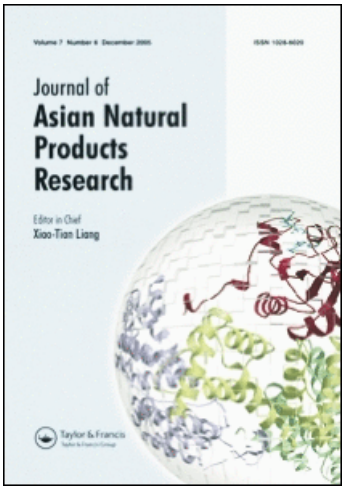


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*Note*

# A new bisabolane sesquiterpenoid from *Euphorbia chrysocoma*

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The new sesquiterpenoid (6*R*)-2-chloro-6-[(1*S*)-1,5-dimethylhex-4-en-1-yl]-3-methylcyclohex-2-en-1-one (**1**), together with ten known compounds, (6*R*)-6-[(1*S*)-1,5-dimethylhex-4-en-1-yl]-3-methylcyclohex-2-en-1-one (**2**), bauerenol acetate (**3**), lupenone (**4**), α-amyrenone (**5**), β-sitosterol (**6**), stigmasterol (**7**), β-amyrin (**8**), ursolic acid (**9**), betulinic acid (**10**), scopolin (**11**), have been isolated from the roots of *Euphorbia chrysocoma* Lévl. et Vant. Their structures have been elucidated by spectroscopic data.

*Keywords*: *Euphorbia chrysocoma* Lévl. et Vant.; Euphorbiaceae; Bisabolane sesquiterpenoid

## 1. Introduction

The roots of *Euphorbia chrysocoma* Lévl. et Vant. (Euphorbiaceae) have been used in folk medicine to treat edema and scabies [1]. To our knowledge, no phytochemical investigation on the roots of this plant has been reported. We have investigated the roots of *Euphorbia chrysocoma* and isolated one new sesquiterpenoid, (6*R*)-2-chloro-6-[(1*S*)-1,5-dimethylhex-4-en-1-yl]-3-methylcyclohex-2-en-1-one (**1**), along with (6*R*)-6-[(1*S*)-1,5-dimethylhex-4-en-1-yl]-3-methylcyclohex-2-en-1-one (**2**) [2], bauerenol acetate (**3**) [3], lupenone (**4**) [4], α-amyrenone (**5**) [5], β-sitosterol (**6**) [6], stigmasterol (**7**) [7], β-amyrin (**8**) [8], ursolic acid (**9**) [9], betulinic acid (**10**) [10], scopolin (**11**) [11]. Compounds **2**–**11** were obtained from this plant for the first time. We report here the isolation and structural elucidation of these compounds.

## 2. Results and discussion

Compound **1** was obtained as a colorless oil. Its CIMS gave a molecular ion peak at *m*/*z* 255.1 $[M + H]^+$, accompanied by an isotopic peak at *m*/*z* 257.1, in a ratio of near 3:1,

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Table 1. $^{1}H$ (500 MHz) and $^{13}C$ (125 MHz) NMR data for compound **1** ($CDCl_3$, $\delta$) and $^{13}C$ NMR (125 MHz) data for compound **2** ($CDCl_3$, $\delta$).

| | ***1*** | | | | ***2*** |
|---|---|---|---|---|---|
| *Position* | $\delta_H$ ($J = Hz$) | $\delta_C$ | *HMBC* | *NOESY* | $\delta_C$ |
| 1 | | 192.4 (s) | | | 200.9 (s) |
| 2 | | 129.4 (s) | | | 127.0 (d) |
| 3 | | 155.0 (s) | | | 161.0 (s) |
| 4 | 2.52 (m) | 32.7 (t) | C-2,3,1,5 | H-5β,5α,7′ | 30.9 (t) |
| 5α | 1.81 (m) | 21.7 (t) | C-1′,4 | H-8′ | 22.4 (t) |
| 5β | 1.93 (m) | | C-4 | H-6 | |
| 6 | 2.34 (m) | 51.0 (d) | C-4,5,1′,8′,1 | H-5β | 49.8 (d) |
| 7 | 2.11 (s) | 22.3 (q) | C-2,3,4 | | 24.1 (q) |
| 1′ | 2.32 (m) | 30.9 (d) | C-2′,3′,1 | H-2′,8′ | 30.3 (d) |
| 2′ | 1.29 (dd, 7.6, 7.6) | 34.6 (t) | C-4′,1′,3′,8′ | H-1′,3′,8′ | 34.7 (t) |
| 3′ | 2.01 (m), 1.98 (m) | 25.9 (t) | C-4′,5′,1′,2′ | H-2′,8′ | 26.0 (t) |
| 4′ | 5.10 (tt, 7.2, 1.3) | 124.1 (d) | C-2′,7′,6′ | H-2′,3′,6′ | 124.4 (d) |
| 5′ | | 131.4 (s) | | | 131.2 (s) |
| 6′ | 1.68 (s) | 25.7 (q) | C-4′,5′,7′ | | 25.7 (q) |
| 7′ | 1.60 (s) | 17.7 (q) | C-4′,5′,6′ | | 17.7 (q) |
| 8′ | 0.82 (d, 6.4) | 15.6 (q) | C-1′,2′ | H-2′,1′,5α | 15.6 (q) |



