

# Two Triterpenoids from *Euphorbia Prolifera* 小狼毒中的两个三萜化合物

Liu Shaohua      Cheng Juying      Wu Dagang  
刘绍华            程菊英\*            吴大刚\*\*

(Pharmacy Department of Guilin Medical College, 8 Pingfenglu, Guilin, Guangxi, 541004)  
(桂林医学院药理学系 桂林市屏风路 8号 541004)

**摘要** 报道从小狼毒植物根部分离出两个新三萜化合物, 分别命名为 Euphorbin A 和 Euphorbin B, 经  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR 和 MS 光谱鉴定, 它们的结构分别是 23-亚甲基-羊毛甾-5(6)-烯醇和 23-亚甲基-24-去甲基-羊毛甾-8(9)-烯醇。

**关键词** 小狼毒 三萜 23-亚甲基-羊毛甾-5(6)-烯醇; 23-亚甲基-24-去甲基-羊毛甾-8(9)-烯醇 结构 小狼毒素

**Abstract** Two new triterpenoids named Euphorbin A and Euphorbin B were isolated from the roots of *Euphorbia prolifera* Buch. - Ham. Their structures were elucidated as 23-methylene-Lanost-5(6)-enol and 23-methylene-24-nor-Lanost-8(9)-enol respectively by spectroscopic methods.

**Key words** *Euphorbia prolifera*, triterpenoid, 23-methylene-Lanost-5(6)-enol, 23-methylene-24-nor-Lanost-8(9)-enol, structure, euphorbin

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The medicinal plants of *Euphorbia prolifera* Buch. - Ham. have been used as the traditional Chinese medicine for the treatment of tumors and edema in Yunnan province, South western China. We collected the roots of *E. prolifera* in Yunnan province and extracted two new triterpenoids, named Euphorbin A (compound 1) and Euphorbin B (compound 2), here are the reports of their isolation and structures.

## 1 Materials and Methods

### 1.1 Plant material

Individuals of *E. prolifera* Buch. - Ham. were collected in Oct. 1994 in Dali county, Yunnan province of southwestern China. The specimen had been deposited in Kunming Institute of Botany, Academia Sinica, Kunming, China.

### 1.2 Apparatus

M. P. S were determined on a MICRO melting point apparatus and corrected. IR spectra were measured in KBr discs on Perkin-Elmer 577 spectrometer. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-400 spectrometer in CDCl<sub>3</sub> with TMS as internal standard, chemical shifts were reported in  $\delta(10^6)$  units. MS was measured in a Finnigan-4510 instrument.

### 1.3 Extracting

2.0 kg roots of *E. prolifera* were pulverized and then extracted with EtOH at room temperature for 2 weeks. The ethanolic extract was concentrated in vacuo into 710 g of the brown residue, in which 700 g was resolved in 2000 mL of water and extracted with petroleum ether (60°~90°). The petroleum ether was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated into 18 g of residue which was subjected to column chromatograph on silica gel, and successively eluted with EtOH-petrol (1:9), (2:8) yielding compound 1 and compound 2, and then further purified by crystallization in methanol affording 200 mg, 100 mg respectively.

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\* 广西植物研究所, 桂林雁山, 541006 (Guangxi Institute of Botany, Yanshan, Guilin, Guangxi, 541006);

\*\* 中国科学院昆明植物研究所 植物化学开放实验室, 昆明, 650204.  
(Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, Yunnan, 650204)

## 2 Results

Euphorbin A (compound 1):

Colourless needles, m. p. 87°C~ 88°C

(methanol); molecular formula C<sub>31</sub>H<sub>50</sub>O; IR<sub>max</sub><sup>KBr</sup> cm<sup>-1</sup> 3370, 3360, (-OH), 3060, 1630, 885 (C=C<sub>alk</sub>), 3030, 850, 810 (C=C<sub>ar</sub>), 1450, 1370, 1095, 1020.

EIMS m/z (%) 440 (M<sup>+</sup>, 5), 422 (9), 408 (14), 393 (15), 383 (4), 365 (5), 357 (5), 315 (2), 300 (5), 286 (10), 243 (20), 217 (40), 187 (50), 166 (10), 149 (12), 148 (10), 139 (15), 121 (18), 107 (22), 95 (50), 41 (82).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.83 (3H, s,  $\beta$ -Me), 0.99 (3H, s,  $\alpha$ -Me), 0.66 (3H, s, Me-13), 0.75 (3H, s, Me-14), 1.04 (6H, d, J = 5.5 Hz, Me-26, 27), 1.06 (3H, s,  $\beta$ -Me), 1.30~1.50 (1H, m, -OH), 3.28 (1H, m,  $\alpha$ -H), 4.67, 4.74 (2H, br. s, C=C<sub>alk</sub>), 5.11 (1H, m, C=C<sub>ar</sub>).

