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## THE CHEMICAL CONSTITUENTS OF *MUNRONIA HENRYI*

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Six compounds were isolated from the MeOH extract of the whole bodies of *Munronia henryi*. Their structures were elucidated as sitosterol-3-*O*-12',13'-epoxy-9'-oxo-(10'*E*)-octadecenoate (**1**),  $\alpha$ -D-glucopyranosyl-6'-*O*-hexadecanoate (**2**), 4 $\alpha$ ,7 $\alpha$ -aromodendranediol (**3**), 2 $\beta$ ,3 $\beta$ ,4 $\beta$ -trihydroxypregnan-16-one (**4**), 4-*O*- $\alpha$ -D-psicofuranos- $\alpha$ -D-glucopyranose (**5**), and glyceryl-1-tetracosanoate (**6**) on the basis of spectroscopic methods. Among them **1** was a new sterol carrying an octadecenyl; **2** and **6** were isolated for the first time from a natural source.

**Keywords:** *Munronia henryi*; Meliaceae; Sitosterol-3-*O*-12',13'-epoxy-9'-oxo-(10'*E*)-octadecenoate;  $\alpha$ -D-Glucopyranosyl-6'-*O*-hexadecanoate

### INTRODUCTION

The genus *Munronia* Wight. (Meliaceae), consisting of 13–15 species, is naturally distributed in China, Sri Lanka, India, Indonesia and Filipino. Three species of this genus have been found in Yunnan province [1]. To date, no details of the chemical constituents of this genus have been published. *M. henryi* is a low, small semi-bush, which has been used for the treatment of many diseases such as tuberculosis, cough, stomach ache and sores in Chinese traditional medicine [1]. During the course of searching new compounds from the family Meliaceae [2–4], we undertook the investigation of *M. henryi*. Six compounds were isolated from the MeOH extract of the whole bodies of *M. henryi*. Their structures were elucidated as sitosterol-3-*O*-12',13'-epoxy-9'-oxo-(10'*E*)-octadecenoate (**1**),  $\alpha$ -D-glucopyranosyl-6'-*O*-hexadecanoate (**2**), 4 $\alpha$ ,7 $\alpha$ -aromodendranediol (**3**) [5], 2 $\beta$ ,3 $\beta$ ,4 $\beta$ -trihydroxypregnan-16-one (**4**) [6], 4-*O*- $\alpha$ -D-psicofuranos- $\alpha$ -D-glucopyranose (**5**) [7] and glyceryl-1-tetracosanoate (**6**), on the basis of spectroscopic methods. Compound **1** is a new sterol carrying an octadecenyl, and **2** and **6** were first isolated for the first time from natural sources.