suggesting the presence of a chlorine atom. Its molecular formula $C_{15}H_{23}OCl$ was determined by HR-ESIMS and $^{13}C$ NMR data. The IR spectrum shows absorption bands for α,β-unsaturated carbonyl (1684 $cm^{-1}$) and a double bond (1616 $cm^{-1}$). The $^{1}H$ NMR (Table 1) spectrum of **1** displays signals for three quaternary methyl groups ($\delta$ 1.60, s; 1.68, s; 2.11, s) and a secondary methyl group ($\delta$ 0.82, d, $J = 6.4$ Hz). The $^{13}C$ NMR spectrum of **1** shows 15 carbon signals belonging to four methyls, four methylenes, three methines, and four quaternary carbons. Comparison of the $^{1}H$ and $^{13}C$ NMR data of **1** with those of **2** [2] suggest that compound **1** is very similar to **2** except that an olefinic proton signal is absent and one methine has been replaced by a quaternary carbon. In addition, compared with the analogous carbon signals for **2** (table 1), C-1 and C-3 in **1** are shifted upfield 8.5 and 6.0 ppm, while C-2 is shifted downfield 2.4 ppm, respectively. All the above evidences indicate that these differences are caused by the chlorine instead of hydrogen on C-2 in compound **1**, which is further supported by **1** having 34 mass units more than **2** ($C_{15}H_{24}O$, MW = 220).

In the HMBC spectrum of **1**, $^{13}C-^{1}H$ long-range correlation signals occur for $CH_3$-7 with C-2, C-3 and C-4; H-6 with C-4, C-5,C-1′, C-8′ and C-1; H-1′ with C-2′, C-3′ and C-1; H-4′ with C-2′, C-6′ and C-7′ (figure 1). All of these data enabled the establishment of a planar structure for compound **1** (figure 2).

Compounds **1** and **2** have similar CD spectra with a negative Cotton effect at 341 and 334 nm, respectively, indicating that both compounds possess an R configuration at C-6. According to the configuration of $CH_3$-8′ in **2**, we deduce that $CH_3$-8′ in **1** also is α-oriented. Therefore the absolute structure of compound **1** is as shown in figure 2.

## 3. Experimental

### *3.1 General experimental procedures*

Optical rotations were measured on a Perkin-Elmer 241 polarimeter. IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR. CD spectra were recorded on a JASCO-600 CD

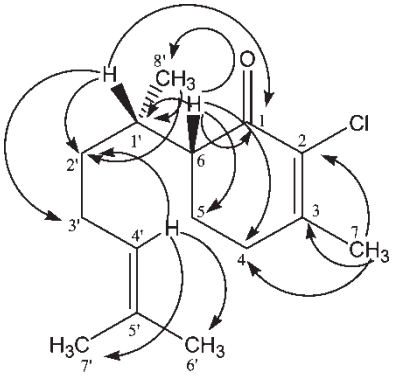



Figure 1. HMBC correlations of **1**.



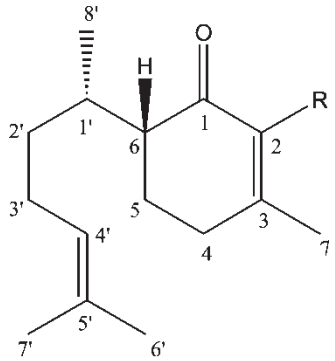
spectrometer. $^{1}H$ (500 MHz), $^{13}C$ (125 MHz) and 2D NMR spectra were recorded on Bruker DRX-500 and JEOL JNM-EX 400 spectrometers. CIMS spectra were recorded on a Finnigan TSQ700 mass spectrometer. HR-ESIMS were obtained on a Bruker APEX FT-MS instrument. Column chromatography was performed on silica gel (Marine Chemical Factory, Qindao, China), and on Sephadex LH-20 (Pharmacia). TLC was conducted on silica gel 60 and silica gel 60 $F_{254}$ plates (Merck).

