

## NOTE

## A New Macrocyclic Diterpene Derived from the Seed of Euphorbia lathyris

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A new macrocyclic diterpene, along with two known macrocyclic diterpenes, was isolated from the seed of *Euphorbia lathyris* L. The new macrocyclic diterpene, designated as *Euphorbia lathyris* A (1), the structure was elucidated on the basis of the spectroscopic data interpretation. In addition, two known macrocyclic diterpenes were also isolated and identified as *Euphorbia* Factor  $L_1$  (2) and *Euphorbia* Factor  $L_2$  (3).

Key Words: Euphorbia lathyris, Euphorbia lathyris A, Spectroscopic methods.

*Euphorbia lathyris* L. has received worldwide attention as a renewable source of industrial raw materials (hydrocarbons and oleic acid) and mass cultivation has been attempted in western Europe and the United States<sup>1</sup>. Owning to therapeutic effect of the plant on the clinic including wart, scabies, hydropsy, boils *etc.*<sup>2</sup>, the seed of *Euphorbia lathyris* L. has been received a large amount of attentions<sup>3-5</sup>.

Present investigation on the seed of *Euphorbia lathyris* L. led to a new macrocyclic diterpene, designated as *Euphorbia lathyris* A (1), together with two additional known macrocyclic diterpene, designated as *Euphorbia Factor* L<sub>1</sub> (2)<sup>5,6</sup> and *Euphorbia* Factor L<sub>2</sub> (3)<sup>5,6</sup>. These known compounds were identified by comparing of the respective spectroscopic data with those reported in the literature. We described herein the separation and structure elucidation of the new macrocyclic diterpene.

*Euphorbia lathyris* L. was collected in Chengdu Chinese herbal medicine market, Sichuan province of China in April 2007 and authenticated by Plant Systematics and Molecular Evolution lab of Sichuan University. A voucher specimen was deposited at Leshan Normal University.

Optical rotations were measured using a Perkin-Elmer model 241 polarimeter. <sup>1</sup>D and <sup>2</sup>D NMR spectra were measured by a Bruker DRX-400 instrument with TMS as internal standard. Mass spectra were obtained by a VG Auto Spec-3000 spectrometer or on a Finnigan MAT 90 instrument. Column chromatography was performed on silica gel (200-300 mesh; Qingdao Marine Chemical Inc.).

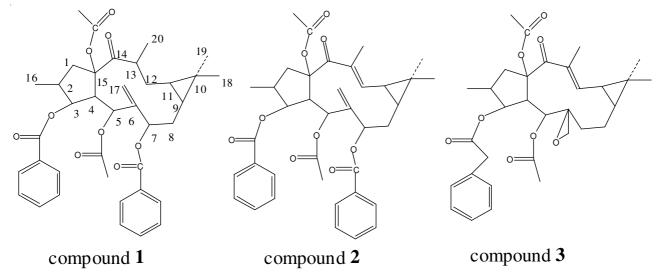
**Extraction and isolation:** Dry seed of *Euphorbia lathyris* L. (5.0 kg) were extracted with ethanol  $(3 \times 7 \text{ L})$  at room

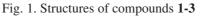
temperature overnight. The extract was suspended in water (2000 mL) to form a suspension and then partitioned with petroleum ether and EtOAc successively to afford petroleum ether extract (980 g) and EtOAc extract (160 g), respectively. The EtOAc extract was chromatographed on a silica gel column employing cyclohexane-acetone ( $10:1 \rightarrow 2:1$ ) as eluent to provided compound **1** (8 mg), compound **2** (61 mg) and compound **3** (73 mg).

Thin-layer chromatography was carried out on silica gel  $60 \text{ F}_{254}$  on glass plates (Qingdao Marine Chemical Inc.) using various solvent systems.

*Euphorbia lathyris* A (1, Fig. 1), amorphous power; m.p. 196-198 °C.  $[\alpha]^{20}_{D}$  103 (*c* 1.0,CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr, v<sub>max</sub>, cm<sup>-1</sup>) 1740, 1712, 1648, 1662 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) data (Table-1); ESIMS *m/z* 645 [M+H]<sup>+</sup>; HRESIMS *m/z* 645.2967 [M+H]<sup>+</sup> (calcd. for C<sub>38</sub>H<sub>44</sub>O<sub>9</sub>, 644.2985).