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## RESULTS AND DISCUSSION

Compound **1** was obtained as white powder. It showed in its negative-ion FABMS spectrum a quasi-molecular ion peak at  $m/z$  705  $[M - 1]^-$  in accordance with the formula  $C_{47}H_{78}O_4$ , as determined by HRFABMS, and confirmed from the  $^{13}C$  and DEPT NMR spectra. Its IR spectrum revealed absorption bands for  $-OH$  at  $3442\text{ cm}^{-1}$ ,  $C=C$  at  $1634\text{ cm}^{-1}$  and  $C=O$  at  $1737\text{ cm}^{-1}$ . The  $^1H$  NMR spectrum of **1** showed the following signals: a one-proton doublet at  $\delta_H$  5.34 (1H, d,  $J = 4.1\text{ Hz}$ ), a proton attached to oxymethine at  $\delta_H$  4.59 (1H, m), Me-18 at  $\delta_H$  0.65 (s), Me-19 at  $\delta_H$  0.99 (s), Me-21 at  $\delta_H$  0.78 (3H, d,  $J = 6.5\text{ Hz}$ ), Me-26 at  $\delta_H$  0.84 (d,  $J = 6.6\text{ Hz}$ ), Me-27 at  $\delta_H$  0.80 (d,  $J = 6.6\text{ Hz}$ ) and Me-29 at  $\delta_H$  0.82 (t,  $J = 7.3\text{ Hz}$ ). These are typical signals for sitosterol. The  $^{13}C$  and DEPT NMR spectra showed the existence of 29 skeleton carbons of the aglycone: six methyls, eleven methylenes, eight methines (one of which was oxygenated), two characteristic quaternary carbons at  $\delta_C$  36.6 and 56.6, and two olefinic carbons at  $\delta_C$  122.6 (d) and 139.7 (s). These data, by comparison with the  $^1H$  and  $^{13}C$  NMR spectral data in the literatures [8–10], suggest that **1** possesses a sitosterol skeleton. This was further supported by the EIMS and HMBC spectra. The EIMS spectrum exhibited mass fragments at  $m/z$  414, 396, 381, 303, 273, 255 and 213 while the HMBC spectrum, showing correlations of  $\delta_H$  5.34 (1H, d,  $J = 4.1\text{ Hz}$ , H-6) with  $\delta_C$  31.8 (t, C-7), 39.7 (t, C-4), 36.6 (s, C-10), and  $\delta_H$  1.58, 1.97 (each 1H, m, H-7), 1.83 (2H, m, H-1) with  $\delta_C$  139.7 (s, C-5), indicated a double bond between C-5 and C-6. The correlations of  $\delta_H$  2.29 (2H, m, H-4), 1.83 (2H, m, H-1), 1.85 (2H, m, H-2) with  $\delta_C$  73.7 (d, C-3) in the HMBC spectrum indicated that C-3 was oxygenated. The  $\beta$ -configuration of the ethyl group at C-24 was confirmed by comparison of chemical shifts of carbons and protons of the side chain in  $^{13}C$  and  $^1H$  NMR spectra of **1** with a series of sterols having similar configuration at C-24 ( $\delta_C$  45.8), particularly  $\beta$ -sitosterol, stigmat-4-en-3-one and stigma-4-en-6 $\beta$ -ol-3-one [11]. The negative-ion FABMS spectrum showed two important peaks at  $m/z$  705  $[M - 1]^-$  and 309  $[M - 1 - 414 + H_2O]$ .  $^1H$  and  $^{13}C$  NMR spectra also showed signals for an unsaturated fatty acid: one methyl, eleven methylenes, one oxirane [ $\delta_C$  56.6 (d) and 61.5 (d),  $\delta_H$  3.19 (1H, d,  $J = 6.9\text{ Hz}$ ) and 2.87 (1H, m)], one carboxy group [ $\delta_C$  173.3 (s)], and an  $\alpha,\beta$ -unsaturated ketone at  $\delta_C$  131.2 (d), 142.4 (d), 199.6 (s) with corresponding proton signals at  $\delta_H$  6.37 (1H, d,  $J = 15.9\text{ Hz}$ ) and 6.50 (1H, dd,  $J = 6.9, 15.9\text{ Hz}$ ). These data suggest that the unsaturated fatty acid is an octadecenoic acid with an oxirane and an  $\alpha,\beta$ -unsaturated ketone, by comparison with the  $^1H$  and  $^{13}C$  NMR spectral data of 16-hydroxy-9-oxo-(10*E*,12*Z*,14*E*)-octadecatrienoate (12*S*, 13*S*)-epoxy-(11*R*)-hydroxy-(9*Z*)-octadecenoate and other related compounds in the literatures [12–14]. This is supported by 2D NMR experiments. In the HMBC spectrum, the correlations of  $\delta_H$  4.59 (1H, m, H-3), 2.24 (2H, t,  $J = 7.3\text{ Hz}$ , H-2'), 1.58 (2H, m, H-3') with  $\delta_C$  173.3 (s, C-1'), indicate a fatty acid attached to C-3; The correlations of  $\delta_H$  6.37 (1H, d,  $J = 15.9\text{ Hz}$ , H-10'), 6.50 (1H, dd,  $J = 6.9, 15.9\text{ Hz}$ , H-11'), 2.50 (2H, t,  $J = 7.0\text{ Hz}$ , H-8') with  $\delta_C$  199.6 (s, C-9'), and H-10', H-11' with  $\delta_C$  56.6 (d, C-12'), and  $\delta_H$  3.19 (1H, d,  $J = 6.9\text{ Hz}$ , H-12'), 1.60 (2H, m, H-14') with  $\delta_C$  61.5 (d, C-13') indicate the presence of an 12',13'-epoxy-10'-ene-9'-oxo unit in the octadecenoate, which was further supported by the  $^1H$ - $^1H$  COSY spectrum showing correlations of H-11' with H-10' and H-12'. The coupling constant  $^3J_{H-H}$  (15.9 Hz) indicates that H-10' and H-11' have a *trans*-relationship. H-12' appeared as a double peak in the  $^1H$  NMR spectrum, indicating a small coupling constant between H-12' and H-13'. This showed that the 12',13'-epoxide group has the *trans* configuration (earlier reported values for *cis*- and *trans*-epoxides are  $J = 4.3$  and  $J = 2.1$ – $2.4\text{ Hz}$ , respectively) [15]. The HMBC spectrum also showed other correlations (Fig. 1). Based on these data, the unsaturated fatty acid was