### *3.2 Plant material*

The roots of *Euphorbia chrysocoma* were collected from Yunnan Province, China in November 2002, and were identified by Mr Bingshu Long (Wenshan Institute of Forestry). A voucher specimen (no. 021102) has been deposited in the herbarium of the China Pharmaceutical University.

### *3.3 Extraction and isolation*

Dried roots of *Euphorbia chrysocoma* (2.0 kg) were extracted 3 × with 95% EtOH for 3 h each time, and the solvent was then removed under reduced pressure The so-obtained




**1** **R** = Cl
**2** **R** = H

Figure 2. Structure of compounds **1** and **2**.

ethanolic extract was suspended in water, and then partitioned with light petroleum, EtOAc and n-BuOH, successively. The light petroleum-soluble fraction (54 g) was concentrated and subjected to silica-gel column chromatography eluting with a gradient of light petroleum-EtOAc to yield ten fractions. Fraction 2 was subjected to silica-gel (light petroleum–EtOAc, 9:1) chromatography to give **3** (25 mg). Fraction 3 was subjected to silica-gel (light petroleum–EtOAc, 9:1) and Sephadex LH-20 ($CHCl_3$) chromatography to give **4** (15 mg) and **5** (10 mg). Fraction 5 was subjected to silica-gel (light petroleum–EtOAc, 8.5:1.5) and Sephadex LH-20 ($CHCl_3$) chromatography to give **1** (40 mg) and **2** (32 mg). Fraction 7 was subjected to silica-gel (light petroleum–EtOAc, 8:2) chromatography to yield a mixture of **6** and **7** (53 mg). Fraction 8 was subjected to silica-gel (light petroleum–EtOAc, 8:2) chromatography to yield **8** (45 mg). The EtOAc-soluble fraction (60 g) was concentrated and subjected to silica-gel column chromatography eluting with a gradient of $CHCl_3$—$CH_3OH$ to yield five fractions, fraction 2 of which was subjected to silica-gel ($CHCl_3$—$CH_3OH$ 9:1) and Sephadex LH-20 ($CHCl_3$—$CH_3OH$ 1:1) chromatography to give **9** (50 mg) and **10** (32 mg). Fraction 3 was subjected to silica-gel ($CHCl_3$—$CH_3OH$ 8:2) chromatography to give **11** (80 mg).

*Compound **1***: a colorless oil; $[\alpha]_D^{25}$ −37.7 ($c = 0.57$, $CHCl_3$); UV ($CHCl_3$) $\lambda_{max}$ ($\log \varepsilon$) 261 (3.04) nm; CD($CHCl_3$) (nm) $\Delta\varepsilon_{341}$ −112.1; IR (KBr) $\nu_{max}$ ($cm^{-1}$): 2964, 1684, 1616, 1452, 1377, 1157, 816; $^1H$ and $^{13}C$ NMR data see table 1; CIMS *m/z* 255 $[M + H]^+$; HR-ESIMS *m/z* $[255.1526]^+$ (calcd. for $C_{15}H_{24}OCl$, 255.1517).

*Compound **2***: a colorless oil; $[\alpha]_D^{25}$ −43.3 ($c = 0.57$, $CHCl_3$); UV ($CHCl_3$) $\lambda_{max}$ ($\log \varepsilon$) 256 (3.15) nm; CD($CHCl_3$) (nm) $\Delta\varepsilon_{334}$ −72.3; IR (KBr) $\nu_{max}$ ($cm^{-1}$): 2970, 1669, 1379, 1209, 820; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 5.85 (1H, d, $J = 1.2$ Hz, H-2), 5.10 (1H, tt, $J = 7.2$ Hz, 1.4 Hz, H-4′), 1.92 (3H, s, $CH_3$-7), 1.67 (3H, s, $CH_3$-6′), 1.58 (3H, s, $CH_3$-7′), 0.79 (3H, d, $J = 6.8$ Hz, $CH_3$-8′); $^{13}C$ NMR data see table 1; CIMS *m/z* 221 $[M + H]^+$.

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