Chinese Chemical Letters Vol. 12, No. 7, pp 601 – 602, 2001

Two New Eremophilane Sesquiterpenes from *Cacalia ainsliaeflora*

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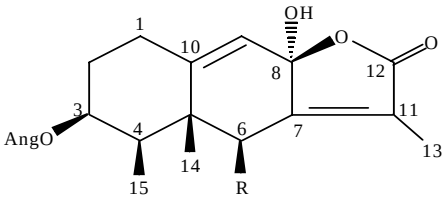
Abstract: Two new eremophilane sesquiterpenes 3β-angeloyloxy-8α-hydroxy-6β-methoxy eremophil-7 (11), 9 (10)-dien-8, 12-olide (**1**) and 3β-angeloyloxy-6β, 8α-dihydroxy-eremophi-7 (11), 9 (10)-dien-8, 12-olide (**2**) were isolated from *Cacalia ainsliaeflora*. Their structures were established by spectroscopic methods and 2D NMR experiments.

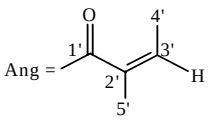
Keywords: *Cacalia ainsliaeflora*, Compositae, eremophilane sesquiterpene.

The root of *C. ainsliaeflora* has been used for curing pellagra, rheumatismal edema and insecticide[1]. In this paper, we report the structure elucidation of two new eremophilane sesquiterpenes (**1**, **2**) from the roots of *C. ainsliaeflora*.

Compound **1**, colorless gum, $[\alpha]_D^{20}$: -50 (c 0.50, $CHCl_3$). HRESI-MS showed $[M+H]^+$ at *m/z* 377.19528 (calcd for $C_{21}H_{29}O_6$ 377.19587), corresponding to a molecular formula $C_{21}H_{28}O_6$. Its IR bands (1655, 1717, 1750cm^{-1}) and UV absorptions (221 nm) displayed the typical of unsaturated γ-lactones. In the ^{1}H-NMR spectra data,

Figure 1. Structures of compounds **1-2**





1 R=OCH_3 **2** R=OH

there are three methyl groups, an angeloyl group and a methoxyl group (**Table**1). Except for the -OAng and a -OCH_3, the ^{13}C-NMR spectra of **1** showed 15 signals for 6×C, 4×CH, 2×CH_2, and 3×CH_3. Therefore, compound **1** was confirmed as eremophilane sesquiterpene[2]. In the HMBC spectrum of **1,** the correlation of H-3 with $C_{1'}$ (δ 167.5) and the methoxy protons with C-6 pointed to the -OAng at C-3 and -OCH_3 at C-6, respectively. Thus, the –OH should be located at C-8 (δ 101.6). In the biogenetic consideration of an eremophilane-type, the methyls at C-4 and C-5 are generally β-configurated. So the NOESY cross-peak between H-6 and H-4α, H-3 and H-4α

showed that the $-OCH_3$ at C-6 was in β-orientation and the -OAng at C-3 was in β-orientation, respectively. Configuration of the 8α-OH was suggested by the presence of a homoallylic spin-coupling (J=1.24) between H-6α and H-13[3]. Thus, the structure of **1** was determined.

Compound **2**, colorless gum, $[\alpha]_D^{20}$: -7 (c 0.71, $CHCl_3$). The molecular formula, $C_{20}H_{26}O_6$ was deduced from its MS (molecular ion at *m/z* 362) and NMR spectra. Its spectral data were very similar to those of **1** except for the presence of a –OH at C-6 in **2** instead of the $-OCH_3$ in **1**. Thus, the structure of compound **2** was confirmed.

Table 1 ^{1}H-NMR (400MHz), ^{13}C-NMR (100MHz) and DEPT data of **1-2** (CD_3COCD_3)

H	**1** δ_H	**2** δ_H	C	**1***δc	DEPT	**2***δc	DEPT
1	2.48dddd	2.51dddd	1	27.7	CH_2	28.0	CH_2
2	1.65ddt	1.65ddt	2	31.9	CH_2	31.9	CH_2
3	5.03ddd (J=3.2, 3.0, 4.5)	5.03ddd (J=3.2, 3.0)	3	74.8	CH	74.9	CH
4	1.80m	1.85m	4	46.6	CH	46.4	CH
6	4.25(q, J=1.24)	4.83(q, J=1.21)	5	50.9	C	51.0	C
9	5.73 (d, J=1.34)	5.71(d, J=1.33)	6	86.8	CH	76.6	CH
13	1.92 (d, J=1.24)	1.95(d, J=1.21)	7	157.4	C	160.0	C
14	1.14 (s)	1.19(s)	8	101.6	C	101.4	C
15	1.15 (d, J= 6.4)	1.25(d, J=7.0)	9	120.8	CH	120.5	CH
3’	6.09 (qq J=7.68, 1.40)	6.10(qq J=7.21,	10	149.7	C	150.2	C
4’	1.96 (dq J=7.60, 1.34)	1.99(dq J=7.21,	11	123.0	C	123.1	C
5’	1.89 (dq J=1.40, 1.34)	1.93(dq J=1.50,	12	171.6	C	172.0	C
			13	8.3	CH_3	8.6	CH_3
			14	14.8	CH_3	14.8	CH_3
			15	15.1	CH_3	15.1	CH_3
O	3.42 s		O	57.7			

* OAng: δ_C 167.5 ($C_{1'}$, s), 128.8 ($C_{2'}$, s), 138.5 ($C_{3'}$, d), 20.99 ($C_{4'}$, q), and 15.7 ($C_{5'}$, q).

Acknowledgments

This work was supported by the National Natural Science Foundation of China No.29972017 and the Foundation of the Ministry of Education of China for Doctoral Program No. 98073003

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Received 5 January, 2001