elucidated as 12',13'-epoxy-9'-oxo-(10'*E*)-octadecenoic acid which is the first to be reported.

So, the structure of compound **1** was established as sitosterol-3-*O*-12',13'-epoxy-9'-oxo-(10'*E*)-octadecenoate.

Compound **2** was obtained as white powder. Its negative-ion FABMS gave a quasi-molecular ion peak at  $m/z$  417  $[M - 1]^{-1}$  suggesting the molecular formula of  $C_{22}H_{42}O_7$ , which was confirmed by the NMR spectra. The  $^{13}C$  NMR and DEPT spectra displayed signals for a long chain fatty acid [ $\delta_C$  173.4 (s), 34.0 (t), 31.7 (t), 29.6–29.0 (t), 24.9 (t), 22.6 (t), 13.9 (q)], and a sugar moiety [ $\delta_C$  93.9 (d), 74.9 (d), 74.1 (d), 71.9 (d), 70.5 (d), 64.8 (t)]. The  $^1H$  NMR spectrum showed an anomeric proton signal at  $\delta_H$  5.88 (1H, d,  $J = 3.6$  Hz) which indicated the  $\alpha$ -configuration of the anomeric proton. All these data suggest that **2** is a fatty acid attached to an  $\alpha$ -D-glucopyranosyl. This is supported by the significant fragment peak at  $m/z$  255  $[M - 162 - H]^{-1}$  which also suggests that the fatty acyl is hexadecanacyl. In the HMBC spectrum, the long-range correlation between  $\delta_H$  4.88–4.81 (2H, m, H-6') and  $\delta_C$  173.4(s, C-1) indicates the fatty acyl is linked to C-6' of the glucopyranose. Thus, the structure of **2** was elucidated as  $\alpha$ -D-glucopyranosyl-6'-*O*-hexadecanoate. When **2** was dissolved in pyridine and placed at room temperature for two weeks, the  $\alpha$ -D-glucopyranosyl was changed into  $\beta$ -D-glucopyranosyl in a proportion of one to one. This could be observed in the  $^1H$  and  $^{13}C$  NMR spectra which showed