<sup>13</sup>C NMR and DEPT spectrum data see Table 1.

Euphorbin B (compound 2):

Colourless needles, m. p. 113°C~ 115°C

(methanol), molecular formula C<sub>30</sub>H<sub>50</sub>O; IR<sub>max</sub><sup>KBr</sup> cm<sup>-1</sup> 3340 (-OH), 3060, 1630, 885 (C=C<sub>alk</sub>), 2940, 2860, 1446, 1365, 1018. EIMS m/z (%) 426 (M<sup>+</sup>, 32), 411 (65), 408 (53), 383 (4), 357 (5), 315 (5), 300 (15), 285 (8), 274 (4), 256 (6), 239 (12), 201 (6), 189 (10), 175 (12), 161 (15), 147 (15), 133 (20), 121 (21), 107 (28), 95 (58), 81 (30), 69 (100), 55 (85), 41 (82).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.85 (3H, s, Me- $\beta$ ), 0.95 (3H, s, Me- $\alpha$ ), 0.68 (3H, s, Me-13), 0.79 (3H, s, Me-14), 1.06 (3H, s, Me-1 $\beta$ ), 1.10 (6H, d, J = 5.0 Hz, Me-26, 27), 1.30~1.50 (1H, m, -OH), 3.23 (1H, m,  $\alpha$ -H), 4.66, 4.74 (2H, br. s, C=C<sub>alk</sub>).

<sup>13</sup>C NMR and DEPT spectrum data see Table 1.

## 3 Discussion

The ethanolic extract from *E. prolifera* was partitioned between petrol and water. The petrol extract on silica gel was chromatographed into euphorbin A (compound 1) and euphorbin B (compound 2).

Table 1 <sup>13</sup>C NMR chemical shift of compounds 1, 2 ( $\delta$ , CDCl<sub>3</sub>, TMS as internal standard)

carbon	compound 1	compound 2
1	35.6	35.5
2	27.0	26.9
3	79.0	79.3
4	42.5	38.9
5	145.9	50.9
6	117.8	18.5
7	28.9	28.1
8	35.1	134.7
9	36.3	134.5
10	37.4	36.4
11	18.2	21.0
12	28.4	28.3
13	44.0	44.7
14	50.4	50.1
15	31.0	30.9
16	29.7	29.7
17	50.5	50.5
18	15.9	15.8
19	19.0	19.0
20	36.7	36.7
21	18.5	18.5
22	36.0	36.0
23	157.2	157.2
24	30.8	-
25	33.9	34.0
26	21.8	21.9
27	22.1	22.1
28	24.5	24.5
29	28.4	28.1
30	15.8	15.5
31	106.0	106.0

### Euphorbin A

The IR spectrum indicated the presence of trisubstituted double bond at 3030 cm<sup>-1</sup>, 850 cm<sup>-1</sup>, 810 cm<sup>-1</sup>, vinylidene group at 3060 cm<sup>-1</sup>, 1630 cm<sup>-1</sup>, 880 cm<sup>-1</sup><sup>[1]</sup>, and a hydroxy group at 3370 cm<sup>-1</sup> and 3360 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum displayed a multiplet at 3.28 ppm for a proton attached to C-3 and the signal at  $\delta$  1.30 ppm~ 1.50 ppm indicated the proton of the hydroxy group at C-3<sup>[1,31]</sup>, the signals at 4.67, 4.72 (br. s) for two protons of the terminal double bond<sup>[2]</sup>, the signal at 5.11 ppm for the proton in a trisubstituted double bond (C=C<sub>alk</sub>)<sup>[1]</sup>. The signal at 145.9 ppm, 117.8 ppm, 157.2 ppm and 106.0 ppm in <sup>13</sup>C NMR and DEPT spe

ctrum are characteristic of double bonds, one of them is a terminal double bond (157.2 ppm, 106.0 ppm), other is trisubstituted double bond (145.9 ppm, 117.8 ppm).

