Chinese Chemical Letters Vol. 13, No. 10, pp 963 – 964, 2002
http://www.imm.ac.cn/journal/ccl.html

Two New Eremophilenolides from *Ligularia sagitta*

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Abstract: Chemical investigation of *L.sagitta* afforded two new eremophilenolides, which were identified as 6β-angeloyloxy-10β-hydroxy-8β-methoxy-eremophil-7(11)-en-12, 8α-olide (**1**) and 6β, 8β-dimethoxy-10β-hydroxy-eremophil-7(11)-en-12, 8α-olide (**2**). Their structures were established by spectroscopic methods including 2D NMR experiments.

Keywords: *Ligularia sagitta*, Compositae, eremophilenolide, sesquiterpene.

Ligularia sagitta has long been used as a folk medicine[1]. From the plant collected in Gansu province, two new eremophilenolides were isolated.

Compound **1**, colorless gum, $[\alpha]_D^{20}$: +135 (*c* 0.43, acetone). Its molecular formula was proposed as $C_{21}H_{30}O_6$ by ^{1}H-NMR, ^{13}C-NMR and DEPT spectra in accordance with $[M+H]^+$ at *m/z* 379 in FAB-MS. Its IR bands (1651, 1714.7, 1774.8 cm^{-1}) and UV absorption (228 nm) displayed the typical unsaturated γ-lactone. In the ^{1}H-NMR spectrum, there are three methyl groups, an angeloyl group, a methoxy group and a hydroxy group. The ^{13}C-NMR spectrum showed 15 signals for 6×C, 2×CH, 4×CH_2, 3×CH_3. Therefore, compound **1** was confirmed as eremophilenolide **(Table 1)**[2]. In the HMBC spectrum of **1**, the correlations of H-6 with $C_{1'}$ (δ 166.4), the methoxy protons with C-8 (δ 105.7) and the hydroxy proton with C-10 (δ 73.6) established locations of the -OAng at C-6, -OCH_3 at C-8 and -OH at C-10, respectively. Stereochemically, Me-14 and Me-15 are biogenetically β orientations[3]. The NOESY cross-peak observed between H-4α and H-9α implied a *cis* eremophilane[2], and 10-OH should be in β-orientation. The configuration at C-8 is β-OMe according to the relative chemical shifts of Me-14 and Me-15 signals[4]. The configuration of 6-OAng was identified as β-substitution from the NOESY cross-peak of H-6 and H-4α, and also from the absence of homoallylic coupling between H-6 and H-13[3]. Thus, the structure of **1** was determined.

Compound **2**, colorless plates, mp:164-166°C, $[\alpha]_D^{20}$: +166.7 (*c* 0.27, acetone). The molecular formula, $C_{17}H_{26}O_5$ was deduced from its molecular ion peak at *m/z* 310 and NMR spectra. Its spectral data were very similar to those of **1 (Table 1)** except for the presence of the -OCH_3 at C-6 in **2** instead of the -OAng in **1**. This was disclosed by

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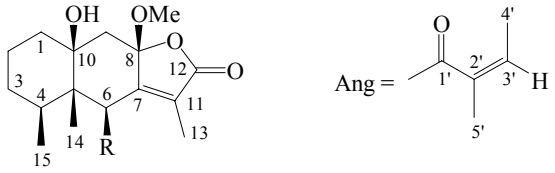
upfield shifted signal of H-6 at δ 4.2 without allylic coupling with H-13, thus, -OCH_3 at C-6 was also in β-substitution. Therefore, compound **2** was confirmed.

Figure 1 Structures of compounds **1**, **2**



1 R = OAng
2 R = OMe

Table 1 ^{1}H-NMR (400MHz), ^{13}C-NMR (100MHz) and DEPT data of **1**, **2** ($CDCl_3$ δppm)

H	**1** δ_H	**2** δ_H	C	**1*** δ_C	DEPT	**2** δ_C	DEPT
4	1.31~1.35 (m)	1.28~1.36 (m)	1	34.2	CH_2	34.3	CH_2
6	5.87 (s)	4.2 (s)	2	21.6	CH_2	21.8	CH_2
9α	2.37 (d, J=14.5)	2.38 (d, J=14.6)	3	29.6	CH_2	29.7	CH_2
9β	2.23 (d, J=14.5)	2.20 (d, J=14.6)	4	33.4	CH	33.4	CH
13	2.08 (s)	1.96 (s)	5	47.5	C	48.0	C
14	1.14 (s)	1.16 (s)	6	71.2	CH	80.9	CH
15	0.92 (d, J=5.8)	0.84 (d, J=5.8)	7	149.5	C	152.7	C
3′	6.25 (qq, J=7.2, 1.35)		8	105.7	C	106.7	C
4′	2.04 (dq, J=7.2, 1.4)		9	42.9	CH_2	41.5	CH_2
5′	1.93 (dq, J=1.4, 1.35)		10	73.6	C	74.1	C
6-OMe		3.31 (s)	11	131.0	C	129.9	C
8-OMe	3.07 (s)	3.35 (s)	12	170.1	C	170.6	C
10-OH	3.71 (s)	3.93 (s)	13	8.9	CH_3	8.8	CH_3
			14	10.5	CH_3	10.7	CH_3
			15	16.5	CH_3	16.5	CH_3
			6-OMe			59.0	CH_3
			8-OMe	50.2	CH_3	51.0	CH_3

*OAng: δ_C 166.4 ($C_{1'}$, s), 126.2 ($C_{2'}$, s), 141.6 ($C_{3'}$, d), 20.4 ($C_{4'}$, q) and 15.7 ($C_{5'}$, q).

Acknowledgments

This work was financed by the NNSFC (No.29972017 and QT Programme).

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Received 18 January, 2002