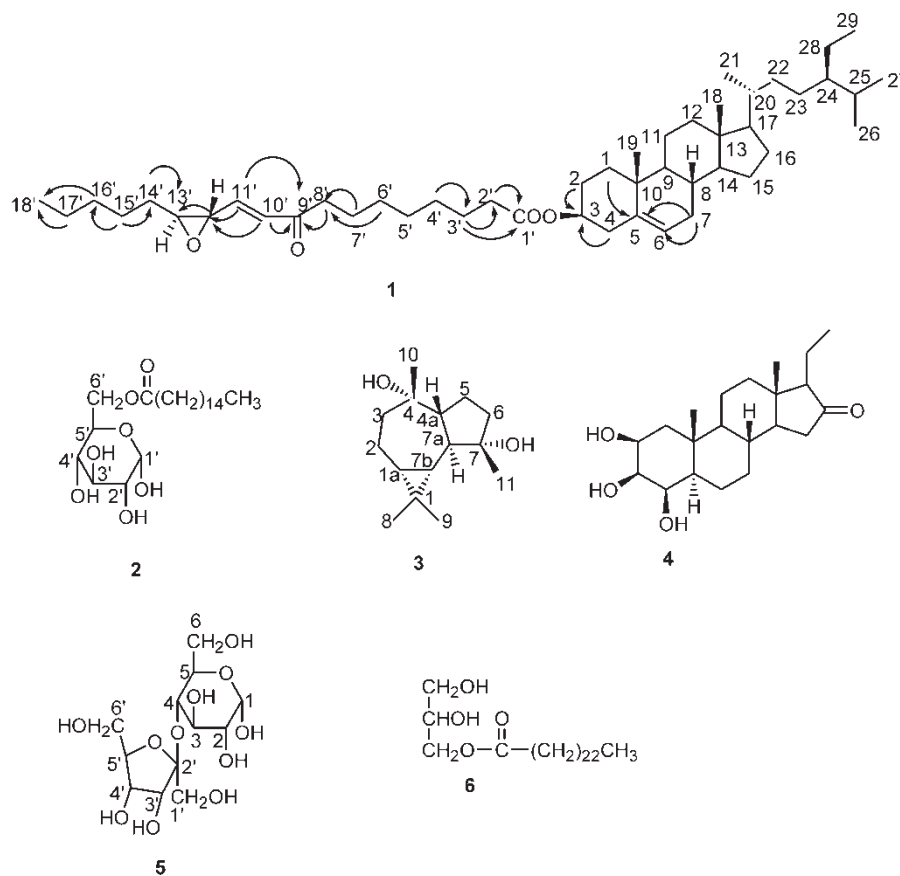


FIGURE 1 Structures of compounds **1**–**6** and selected HMBC correlations of **1**.

the signals for an additional oxymethylene [ $\delta_{\text{C}}$  65.1,  $\delta_{\text{H}}$  5.12 (1H, d,  $J = 11.2$  Hz), 4.90 (1H, m)], four more oxymethines [ $\delta_{\text{C}}$  71.0, 74.9, 77.1, 78.2] and one more anomeric carbon [ $\delta_{\text{C}}$  98.6,  $\delta_{\text{H}}$  5.34 (1H, d,  $J = 8.0$  Hz)] than the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2**. Compound **6** was determined by extensive analysis of its NMR spectra and comparison with other analogous compounds [16].

## EXPERIMENTAL

### General Experimental Procedures

All the mps were obtained on an XRC-1 micromelting apparatus and are uncorrected. Optical rotations were measured with a Horiba SEAP-300 spectropolarimeter. UV spectra were measured with a Shimadzu double-beam 210A spectrophotometer in MeOH solution. IR (KBr) spectra were obtained on a Bio-Rad FTS-135 infrared spectrophotometer.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and 2D NMR spectra were recorded on Bruker AM-400 and a DRX-500 MHz NMR spectrometers with TMS as internal standard. MS spectral data were obtained on a VG Autospec-3000 spectrometer; 70 eV for EI. Silica gel (200–300 mesh) for column chromatography and GF<sub>254</sub> for TLC were obtained from the Qindao Marine Chemical Factory, Qindao, China.

### Plant Material

The whole body of *M. henryi* was collected from Xishuangbanna, Yunnan province, People's Republic of China, in December 2001. It was identified by Professor J.Y. Cui, Xishuangbanna Botany Garden, Academia Sinica. A Voucher specimen (No. 3386) was deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia Sinica, Kunming, China.