In the MS spectrum, peaks appearing at 383 ( $M^+$ , - C<sub>6</sub>H<sub>8</sub>), 357 ( $M^+$ , - C<sub>6</sub>H<sub>10</sub>) indicated the terminal double bond was located at C-23<sup>[1]</sup>. The typical retro-Diels-Alder fragmentation of ring B in compound 1 produced fragments at 166, 148, 149

(Fig. 1). The mass spectral fragmentation confirmed that the trisubstituted double bond was located at  $\Delta^{5(6)}$ . Consequently, the structure of compound 1 should be 23-methylene-Lanost-5(6)-enol.

#### Euphorbin B

The appearance of strong absorption at 3340  $cm^{-1}$  and 3060  $cm^{-1}$ , 1630  $cm^{-1}$ , 880  $cm^{-1}$  in IR spectrum showed a hydroxy group (-OH) and a vinylidene group (C=C<sub>2</sub>H<sub>5</sub>)<sup>[1]</sup>. In the <sup>1</sup>H NMR spectrum, the signal at 1.30 ppm~ 1.50 ppm indicated a proton of the hydroxy group at C-3, the multiplet at  $\delta$  3.23 ppm was characteristic of the proton at C-3<sup>[1,3]</sup>, the signal at 4.67 ppm (br. s) and 4.72 ppm (br. s) for two protons of vinylidene group (C=C<sub>2</sub>H<sub>5</sub>)<sup>[2]</sup>. The <sup>13</sup>C NMR and DEPT spectrum appearing at  $\delta$  134.7 ppm, 134.5 ppm and 157.2 ppm, 106.0 ppm for the carbons of two double bonds, one of them was vinylidene (157.2 ppm, 106.0 ppm)<sup>[2]</sup>. In the MS spectrum the peaks appearing at 357 ( $M^+$ , - C<sub>6</sub>H<sub>8</sub>), 383 ( $M^+$ , - C<sub>6</sub>H<sub>8</sub>) indicated that the vinylidene group was located at C-23, there evidence that compound 2 has its unsaturated centres at  $\Delta^{8(9)}$ , as shown by the species in the following scheme<sup>[1]</sup>.

Thus compound 2 should be as identified as 23-methylene-24-nor-Lanost-8(9)-enol.

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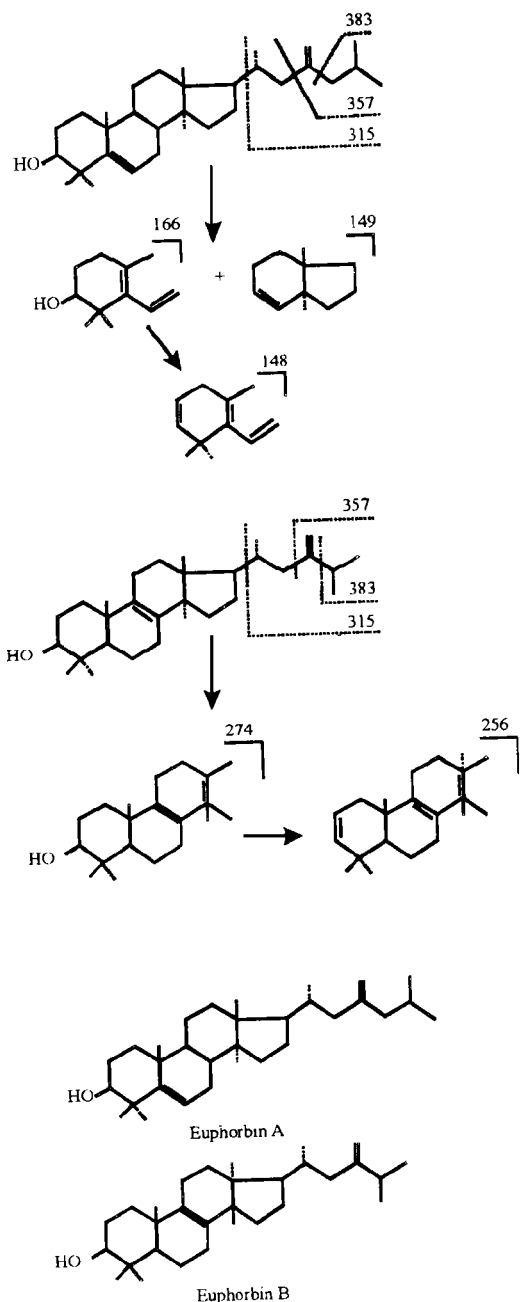


Fig. 1