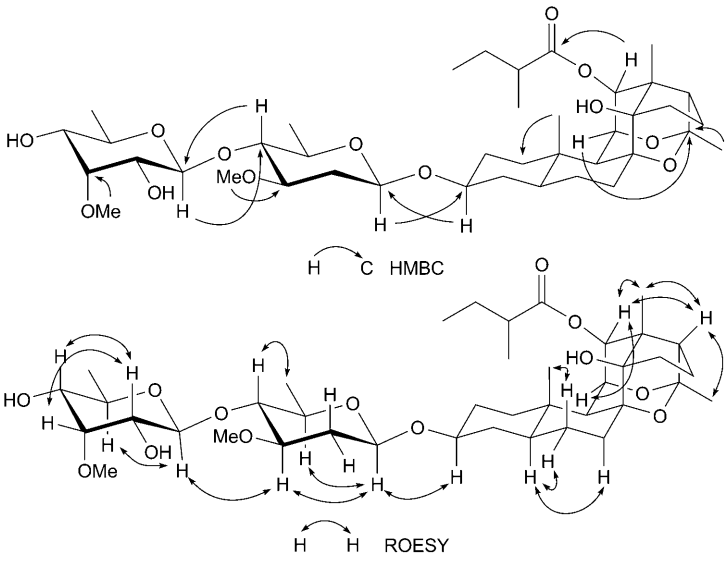


Fig. 2. *Key HMBC and NOESY correlations of* **2**

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

| | $\delta$(C)[a]) | $\delta$(H)[b]) | | $\delta$(C)[a]) | $\delta$(H)[b]) |
|---|---|---|---|---|---|
| $H_a$–C(1) | 38.3 | 1.58–1.65 (*m*) | 2-Methylbutanoyl: | | |
| $H_b$–C(1) | | 1.13–1.18 (*m*) | H–C(1‴) | 176.3 | |
| $H_a$–C(2) | 28.4 | 1.84–1.90 (*m*) | H–C(2‴) | 41.6 | 2.33–2.44 (*m*) |
| $H_b$–C(2) | | 1.44–1.49 (*m*) | $H_a$–C(3‴) | 26.3 | 1.38–1.46 (*m*) |
| H–C(3) | 77.1 | 3.59–3.68 (*m*) | $H_b$–C(3‴) | | 1.69–1.77 (*m*) |
| $H_a$–C(4) | 34.3 | 1.56–1.65 (*m*) | H–C(4‴) | 11.9 | 0.89 (*t*, $J$ = 7.5) |
| $H_b$–C(4) | | 2.35–2.37 (*m*) | H–C(5‴) | 17.6 | 1.18 (*d*, $J$ = 7.0) |
| H–C(5) | 45.8 | 1.21–1.30 (*m*) | Oleandropyranose: | | |
| $H_a$–C(6) | 27.7 | 1.24–1.31 (*m*) | H–C(1′) | 97.3 | 4.57 (*dd*, $J$ = 9.5, 2.0) |
| $H_b$–C(6) | | 1.48–1.52 (*m*) | $H_a$–C(2′) | 36.1 | 1.43–1.52 (*m*) |
| $H_a$–C(7) | 33.5 | 1.25–1.33 (*m*) | $H_b$–C(2′) | | 2.27–2.34 (*m*) |
| $H_b$–C(7) | | 1.62–1.66 (*m*) | H–C(3′) | 78.8 | 3.36–3.42 (*m*) |
| C(8) | 77.8 | | H–C(4′) | 79.3 | 3.32–3.35 (*m*) |
| H–C(9) | 57.4 | 2.36–2.39 (*m*) | H–C(5′) | 71.4 | 3.31–3.35 (*m*) |
| C(10) | 35.3 | | Me(6′) | 18.5 | 1.36 (*d*, $J$ = 5.5) |
| H–C(11) | 68.5 | 4.28–4.29 (*m*) | MeO | 55.7 | 3.37 (*s*) |
| H–C(12) | 71.7 | 5.26 (*d*-like, $J$ = 4.0) | Allopyranose: | | |
| C(13) | 44.4 | | H–C(1″) | 99.2 | 4.79 (*d*, $J$ = 8.5) |
| C(14) | 81.0 | | H–C(2″) | 71.9 | 3.46–3.50 (*m*) |
| $H_a$–C(15) | 34.0 | 1.28–1.36 (*m*) | H–C(3″) | 81.1 | 3.77–3.79 (*m*) |
| $H_b$–C(15) | | 2.23–2.33 (*m*) | H–C(4″) | 72.9 | 3.18 (*dd*, $J$ = 9.5, 2.5) |
| $H_a$–C(16) | 22.9 | 1.43–1.47 (*m*) | H–C(5″) | 71.4 | 3.52–3.58 (*m*) |
| $H_b$–C(16) | | 1.82–1.88 (*m*) | Me(6″) | 17.8 | 1.26 (*d*, $J$ = 6.0) |
| H–C(17) | 55.3 | 1.96–1.97 (*m*) | MeO | 61.9 | 3.65 (*s*) |
| H–C(18) | 16.1 | 1.06 (*s*) | | | |
| H–C(19) | 15.7 | 1.09 (*s*) | | | |
| C(20) | 99.7 | | | | |
| H–C(21) | 24.2 | 1.19 (*s*) | | | |