### Extraction and Isolation

The air-dried and powdered whole body (4.5 kg) of *M. henryi* was extracted with MeOH three times under reflux, and the solvent was evaporated *in vacuo*. The residue was partitioned in H<sub>2</sub>O and extracted with EtOAc three times. The EtOAc extracts were concentrated *in vacuo* to afford 135 g of residue, which was subjected to column chromatography (CC) on a silica gel column, using CHCl<sub>3</sub>–Me<sub>2</sub>CO (from CHCl<sub>3</sub> to CHCl<sub>3</sub>–Me<sub>2</sub>CO 1:1) as eluent. Upon combining the fractions with TLC (GF<sub>254</sub>) monitoring, eleven fractions were obtained. The first fraction (20 g) was then subjected to CC on silica gel, eluted with light petroleum (petrol)–EtOAc (from 50:1 to 5:1) to give six subfractions (A–F). Fraction E (1.5 g) was subjected to CC on silica gel, eluted with petrol–EtOAc (15:1), to give **1** (5 mg). The third fraction (3.6 g) was repeatedly subjected to CC on silica gel, eluted with petrol–acetone (8:2), then crystallized from MeOH to give **3** (7 mg). The fourth fraction (2.0 g) was repeatedly subjected to CC on silica gel, eluted with CHCl<sub>3</sub>–Me<sub>2</sub>CO (10:1), to give **6** (6 mg). The fifth fraction (15 g) was subjected to CC on silica gel, eluted with CHCl<sub>3</sub>–Me<sub>2</sub>CO (from 7:3 to 2:1), to give four subfractions (A–D). Fraction D (1.6 g) was subjected to CC on silica gel, eluted with CHCl<sub>3</sub>–Me<sub>2</sub>CO (2:1) to give **2** (9 mg). The eighth fraction (4.2 g) was repeatedly subjected to CC on silica gel, repeatedly eluted with CHCl<sub>3</sub>–MeOH (12:1), then crystallized from Me<sub>2</sub>CO to give **4** (13 mg). The ninth fraction (2.6 g) was subjected to CC on silica gel, repeatedly eluted with CHCl<sub>3</sub>–MeOH (8:2), to give **5** (6 mg).

**Sitosterol-3-*O*-12',13'-epoxy-9'-oxo-(10'E)-octadecenoate (1)**

White powder; mp 72–73°C;  $[\alpha]_D^{18.4} - 18.0$  (*c* 0.25, CHCl<sub>3</sub>); UV (MeOH)  $\lambda_{\max}$  (nm): 202, 227; IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3442, 2936, 2865, 1737, 1699, 1634, 1464, 1377, 1179; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.83 (2H, m, H-1), 1.85 (2H, m, H-2), 4.59 (1H, m, H-3), 2.29 (2H, m, H-4), 5.34 (1H, d, *J* = 4.1 Hz, H-6), 1.58, 1.97 (each 1H, m, H-7), 1.20 (1H, m, H-8), 0.93 (1H, m, H-9), 1.44, 1.36 (each 1H, m, H-11), 2.01 (2H, m, H-12), 0.96 (1H, m, H-14), 1.57, 1.05 (each 1H, m, H-15), 1.67, 1.25 (each 1H, m, H-16), 1.08 (1H, m, H-17), 0.65 (3H, s, Me-18), 0.99 (3H, s, Me-19), 1.32 (1H, m, H-20), 0.78 (3H, d, *J* = 6.5 Hz, Me-21), 1.29 (2H, m, H-22), 1.26 (2H, m, H-23), 0.89 (1H, m, H-24), 1.30 (1H, m, H-25), 0.84 (3H, d, *J* = 6.6 Hz, Me-26), 0.80 (3H, d, *J* = 6.6 Hz, Me-27), 1.23 (2H, m, H-28), 0.82 (3H, d, *J* = 7.3 Hz, Me-29), 2.24 (2H, t, *J* = 7.3 Hz, H-2'), 1.58 (2H, m, H-3'), 1.26 (6H, m, H-4', 5', 6'), 1.57 (2H, m, H-7'), 2.50 (2H, t, *J* = 7.0 Hz, H-8'), 6.37 (1H, d, *J* = 15.9 Hz, H-10'), 6.52 (1H, dd, *J* = 15.9, 6.9 Hz, H-11'), 3.19 (1H, d, *J* = 6.9 Hz, H-12'), 2.87 (1H, m, H-13'), 1.60 (2H, m, H-14'), 1.44 (2H, m, H-15'), 1.14 (2H, m, H-16'), 1.28 (2H, m, H-17'), 0.86 (3H, t, *J* = 6.7 Hz, Me-18'); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  36.9 (t, C-1), 28.2 (t, C-2), 73.7 (d, C-3), 39.7 (t, C-4), 139.7 (s, C-5), 122.6 (d, C-6), 31.8 (t, C-7), 31.5 (d, C-8), 50.0 (d, C-9), 36.6 (s, C-10), 21.1 (t, C-11), 29.1 (t, C-12), 42.3 (s, C-13), 56.6 (d, C-14), 24.2 (t, C-15), 38.1 (t, C-16), 56.0 (d, C-17), 11.8 (q, C-18), 19.3 (q, C-19), 36.2 (d, C-20), 18.7 (q, C-21), 34.6 (t, C-22), 27.8 (t, C-23), 45.8 (d, C-24), 29.1 (d, C-25), 19.0 (q, C-26), 19.8 (q, C-27), 23.0 (t, C-28), 11.9 (q, C-29), 173.3 (s, C-1'), 34.6 (t, C-2'), 24.9 (t, C-3'), 28.9 (t, C-4'), 29.0 (t, C-5'), 29.0 (t, C-6'), 23.7 (t, C-7'), 38.8 (t, C-8'), 199.6 (s, C-9'), 131.3 (d, C-10'), 143.7 (d, C-11'), 56.6 (d, C-12'), 61.5 (d, C-13'), 31.8 (t, C-14'), 25.4 (t, C-15'), 26.0 (t, C-16'), 22.4 (t, C-17'), 13.9 (q, C-18'); EIMS *m/z* 414 (25), 396 (80), 381 (21), 303 (4), 273 (10), 255 (11); negative-ion FABMS *m/z* 705 [M – H]<sup>–</sup> (100), 309 [M – H – 414 + H<sub>2</sub>O] (50); HRFABMS *m/z* [M – H]<sup>–</sup> 705.5837 (calcd for C<sub>47</sub>H<sub>77</sub>O<sub>4</sub>, 705.5821).