The HRESIMS at m/z 645.2967 corresponded to the protonated molecular ion  $[M + H]^+$  (C<sub>38</sub>H<sub>44</sub>O<sub>9</sub>). The NMR spectra of **1** showed that the presence of four methyl groups ( $\delta_{\rm H}$  1.21, 1.25, each 3H, s;  $\delta_{\rm H}$  0.96, 1.09, each 3H, d, J = 6.8 Hz), two acetyl groups ( $\delta_{\rm H}$  2.12, 2.25, each 3H), two benzoyl groups ( $\delta_{\rm H}$  7.37-7.96, 10H, m) (Table-1), an exocyclic double bond [ $\delta_{\rm H}$  5.76, 5.75, each 1H, s;  $\delta_{\rm C}$  140.7 (s), 120.6 (t)]. In addition, the close resemblance of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of *Euphorbia* Factor (L<sub>2</sub>) (**3**)<sup>4</sup> and **1** except for absence of an double bond, which suggest that compound **1** is very similar to the *Euphorbia* Factor (L<sub>2</sub>) except for absence of an double bond. The difference of **2** mass units in their molecular weights





also supports the above-mentioned difference. Consequently, the group assignments were achieved from the HMBC for **1** (Fig. 2). Therefore, the structure of compound **1** was assigned as *Euphorbia lathyris* A.

TABLE-1		
<sup>1</sup> H NMR AND <sup>13</sup> C NMR DATA OF COMPOUND		
<b>1</b> (CDCl <sub>3</sub> ), $\delta$ IN ppm, <i>J</i> IN Hz		
Position	δ <sub>H</sub>	δ <sub>c</sub>
1	3.30 (1H, m),1.64 (1H, m)	44.3
2	2.30 (1H, m)	37.8
3	5.81 (1H, m)	78.4
4	2.90 (1H, m)	51.1
5	6.09(1H, d, <i>J</i> =8.8)	71.0
6	-	147.0
7	5.58 (1H, dd, J=8.8, 4.0)	78.4
8	2.34 (1H, m) 2.18 (1H, m)	29.6
9	1.30 (1H, m)	30.3
10	-	25.6
11	1.46 (1H, m)	28.7
12	1.50 (1H, m), 1.88 (1H, m)	38.3
13	1.90 (1H, m)	37.8
14	-	211.1
15	-	91.8
16	0.96 (3H, d, <i>J</i> =6.8)	13.2
17	5.76 (1H, m), 5.75 (1H, s)	120.6
18	1.21 (3H, s)	28.7
19	1.25 (3H, s)	15.2
20	1.09 (3H, s)	19.2
5-OAc: $\delta_{C}$ 169.0, 20.8; $\delta_{H}$ 2.25 (3H, s);		

15-OAc:  $\delta_{\rm C}$  169.7, 21.5;  $\delta_{\rm H}$  2.25 (3H, s); 3-OBz:  $\delta_{\rm C}$  165.7, 130.3, 129.6, 129.6, 128.3, 128.3, 133.0; 7-OBz:  $\delta_{\rm C}$  165.0, 130.0, 129.6, 129.6, 128.3, 128.3, 132.9; 3-OBz and 7-OBz:  $\delta_{\rm H}$ 7.37-7.96 (m, 10H)

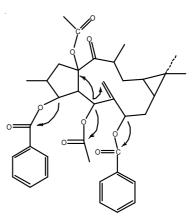


Fig. 2. Key HMBC ( $\frown$ ) correlations of compound 1

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## REFERENCES

- 1. M. Moresi, Chim. Ind., 78, 43 (1996).
- Nanjing University of Chinese Medicine: Dictionary of Chinese Traditional Drugs. Shanghai Scientific and Technical Publishers, Shanghai, p. 287 (2006).
- 3. G. Appendino, C.D. Porta and G. Conseil, J. Nat. Prod., 66, 140 (2003).
- 4. G. Appendino, G.C. Tron and T. Sterner, Org. Lett., 3, 1609 (2001).
- 5. H. Itokawa, Y. Yoshitatsu and M. Yahagi, *Phytochemistry*, **29**, 2025 (1990).
- 6. G. Appendino and G.C. Tron, J. Nat. Prod., 62, 76 (1999).