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Note

Capitulatin B, A new eudesmane derivative from *Curculigo capitulata*, and revised assignment of ^{13}C NMR data of $6\alpha,15\alpha$ -epoxy- $1\beta,4\beta$ -dihydroxyeudesmane

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A new eudesmane derivative named capitulatin B (**1**) along with $6\alpha,15\alpha$ -epoxy- $1\beta,4\beta$ -dihydroxyeudesmane (**2**) has been isolated from the rhizomes of *Curculigo capitulata*. The structure of compound **1** was established as $4\alpha,6\alpha$ -epoxy- 1β -hydroxy- 4β -methyleudesmane, and the ^{13}C NMR data of compound **2** was reassigned on the basis of the spectral data, including 1D and 2D NMR (HMQC, HMBC, COSY, ROESY).

Keywords: *Curculigo capitulata*; Hypoxidaceae; Eudesmane; Capitulatin B; Revised assignment of ^{13}C NMR data

1. Introduction

Our previous investigation on *Curculigo capitulata* (Hypoxidaceae), which is used as a tonic and as a drug to treat dysmenorrhea and rheumatism [1], led to the identification of a new chlorine-containing phenoloid [2] and three new norlignans [3]. As part of our studies, further investigation on the less polar fraction of *C. capitulata* resulted in the isolation of two eudesmane derivatives. This report deals with the isolation and structural elucidation of a new compound – capitulatin B (**1**), and revised assignment of ^{13}C NMR data of $6\alpha,15\alpha$ -epoxy- $1\beta,4\beta$ -dihydroxyeudesmane (**2**) based on 1D and 2D NMR spectroscopy, including HMQC, HMBC, COSY and ROESY experiments.

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2. Results and discussion

The 1D NMR spectral data of **1** and **2** are typical of those of the eudesmane skeleton. Compound **1** was assigned a molecular formula of $C_{15}H_{26}O_2$ based on the HR-ESIMS, implying three degrees of unsaturation. No sp^2 carbons were revealed by the ^{13}C NMR spectrum, suggesting three rings for compound **1**. A broadened double doublet (1H, $J = 10.84, 4.28$ Hz) at δ 3.28 could be ascribed to H α -1 [4,5], which indicated a β -hydroxyl group at C-1 (δ 78.8). The 1D NMR spectral data and a selective 1H -decoupling experiment show the presence of an isopropyl group. Correlations between protons of the isopropyl group and C-7 (δ 51.3), protons of methyl at δ 1.32 and C-4 (δ 73.6), protons of methyl at δ 0.83 and C-10 (δ 40.3) in the HMBC spectrum of **1** (table 1) confirm that $CH(Me)_2$ is linked with C-7 and two CH_3 with C-4 and C-10, respectively. The downfield δ s at C-4 (73.6) and C-6 (70.8) in combination with the molecular formula of $C_{15}H_{26}O_2$, which imply three rings in **1**, suggest the presence of a 4,6-epoxide in **1**. A double doublet (1H, $J = 10.08$ and 10.32 Hz) at δ 3.86 due to H-6 shows that H-5, H-6 and H-7 should be at an axial orientation, indicating the presence of a β -isopropyl group and a 4 α ,6 α -epoxide. Careful analyses and comparison of NOE spectra (figure 1) of **1** confirmed the stereochemistry of **1** as assigned. Thus the structure of **1** was established as 4 α ,6 α -epoxy-1 β -hydroxy-4 β -methyldeudesmane.

Compound **2** was assigned a molecular formula of $C_{15}H_{26}O_3$ on the basis of a molecular ion peak at m/z 254 (15%). Its structure was identified by 1D NMR (1H and ^{13}C), 2D NMR (HMQC, COSY, HMBC and NOESY) and comparison of its spectral data (FABMS, 1H and ^{13}C) with those reported in the literature [6]. Its stereochemistry was identified by analyzing the coupling constants of H-1, H-6 and H-15 and NOE spectra. The spectral data support the assignment of **2** as 6 α ,15 α -epoxy-1 β ,4 β -dihydroxyeudesmane. The stereochemical configuration of **2** is consistent with that reported in the literature [6]. However, the δ values in ^{13}C NMR (DEPT) between C-4 (s) and C-15 (t), and C-9 (t) and C-10 (s) for compound **2** are contrary to the literature [6]. Those exchanges of the δ _Cs were further confirmed by ^{13}C NMR (DEPT), COSY, HMQC and HMBC spectra. Thus the chemical shifts of C-4, C-15, C-9 and C-10 were reassigned (Experimental section).

Table 1. 1H and ^{13}C NMR and HMBC data for **1** ($CDCl_3$).

Position	δ (C) ^a	δ (H) ^b	HMBC ^c (H → C)
1	78.8 d	3.28 (1H, dd, $J = 4.28, 10.84$ Hz)	2, 9, 14
2	28.0 t	1.52 (1H, m), 1.70 (1H, m)	3, 10
3	40.2 t	1.55 (1H, m), 1.72 (1H, m)	1, 5, 15
4	73.6 s		
5	60.0 d	1.35 (1H, d, $J = 10.32$ Hz)	6, 7, 14, 15
6	70.8 d	3.86 (1H, dd, $J = 10.08, 10.32$ Hz)	4, 5, 7, 8, 11
7	51.3 d	1.30 (1H, m)	5, 12, 13
8	18.3 t	1.46 (1H, m), 1.53 (1H, m)	6, 9
9	39.3 t	1.05 (1H, m), 1.80 (1H, m)	5, 7
10	40.3 s		
11	25.3 d	2.14 (1H, m)	7, 8, 12, 13
12	15.8 q	0.82 (3H, d, $J = 6.80$ Hz)	7, 11, 13
13	21.1 q	0.90 (3H, d, $J = 6.80$ Hz)	7, 11, 12
14	13.9 q	0.83 (3H, s)	1, 5, 9, 10
15	23.6 q	1.32 (3H, s)	3, 5

Recorded at ^a100, ^b400 and ^c500 MHz.