**α-D-Glucopyranosyl-6'-*O*-hexadecanoate (2)**

C<sub>22</sub>H<sub>42</sub>O<sub>7</sub>; White powder; mp 106–107°C;  $[\alpha]_D^{18.6} + 67.7$  (*c* 0.20, pyridine); IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3437, 2923, 2850, 2362, 2337, 1732, 1634, 1471, 1173; <sup>1</sup>H NMR (Pyri-d<sub>5</sub>, 400 MHz)  $\delta$  0.83 (3H, t, *J* = 6.8 Hz, Me-16), 1.22 (24H, brs, H-4 to H-15), 1.58 (2H, m, H-3), 2.31 (2H, t, *J* = 7.5 Hz, H-2), 5.87 (1H, d, *J* = 3.6 Hz, H-1'), 4.22 (1H, dd, *J* = 3.6, 9.3 Hz, H-2'), 4.13 (1H, dd, *J* = 9.3, 8.8 Hz, H-3'), 4.75 (1H, t, *J* = 7.2 Hz, H-5'), 4.92 (1H, m, H-4'), 4.88–4.81 (2H, m, H-6'); <sup>13</sup>C NMR (Pyri-d<sub>5</sub>, 100 MHz)  $\delta$  173.4 (s, C-1), 34.0 (t, C-2), 24.9 (t, C-3), 29.6–29.0 (t, C-4 to 13), 22.5 (t, C-14), 31.7 (t, C-15), 13.9 (q, C-16), 93.9 (d, C-1'), 74.1 (d, C-2'), 74.9 (d, C-3'), 70.5 (d, C-4'), 71.9 (t, C-5'), 64.8 (t, C-6'); FABMS *m/z* 417 [M – H]<sup>–</sup> (60), 255 [M – 162 – H]<sup>–</sup> (100).