[a]) Recorded at 125 MHz in $CDCl_3$. [b]) Recorded at 500 MHz in $CDCl_3$.

allopyranosyl-(1 → 4)-$\beta$-D-oleandropyranosyl-11-*O*-isobutyryl-12-*O*-acetyltenacigenin B[2]).

## Experimental Part

*General.* Silica gel ($SiO_2$; 200–300 mesh) and TLC precoated silica-gel *G* plates were from *Qingdao Marine Chemical Plant*, Qingdao, P. R. China. *Sephadex LH-20* was purchased from *GE Healthcare Bio-Sciences AB* (USA). *YMC*GEL® ODS-A rp-filler* (500 mesh) was obtained from *YMC Co., Ltd.* (Japan). Prep. HPLC: *Waters delta 600* pump and *Waters 2487 UV* detector purchased from *Waters Corporation* (USA). Prep. HPLC column: *Waters sunfire™ prep. $C_{18}$ 5 μm* (10 × 250 mm) obtained from *Waters Corporation* (USA). Optical rotations: *RUDOLPH Automatic* polarimeter. UV Spectra: *Shimadzu 2410PC*. IR Spectra (KBr): *Nicolet Impact 410*; in $cm^{-1}$. $^1$H-, $^{13}$C-, and 2D-NMR spectra: *Bruker-AV-500* spectrometer ($\delta$ in ppm rel. to $Me_4Si$, $J$ in Hz). HR-ESI-MS: *Micro-Q-TOF* spectrometer.

*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 Chinese Pharmaceutical University, Nanjing, P. R. China (reference No. 20060628).

Table 3. *$^1$H- and $^{13}$C-NMR Data of Compound* **3**. $\delta$ in ppm, $J$ in Hz.