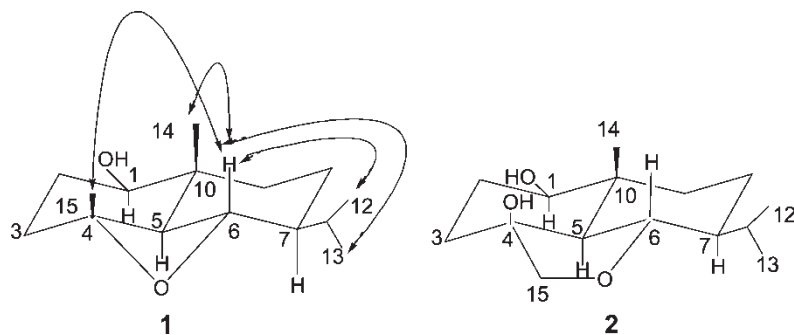


Figure 1. The structures and key NOESY correlations of compounds **1** and **2**.

3. Experimental

3.1 General experimental procedures

The melting point was determined on an XRC-1 micro-melting point apparatus and is uncorrected. The $[\alpha]_D$ was determined on a Jasco-20. The IR spectrum was recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. The UV spectrum was recorded on an UV 210A spectrometer using MeOH as solvent. 1D and 2D NMR spectra were run on Bruker AM-400 and DRX-500 spectrometers with TMS as an internal standard using CDCl_3 as a solvent. MS was run on a VG Auto Spec-3000 spectrometer. TLC was carried on silica-gel G (Meijing) precoated plates. Spots were detected by spraying with 5% sulfuric acid–ethanol solution followed by heating.

3.2 Plant material

Rhizomes of *Curculigo capitulata* (Lour.) O. Ktze were collected from Xishuangbanna in July 2001 and identified by Professor Xu Zai Fu of Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences. A voucher specimen has been deposited in the herbarium of the Botanical Garden.

3.3 Extraction and isolation

The air-dried and powdered rhizomes of *C. capitulata* (3 kg) were extracted with 85% EtOH ($3 \times 20\text{ L}$) at room temperature, and the combined extracts were then evaporated *in vacuo* to give a residue. The residue was suspended in H_2O and then applied to a D101 reticular resin column eluted with H_2O and EtOH. The EtOH eluent was concentrated *in vacuo* to give a residue (240 g) that was chromatographed on silica gel column (200–300 mesh) with CHCl_3 –MeOH (7:2) to give 8 fractions. Fraction 1 (10.0 g) was subjected to column chromatography over silica gel eluted with CHCl_3 –MeOH (15:2) to afford 7 further fractions. Sub-fractions 1–5 (600 mg) were then rechromatographed on a silica-gel column with light petroleum–chloroform and light petroleum–acetone to afford compounds **1** (14 mg) and **2** (3 mg), respectively.

3.3.1 4 α ,6 α -Epoxy-1 β -hydroxy-4 β -methyleudesmane (1). Yellowish oil, $[\alpha]_D^{16} - 7.6$ (*c* 0.79, CHCl₃); IR (KBr) ν_{\max} (cm⁻¹): 3432, 2925, 2854, 1463, 1383, 1065, 985; HRESI-MS (+), *m/z* 239.2044 [M + 1]⁺ (calcd for C₁₅H₂₇O₂ 239.2011). EI-MS *m/z* (%): 238 [M]⁺ (15.1), 223 (39.2), 220 (14.7), 205 (16.3), 167 (32.5), 155 (77.2), 101 (100). ¹H NMR (CDCl₃, 400 MHz) and ¹³C NMR (CDCl₃, 100 MHz) data are shown in table 1.

3.3.2 6 α ,15 α -Epoxy-1 β ,4 β -dihydroxyeudesmane (2). Colorless needles (EtOH), mp 126–128°C. $[\alpha]_D^{16} - 28$ (*c* 0.15, CHCl₃). EI-MS *m/z*: 254 [M]⁺ (15.5), 239 (6.7), 236 (3.9), 222 (42.0), 209 (18.6), 206 (19.1), 180 (35.8), 81 (100). ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 3.38 (1H, dd, *J* = 4.25, 11.19 Hz, H-1), 1.71 (1H, m, H-2), 1.94 (1H, m, H-2), 1.78 (2H, m, H-3), 1.03 (1H, d, *J* = 11.56 Hz, H-5), 3.73 (1H, dd, *J* = 9.56, 11.69 Hz, H-6), 1.27 (1H, m, H-7), 1.35 (1H, m, H-8), 1.60 (1H, m, H-8), 1.52 (1H, m, H-9), 1.91 (1H, m, H-9), 1.87 (1H, m, H-11), 0.90 (3H, d, *J* = 6.91 Hz, H-12), 0.96 (3H, d, *J* = 6.91 Hz, H-13), 1.03 (3H, s, H-14), 3.62 (1H, d, *J* = 9.18 Hz, H-15), 3.72 (1H, d, *J* = 9.18 Hz, H-15); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 80.5 (d, C-1), 28.0 (t, C-2), 39.7 (t, C-3), 77.2 (s, C-4), 57.5 (d, C-5), 75.6 (d, C-6), 51.1 (d, C-7), 22.2 (t, C-8), 33.2 (t, C-9), 39.1 (s, C-10), 29.5 (d, C-11), 18.5 (q, C-12), 20.7 (q, C-13), 12.8 (q, C-14), 80.4 (t, C-15).

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