**4α,7α-Aromodendranediol (3)**

C<sub>15</sub>H<sub>26</sub>O<sub>2</sub>; white needle crystals (MeOH); mp 135–136°C; IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3394, 2980, 2949, 2925, 2866, 1456, 1379, 1299, 1247, 1110, 1085, 987; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  1.55–1.95 (m, CH<sub>2</sub> and CH), 1.25 (3H, s, CH<sub>3</sub>), 1.17 (3H, s, CH<sub>3</sub>), 1.04 (6H, s, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  19.6 (s, C-1), 28.3 (d, C-1a), 20.2 (t, C-2), 44.5 (t, C-3), 75.0 (s, C-4), 56.4 (d, C-4a), 23.8 (t, C-5), 41.2 (t, C-6), 80.1 (s, C-7), 48.5 (d, C-7a), 26.6 (d, C-7b), 28.6 (q, C-8), 16.4 (q, C-9), 20.3 (q, C-10), 24.5 (q, C-11); EIMS *m/z* 238 [M]<sup>+</sup> (42), 220 (45), 205 (41), 187 (17), 177 (35), 162 (90), 149 (65), 134 (30), 121 (54), 107 (55), 93 (66), 83 (72), 69 (70), 55 (100).



**2 $\beta$ ,3 $\beta$ ,4 $\beta$ -Trihydroxypregnan-16-one (4)**

White crystal (Me<sub>2</sub>CO); mp 228–230°C; IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3355, 2924, 2843, 1737, 1444, 1298, 1159, 1146, 1097, 960, 911, 801; <sup>1</sup>H NMR (Pyri-d<sub>5</sub>, 400 MHz)  $\delta$  4.56 (1H, d,  $J$  = 2.2 Hz, H-2), 4.19 (1H, brs, H-4), 3.86 (1H, t,  $J$  = 3.5 Hz, H-3), 2.34 (1H, dd,  $J$  = 14.0, 3.1 Hz, H-1a), 1.22 (1H, m, H-1b), 2.16 (1H, m, H-15a), 1.46 (1H, m, H-15b), 1.73 (2H, m, H-12), 1.70 (2H, m, H-6), 1.63 (1H, m, H-17), 1.60 (3H, s, Me-19), 1.62, 0.95 (each 1H, m, H-7), 1.47 (1H, m, H-8), 1.35 (3H, m, H-11, 14), 1.22 (2H, m, H-20), 1.18 (1H, m, H-5), 1.04 (3H, t,  $J$  = 7.4 Hz, Me-21), 0.72 (1H, m, H-9), 0.58 (3H, s, Me-18); <sup>13</sup>C NMR (Pyri-d<sub>5</sub>, 100 MHz)  $\delta$  218.4 (s, C-16), 77.3 (d, C-4), 72.9 (d, C-2), 72.8 (d, C-3), 65.3 (d, C-17), 56.9 (d, C-9), 50.7 (d, C-14), 50.3 (d, C-5), 44.6 (t, C-1), 42.3 (s, C-13), 38.6 (t, C-6), 38.3 (t, C-12), 35.8 (s, C-10), 34.2 (d, C-8), 32.8 (t, C-7), 26.6 (t, C-15), 20.5 (t, C-11), 18.1 (t, C-20), 17.5 (q, C-19), 13.7 (q, C-21), 13.6 (q, C-18); EIMS  $m/z$  350 [M]<sup>+</sup> (23), 332 (60), 314 (18), 288 (35), 275 (18), 264 (21), 246 (35), 229 (917), 191 (8), 161 (13), 149 (28), 135 (15), 121 (24), 107 (25), 95 (37), 81 (15), 69 (67), 55 (100).

**4-*O*- $\alpha$ -D-Psicofuranose- $\alpha$ -D-glucopyranose (5)**

<sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$  5.23 (1H, d,  $J$  = 3.8 Hz, H-1), 4.04 (1H, t,  $J$  = 8.8 Hz, H-4), 3.49 (2H, s, H-1'), 3.39 (1H, dd,  $J$  = 3.8, 9.8 Hz, H-2), 3.28 (1H, t,  $J$  = 9.4 Hz, H-3), 3.84–3.64 (8H, m, H-5, 6, 3', 4', 5', 6'); <sup>13</sup>C NMR (D<sub>2</sub>O, 100 MHz)  $\delta$  64.0 (t, C-1'), 106.3 (s, C-2'), 75.2 (d, C-3'), 71.9 (d, C-4'), 84.0 (d, C-5'), 62.8 (t, C-6'), 94.8 (d, C-1), 73.7 (d, C-2), 75.0 (d, C-3), 79.1 (d, C-4), 76.6 (d, C-5), 65.0 (t, C-6); FABMS  $m/z$  341 [M – H]<sup>–</sup>.