| | $\delta$(C)[a]) | $\delta$(H)[b]) | | $\delta$(C)[a]) | $\delta$(H)[b]) |
|---|---|---|---|---|---|
| $H_a$–C(1) | 37.6 | 1.48–1.54 (*m*) | Acetyl: | | |
| $H_b$–C(1) | | 1.20–1.27 (*m*) | C(1‴) | 170.6 | |
| $H_a$–C(2) | 29.0 | 1.45–1.48 (*m*) | H–C(2‴) | 20.8 | 1.97 (*s*) |
| $H_b$–C(2) | | 1.74–1.80 (*m*) | Isobutyryl: | | |
| H–C(3) | 76.2 | 3.58–3.65 (*m*) | H–C(1⁗) | 176.0 | |
| $H_a$–C(4) | 34.7 | 1.64–1.70 (*m*) | H–C(2⁗) | 34.5 | 2.39 (*qq*, $J$ = 7.0, 7.0) |
| $H_b$–C(4) | | 1.30–1.35 (*m*) | H–C(3⁗) | 18.9 | 1.07 (*d*, $J$ = 7.0) |
| H–C(5) | 43.9 | 1.30–1.34 (*m*) | H–C(4⁗) | 18.6 | 1.08 (*d*, $J$ = 7.0) |
| $H_a$–C(6) | 26.8 | 1.37–1.43 (*m*) | Oleandropyranose: | | |
| $H_b$–C(6) | | 1.54–1.62 (*m*) | H–C(1′) | 96.9 | 4.58 (*dd*, $J$ = 10.0, 1.5) |
| $H_a$–C(7) | 31.7 | 1.23–1.27 (*m*) | $H_a$–C(2′) | 36.1 | 1.45–1.51 (*m*) |
| $H_b$–C(7) | | 1.85–1.92 (*m*) | $H_b$–C(2′) | | 2.28–2.34 (*m*) |
| C(8) | 66.7 | | H–C(3′) | 78.8 | 3.36–3.42 (*m*) |
| H–C(9) | 51.1 | 2.00 (*d*, $J$ = 10.5) | H–C(4′) | 79.2 | 3.30–3.42 (*m*) |
| C(10) | 39.1 | | H–C(5′) | 71.4 | 3.31–3.35 (*m*) |
| H–C(11) | 68.5 | 5.35 (*t*-like, $J$ = 10.0) | Me(6′) | 18.4 | 1.37 (*d*, $J$ = 5.5) |
| H–C(12) | 75.1 | 4.98 (*d*, $J$ = 10.0) | MeO | 55.6 | 3.37 (*s*) |
| C(13) | 45.8 | | Allopyranose: | | |
| C(14) | 71.3 | | H–C(1″) | 99.1 | 4.79 (*d*, $J$ = 8.5) |
| $H_a$–C(15) | 26.5 | 1.97–2.02 (*m*) | H–C(2″) | 71.9 | 3.46–3.50 (*m*) |
| $H_b$–C(15) | | 1.54–1.62 (*m*) | H–C(3″) | 81.0 | 3.79 (*t*, $J$ = 3.0) |
| $H_a$–C(16) | 24.9 | 2.17–2.20 (*m*) | H–C(4″) | 72.9 | 3.15–3.18 (*m*) |
| $H_b$–C(16) | | 1.58–1.64 (*m*) | H–C(5″) | 71.3 | 3.50–3.57 (*m*) |
| H–C(17) | 60.1 | 2.91 (*d*-like, $J$ = 7.0) | Me(6″) | 17.9 | 1.26 (*d*, $J$ = 6.0) |
| H–C(18) | 16.7 | 1.07 (*s*) | MeO | 61.9 | 3.66 (*s*) |
| H–C(19) | 12.7 | 1.04 (*s*) | | | |
| C(20) | 210.6 | | | | |
| H–C(21) | 29.8 | 2.20 (*s*) | | | |

[a]) Recorded at 125 MHz in $CDCl_3$. [b]) Recorded at 500 MHz in $CDCl_3$.

*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). Concentrating the AcOEt extract *in vacuo* afforded a residue (408.5 g), which was separated by CC ($SiO_2$; petroleum ether (PE)/acetone 15:1 → acetone) to give 154 fractions (*Fr. 1*).

*Fr. 1* (*86–92*) was further subjected to CC ($SiO_2$; $CHCl_3$/MeOH/PE 20:1:20), CC (*Sephadex LH-20*; MeOH), and CC (*ODS-A*; acetone/$H_2O$ 3:2), and finally to a prep. HPLC column (MeCN/$H_2O$ 42:58) to yield **3** (12 mg).

*Fr. 1* (*93–98*) was further submitted to CC ($SiO_2$; $CHCl_3$/MeOH/PE 15:1:15), CC (*Sephadex LH-20*; MeOH), and CC (*ODS-A*; acetone/$H_2O$ 11:9), and finally to a prep. HPLC (MeCN/$H_2O$ 40:60) to yield **1** (10 mg) and **2** (9 mg).

