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大果大戟中的一个对映-贝壳杉烷型二萜

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摘　要: 从大果大戟的根部首次分离得到一个对映-贝壳杉烷型二萜, 利用波谱方法鉴定为 ent-16α, 17-dihydroxykauran-3-one (**1**)。首次对化合物 **1** 在甲醇中的碳谱和氢谱数据进行了全归属。

关键词: 大果大戟; 大戟科; 贝壳杉烷型二萜

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An ent-Kaurane Diterpene from *Euphorbia wallichii*

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Abstract: One known ent-kaurane diterpene, ent-16α, 17-dihydroxykauran-3-one, were isolated from the roots of Euphorbia wallichii for the first time. Its structure was elucidated on the basis of spectral methods. And the NMR assignments of the compound in CD_3OD were given for the first time.

Key words: *Euphorbia wallichii*; Euphorbiaceae; kaurane diterpene

Euphorbia wallichii hook. f. is a traditional Tibetan medicine used for curing furuncle, exanthema and cutaneous anthrax. Our previous investigation on the species resulted in the isolation of 24 compounds[1-3]. In our continuous study, an ent-kaurane diterpene, ent-16α, 17-dihydroxykauran-3-one (**1**[4]), was obtained from the alcohol extract of the roots of the plant. In this paper, we report the isolation and structure elucidation of the compound.

Results and Discussion

Compound **1** has a molecular formula of $C_{20}H_{32}O_3$ as determined by EIMS and ^{13}C NMR spectra. The 1D NMR spectra showed signals of three tertiary methyls, eight methylenes, three methines, three quaternary carbons, a carbonyl (δ_C 221.0), a primary (δ_C 70.5) and a tertiary (δ_C 80.6) hydroxyl groups. These features are similar to those of ent-16α, 17-dihydroxyatisan-3-one[3] and ent-16α, 17-dihydroxykauran-3-one[4]. Compound **1** was detected in CD_3OD, while the latter two compounds were detected in CD_3Cl or C_6D_6, so it is hard to confirm the skeleton of compound **1**. To determine its skeleton and give the NMR assignments, HMQC, HMBC and ROESY spectra of **1** were tested. Correlations in HMBC (see table **1**) from H-14 to G-7, G-8, G-9, G-12, G-13, G-15 and G-16, H-15 to G-7, G-8, G-9, G-13, G-14, G-16 and G-17, H-17 to G-13, G-15 and G-16 revealed that compound 1 isn't an ent-atisane diterpene but an ent-kaurane diterpene. The relative stereochemistry of the compound was finally determined by Roesy spectrum, in whose NOE interaction between H-9 with H-5, and H-11β, H-20 with H-1α, H-13, H-14α, and H-17 were observed. Thus **1** was elucidated to be ent-16α, 17-dihydroxykauran-3-one. In comparison with the reported data of compound **1** in C_6D_6[4], the ^{13}C NMR spectra in CD_3OD provided increased signal, especially G-3, whose chemical shift was bigger than that in C_6D_6 (δ_C 215.6) by 5.4 ppm.

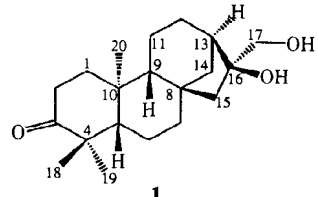

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Table 1 1D NMR data and HMBC of compound 1[a] (CD_3OD)

	δ_H	δ_C	HMBC
1	1.93, 1.35 (m, each 1H)	40.4 (t)	C-2, C-3, C-5, C-6, C-9, C-10, C-20
2	2.39 (m, 2H)	35.0 (t)	C-1, C-3, C-4
3	–	221.0 (s)	–
4	–	48.2 (s)	–
5	1.39 (m, 1H)	55.5 (d)	C-1, C-4, C-6, C-7, C-9, C-10, C-18, C-19, C-20
6	1.37 (m, 2H)	22.3 (t)	C-4, C-5, C-7, C-9, C-10
7	1.38 (m, 2H)	42.0 (t)	C-5, C-6, C-9, C-14
8	–	44.6 (s)	–
9	1.12 (brd, J = 8.6 Hz, 1H)	57.2 (d)	C-8, C-10, C-11, C-12, C-14, C-15, C-20
10	–	39.7 (s)	–
11	2.05 (m, 1H), 1.49 (d, J = 6.3 Hz, 1H)	20.2 (t)	C-8, C-9, C-10, C-12, C-13
12	1.44, 1.74 (m, each 1H)	27.7 (t)	C-9, C-11, C-13, C-14, C-16
13	1.96 (m, 1H)	42.1 (d)	C-12, C-14
14	1.01 (m, 1H), 1.85 (dd, J = 1.9, 12.2 Hz, 1H)	38.8 (t)	C-7, C-8, C-9, C-12, C-13, C-15, C-16
15	1.34, 1.31 (m, each 1H)	52.8 (t)	C-7, C-8, C-9, C-13, C-14, C-16, C-17
16	–	80.6 (s)	–
17	3.31 (d, J = 11.2 Hz, 1H), 3.20 (d, J = 11.2 Hz, 1H)	70.5 (t)	C-13, C-15, C-16
18	0.96 (s, 3H)	27.7 (q)	C-3, C-4, C-5, C-19
19	0.92 (s, 3H)	21.4 (q)	C-3, C-4, C-5, C-18
20	1.00 (s, 3H)	18.2 (q)	C-1, C-5, C-9, C-10

[a] 1D NMR data were measured at 400 MHz, and 2D NMR data at 500 MHz.

Experimental

Apparatus and plant materials (see previously described[1])

Extraction and isolation

The air-dried roots (10 kg) of *Euphorbia wallichii* were extracted with EtOH (95%) four times at room temperature, and the combined extracts were evaporated in vacuo. The residue was suspended in H_2O and then extracted with $CHCl_3$ for three times. The $CHCl_3$ layer was concentrated in vacuo to give 200 g of residue, which was chromatographed over silica gel. The column was eluted with petroleum ether-EtOAc (from petroleum ether to petroleum-EtOAc 1:1). According to differences in composition monitored by TLC (GF_{254}), 17 fractions were obtained. Fraction 11 (6.8 g) was subjected to CC on silica gel with petrol-Me_2CO (from 17:3 to 7:3). Five subfractions (a-e) were collected. Fraction e (1.2 g) was subjected to CC on silica gel with $CHCl_3$-Me_2CO (90:10) to give three subfractions (Ⅰ-Ⅲ). Sediment from fraction Ⅱ (140 mg) was washed intensively with petrol-acetone (10:1) and recrystallized by MeOH, then it was washed intensively again to afford **1** (45 mg).

Identification

ent-16α, 17-dihydroxykauran-3-one (1) $C_{20}H_{32}O_3$, colorless needles; ^1H NMR and ^{13}C NMR (CD_3OD) see table 1; EIMS *m/z* 320 $[M]^+$ (1), 302(3), 289(100), 271(47), 259(11), 253(4), 247(25), 229(13), 216(9), 203(16), 189(18), 177(12), 171(4), 165(7), 159(10), 151(13), 145(21), 137(15), 121(21), 107(28), 97(11), 91(32), 81(29), 67(29), 55(53).

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