**Glyceryl-1-docosoicate (6)**

C<sub>27</sub>H<sub>54</sub>O<sub>4</sub>; colorless wax; mp 66–67°C; <sup>1</sup>H NMR (Pyri-d<sub>5</sub>, 400 MHz)  $\delta$  0.88 (3H, t,  $J$  = 6.8 Hz, Me-24'), 1.27 (38H, m, H-4'-23'), 1.64 (2H, m, H-3'), 2.35 (2H, t,  $J$  = 7.5 Hz, H-2'), 4.70 (2H, m, H-1), 4.41 (1H, m, H-2), 4.08 (2H, d,  $J$  = 5.3 Hz, H-3); <sup>13</sup>C NMR (Pyri-d<sub>5</sub>, 100 MHz)  $\delta$  14.5 (q, C-24'), 23.1 (t, C-22'), 25.4 (t, C-3'), 29.5–29.9 (t, C-4'-21'), 32.3 (t, C-23'), 34.6 (t, C-2'), 64.4 (t, C-3), 66.9 (t, C-2), 71.0 (d, C-1), 174.0 (s, C-1'); EIMS  $m/z$  442 [M]<sup>+</sup> (1), 425 (2), 411 (5), 397 (4), 382 (7), 368 (13), 134 (45), 112 (49), 97 (67), 57 (100).

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**References**

- [1] Yunnan Institute of Botany (1977), *Flora Yunnanica Tomus I* (Science Press, Beijing), pp. 214–216.
- [2] Luo, X.D., Wu, S.H., Wu, D.G., Ma, Y.B. and Qi, S.H. (2002), *Tetrahedron* **58**, 7797–7804.
- [3] Luo, X.D., Wu, S.H., Wu, D.G., Ma, Y.B. and Qi, S.H. (2002), *Tetrahedron* **58**, 6691–6695.
- [4] Luo, X.D., Ma, Y.B., Wu, S.H. and Wu, D.G. (2000), *J. Nat. Prod.* **63**, 947–951.
- [5] Beechan, C.M., Djerassi, C. and Eggert, H. (1978), *Tetrahedron* **34**, 2503.
- [6] Ketwaru, P., Klass, J.T.W.F., Mclean, S. and Reynolds, W.F. (1993), *J. Nat. Prod.* **56**, 430–431.
- [7] Zhang, G.L., Zhou, Z.Z. and Li, P.G. (1997), *Nat. Prod. Res. Dev.* **9**(4), 10–12.
- [8] Gupta, S., Ali, M., Alam, M.S., Niwa, M. and Sakai, T. (1992), *Phytochemistry* **31**(7), 2558–2560.
- [9] Geng, P.W., Yoshiyasu, F., Wang, R., Bao, J. and Kazuyuki, N. (1988), *Phytochemistry* **27**(6), 1895–1896.

- [10] Adolfo, M.I. and Alicia, B.P. (1984), *Phytochemistry* **23**(9), 2087–2088.
- [11] Greca, M.D., Manaco, P. and Previtera, L. (1990), *J. Nat. Prod.* **53**, 1430.
- [12] Bernart, M.W., Whatley, G.G. and Gerwick, W.H. (1993), *J. Nat. Prod.* **56**, 245–259.
- [13] Hamberg, M., Herman, R.P. and Jacobsson, U. (1986), *Biochim. Biophys. Acta* **879**, 410–418.
- [14] Dix, T.A. and Marnett, L.J. (1985), *J. Biol. Chem.* **260**(9), 5351–5357.
- [15] Pierre, J.-L., Chautemps, P. and Arnaud, P. (1968), *Chim. Anal.* **50**, 494–500.
- [16] Yang, H., Jiang, B., Hou, A.J., Lin, Z.W. and Sun, H.D. (2000), *J. Asian Nat. Prod. Res.* **2**, 177–185.