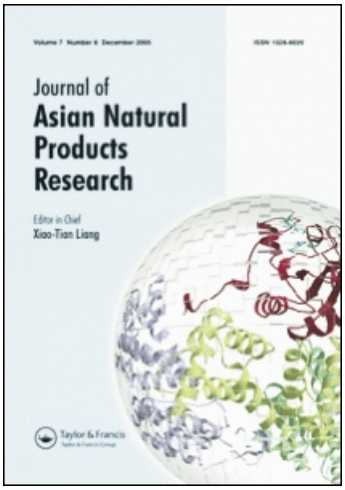

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Note

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

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A new eudesmane derivative named capitulatin B (**1**) along with 6α,15α-epoxy-1β,4β-dihydroxy-eudesmane (**2**) has been isolated from the rhizomes of *Curculigo capitulata.* The structure of compound **1** was established as 4α,6α-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 6α,15α-epoxy-1β,4β-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 Hα-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 δs 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 4α,6α-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 4α,6α-epoxy-1β-hydroxy-4β-methyleudesmane.

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 6α,15α-epoxy-1β,4β-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 [a]100, [b]400 and [c]500 MHz.

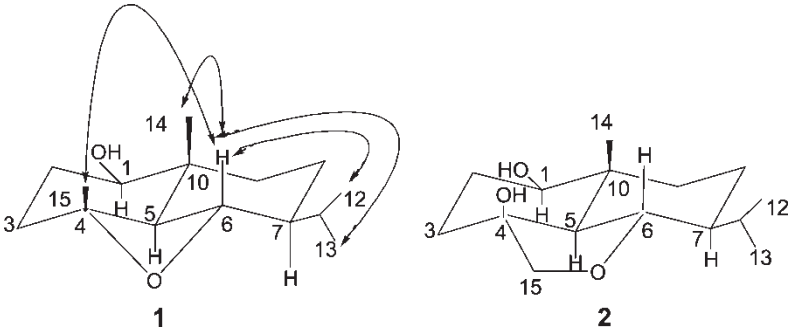

Figure 1. The structures and key NOESY correlations of compounds **1** and **2**.

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 powered rhizomes of *C. capitulata* (3 kg) were extracted with 85% EtOH (3×20 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 4α,6α-Epoxy-1β-hydroxy-4β-methyleudesmane (1). Yellowish oil, $[\alpha]_D^{16}$ − 7.6 (*c* 0.79, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}): 3432, 2925, 2854, 1463, 1383, 1065, 985; HRESI-MS (+), *m/z* 239.2044 $[M + 1]^+$ (calcd for $C_{15}H_{27}O_2$ 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 ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) data are shown in table 1.

3.3.2 6α,15α-Epoxy-1β,4β-dihydroxyeudesmane (2). Colorless needles (EtOH), mp 126–128°C. $[\alpha]_D^{16}$ − 28 (*c* 0.15, $CHCl_3$). 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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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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