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Two New Eremophilenolides from *Ligularia fischeri*

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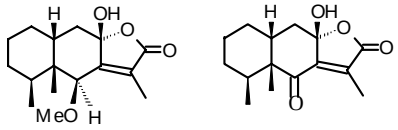
Abstract: Chemical investigation of *L. fischeri* afforded two new eremophilenolides, which were identified as 6β-methoxy-8β-hydroxy-eremophil-7(11)-en-12,8α-olide **1**; 6-oxo-8β-hydroxy-eremophil-7(11)-en-12,8α-olide **2**.

Keywords: *Ligularia fischeri*, compositae, eremophilenolide, sesquiterpene.

Ligularia fischeri has long been used as traditional medicine to relieve cough, invigorate the circulation of blood and stop pain[1]. From the plant growing in Shengnongjia, Hubei,China, two new eremophilenolides have been isolated.

Compound **1** was needle crystals from petrol ether (60-90^{0}C), m.p. =148-150^{0}C. Its formula was determined as $C_{16}H_{24}O_4$ by ^{13}C-NMR and DEPT spectra in accordance with the molecular ion peak m/z=280 in EIMS. The type of carbon signals (5×C, 3×CH, 4×CH_2 , 4×CH_3) (**Table 2**) showed it had a bicyclic sesquiterpene skeleton bearing a methoxy, a hemi-ketal group and an α,β-unsaturated lactone ring which was verified by its IR absorptions. Three methyl signals δ1.91 (s, 3H), δ 1.10 (s, 3H) and δ 0.76 (d, J=5.7Hz, 3H) indicated it was a characteristic 12,8α-eremophilenoide[2,3]. Comparing with the corresponding ^{13}C-NMR signals of known eremophilenolides[4], we attributed δ 103.68 (s), δ 80.46 (d) of this compound to hemi-ketal at C-8, and methoxy at C-6. Since there was no long range coupling between H -6 and the olefinic methyl (CH_3-13), H-6 should be in α-orientation[5]. Thus this compound was deduced as 6β-methoxy-8β-hydroxy-eremophil-7(11)-en-12,8α-olide.

Compound **2** was obtained as needle crystals by recrystallization from petrol ether (60-90^{0}C), m.p.=216-218^{0}C. The typical methyl signals δ 0.85 (d, J=6.8Hz, 3H), δ 1.13 (s, 3H) and δ 2.03 (s, 3H) in ^{1}H-NMR indicated an eremophilane skeleton[2,3] obviously. Compared its NMR data with those of **1 (Table1, 2)**, it was deduced as another 12,8α -eremophilenolide with 8β hydroxy. The highest mass peak in EIMS m/z=264 indicated a formula of $C_{15}H_{20}O_4$ in good agreement with its ^{13}C-NMR and DEPT spectral information. However, the lowest field signal δ 186.67 in ^{13}C-NMR which had a correlation with δ 1.13 (CH_3-14, s, 3H) in HMBC showed a carbonyl in this compound at C-6. Therefore, the compound was identified as 6-oxo-8β-hydroxy-eremophil-7(11)-en-12,8α -olide.



1 **2**

Table 1. ^{1}H-NMR spectral data of compounds 1 and 2 (400 MHz, $CDCl_3$, TMS as internal standard)

H	1	2
6	4.11 s	----
9α	2.04-2.11 m	2.63 d (16.0)
9β	2.04-2.11 m	2.30 dd (16.0,4.0)
13	1.91 s	2.03 s
14	1.10 s	1.13 s
15	0.76 d (5.7)	0.85 d (6.8)
OMe	3.37 s	----

Table 2. ^{13}C-NMR (DEPT) spectral data of compounds 1 and 2 (100MHz, $CDCl_3$)

C	1	2	DEPT	C	1	2	DEPT
1	29.18	29.95	CH_2	9	39.01	39.80	CH_2
2	25.36	26.51	CH_2	10	34.30	38.78	CH
3	30.38	30.85	CH_2	11	127.00	134.85	C
4	28.91	35.81	CH	12	171.21	171.49	C
5	42.87	47.01	C	13	8.35	9.00	CH_3
6	80.46	186.67*	CH	14	16.28	20.01	CH_3
7	154.07	162.93	C	15	16.09	16.18	CH_3
8	103.68	103.28	C	OMe	58.25		CH_3

* quaternary C in DEPT.

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