*(3β,5α,8α,11α,12β,14β,17α,20*R*)-3-{[2,6-Dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-β-*D*-allopyranosyl)-3-*O*-methyl-β-*D*-arabino-hexopyranosyl]oxy}-14-hydroxy-8,20:11,20-diepoxypregnan-12-yl (2*E*)-2-Methylbut-2-enoate* (**1**). Colorless, amorphous solid. $[\alpha]_D^{25} = -5.3$ ($c$ = 0.31M, MeOH). IR (KBr): 3440, 2944, 1707, 1380, 1245, 1082. $^1$H- and $^{13}$C-NMR: see *Table 1*. Key correlations of HMBC and ROESY: see *Fig. 1*. HR-ESI-MS (pos.): 773.4094 ($[M+Na]^+$, $C_{40}H_{62}NaO_{13}^+$; calc. 773.4088).

*(3β,5α,8α,11α,12β,14β,17α,20*R*)-3-{[2,6-Dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-β-*D*-allopyranosyl)-3-*O*-methyl-β-*D*-arabino-hexopyranosyl]oxy}-14-hydroxy-8,20:11,20-diepoxypregnan-12-yl 2-Methylbuta-*

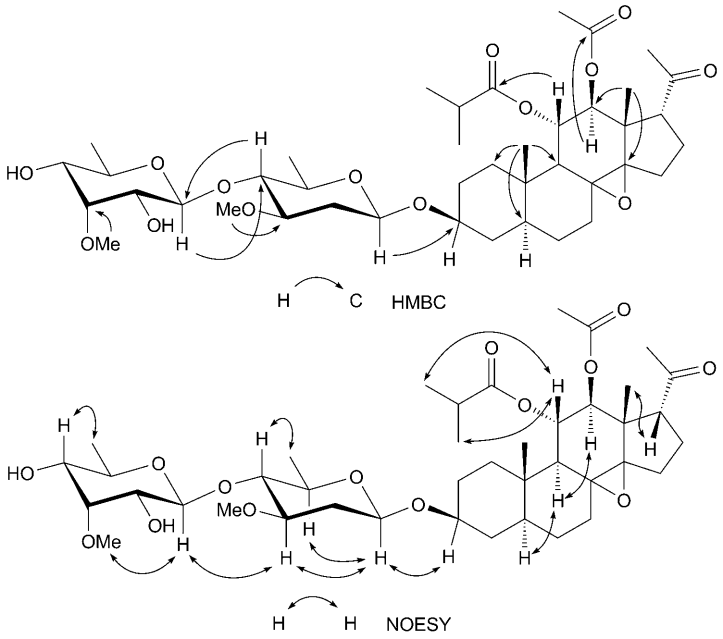


Fig. 3. *Key HMBC and NOESY correlations of* **3**

*noate* (**2**). Colorless, amorphous solid. IR (KBr): 3439, 2937, 1707, 1380, 1270, 1076. $[\alpha]_D^{25} = -4.7$ ($c =$ 0.28M, MeOH). $^1$H- and $^{13}$C-NMR: see *Table 2*. Key correlations of HMBC and ROESY: see *Fig. 2*. HR-ESI-MS (pos.): 775.4224 ($[M+Na]^+$, $C_{40}H_{64}NaO_{13}^+$; calc. 775.4245).

*(3β,5α,11α,12β,14β,17α)-12-(Acetyloxy)-3-{[2,6-dideoxy-4-*O*-(6-deoxy-3-*O*-methyl-β-*D*-allopyranosyl)-3-*O*-methyl-β-*D*-*arabino*-hexopyranosyl]oxy}-20-oxo-8,14-epoxypregnan-11-yl 2-Methylpropanoate* (**3**). Colorless, amorphous solid. IR (KBr): 3433, 2971, 2933, 1736, 1374, 1252. $[\alpha]_D^{25} = +26.3$ ($c =$ 0.23M, MeOH). $^1$H- and $^{13}$C-NMR: see *Table 3*. Key correlations of HMBC and ROESY: see *Fig. 3*. HR-ESI-MS (pos.): 803.4202 ($[M+Na]^+$, $C_{41}H_{64}NaO_{14}^+$; calc. 803.4194).

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