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New Sesquiterpenes from *Cacalia ainsliaeflora*

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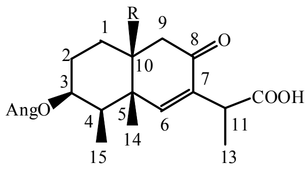
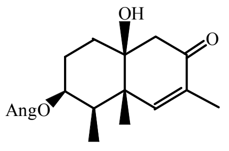
Abstract: Two new eremophilane sesquiterpenes, 3*β*-angeloyloxy-8-oxo-eremophil-6(7)-en-12-oic acid **1** and 3*β*-angeloyloxy-10*β*-hydroxy-8-oxo-eremophil-6 (7)-en-12-oic acid **2**, and a novel nor-eremophilane derivative, 3*β*-angeloyloxy-10*β*-hydroxy-8-oxo-eremophil-6(7)-en **3** were isolated from the roots of *Cacalia ainsliaeflora*. Their structures were elucidated by spectroscopic methods, including 2D NMR.

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

In a previous study, we reported five eremophilane sesquiterpenes from *Cacalia ainsliaeflora*[1]. In continuation of our investigation on sesquiterponoids from this plant, here we describe the structural elucidation of two new eremophilane sesquiterpenes and a novel nor-eremophilane derivative.



1 R = H
2 R = OH



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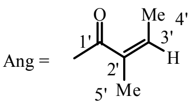

Compound **1**, colorless gum; $[\alpha]_D^{20}$ +10.8 (*c* 0.55, $CHCl_3$). The IR spectrum indicated the presence of a typical *α*, *β*-unsaturated ketone ($1675cm^{-1}$) and carboxyl group (1710, $1736cm^{-1}$). The molecular formula, $C_{20}H_{28}O_5$, was determined by HRESIMS *m/z* 349.2013 ($[M+H]^+$, calcd. 349.2010). The NMR data of **1** were similar to those reported in the literature[2]. The ^1H, ^{13}C NMR and DEPT-NMR (**Table 1**) indicated the presence of three methyl groups characterized of an eremophilenolide [δ 1.34 (d, 3H, *J*=7.1, H-13), δ 1.24 (s, 3H, H-14), δ 1.00 (d, 3H *J*=7.0, H-15)], an angeloyl group and an olefin [δ 6.63 (br s, 1H, H-6), δ 154.6 (C-6)], an oxygen-bearing methine [δ 4.90 (dt, 1H, *J*=5.4, 3.9Hz, H-3), δ 73.0 (C-3)] and a carbonyl group [δ 197.9 (C-8)]. The signal of H-9 was double doublets [δ 2.38 (dd, 1H, *J*=17.5, 4.8Hz, H-9*α*), δ 2.64

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Table 1 ^{1}H (400MHz) and ^{13}CNMR (100MHz) and DEPT data of **1-3** (CDCl$_3$) (δ ppm, *J* Hz)

H	**1** δ$_H$	**2** δ$_H$	**3** δ$_H$
1	2.10 m	2.38 m	2.24 m
	1.95 m	2.12 m	2.00 m
2	1.73 m	1.85 m	1.83 m
	1.25 m	1.71 m	1.68 m
3	4.90 ddd (6.0, 3.9, 3.9)	4.96ddd (5.4, 3.0, 3.0)	4.98 ddd (5.4, 3.3, 3.1)
4	1.53 dq	1.65 dq	1.60 dq
6	6.63 brs	6.59 brs	6.66 d (2.1)
9	2.64 dd(17.5,4.8)	2.85 d (16.5)	2.90 d (16.7)
	2.38 dd(17.5,4.8)	2.51 d (16.5)	2.55 d (16.7)
10	2.10 m		
11	3.58 brq (7.2)	3.57 brq (7.0)	2.34 s
12			1.24 s
13	1.34 d (7.1)	1.25 d (7.0)	1.03 d (7.2)
14	1.24 s	1.32 s	
15	1.00 d (7.0)	1.14 d (7.0)	
OAng	6.09 brq (7.2)	6.08 brq (7.1)	6.09 brq (7.0)
	1.99 dq (7.2, 1.2)	1.95 brd (7.1)	2.03 dq (7.0, 1.5)
	1.90 brs	1.89 brs	1.94 brd (1.4)

C	**1** δ$_C$	**2** δ$_C$	**3** δ$_C$
1	24.6 (CH$_2$)	25.4 (CH$_2$)	27.1 (CH$_2$)
2	25.8 (CH$_2$)	33.3 (CH$_2$)	30.1 (CH$_2$)
3	73.0 (CH)	73.6 (CH)	72.0 (CH)
4	41.2 (CH)	43.3 (CH)	41.8 (CH)
5	39.9 (C)	45.2 (C)	55.1 (C)
6	154.6 (CH)	154.2 (CH)	152.5 (CH)
7	136.6 (C)	137.1 (C)	141.5 (C)
8	197.9 (C)	197.1 (C)	197.3 (C)
9	39.7 (CH$_2$)	48.6 (CH$_2$)	41.5 (CH$_2$)
10	36.2 (CH)	74.5 (C)	81.3 (C)
11	38.6 (CH)	38.2 (CH)	8.7 (CH$_3$)
12	178.4 (C)	175.6 (C)	14.9 (C H$_3$)
13	15.8 (CH$_3$)	16.4 (CH$_3$)	13.6 (CH$_3$)
14	24.6 (CH$_3$)	18.8 (CH$_3$)	
15	8.8 (CH$_3$)	11.4 (CH$_3$)	
OAng	167.3 (C)	167.4 (C)	167.7 (C)
	138.0 (CH)	138.0 (CH)	138.6 (CH)
	128.0 (C)	129.0 (C)	127.7 (C)
	20.7 (CH$_3$)	20.9 (CH$_3$)	20.9 (CH$_3$)
	15.8 (CH$_3$)	15.8 (CH$_3$)	15.7 (CH$_3$)

(dd, 1H, *J*=17.5, 4.8Hz, H-9*β*)] due to the coupling $J_{9\alpha 9\beta}$ and $J_{9,10}$. These spectral data agreed with the proposed structure **1**. The localization of the angeloyloxy moiety at the C-3 position was deduced from the HMBC spectrum in which H-3 gave a long-range coupling with $C_{1'}$ (δ 167.3) and C-3 gave a long-range coupling with H-15. The long-range coupling between C-12 and H-13, H-11 (δ 3.58 brq, 1H, *J*=7.2 Hz) indicated that a carboxyl group was at C-11 position. The coupling pattern observed for H-3 at δ 4.90 (ddd, 1H, *J*=6.0, 3.9, 3.9Hz) implied that the angeloyl group at C-3 was *β*-equatorial[2, 3], and this was supported by the NOESY cross peak between H-3 and H-4*α*.

The NOESY cross-peak between H-4 and H-9α (δ 2.38, dd, 1H), H-10 and H-14, H-6 and H-3α further confirmed an A/B *cis*-fused eremophilane. Therefore compound **1** was determined as 3β-angeloyloxy -8-oxo- eremophil-6 (7)-en-12-oic acid.

Compound **2**, colorless gum, $[\alpha]_D^{20}$ +33.8 (*c* 0.68, $CHCl_3$). The molecular formula, $C_{20}H_{28}O_6$, was deduced by HRESIMS *m/z* 382.2228 ($[M+NH_4]^+$, calcd. 382.2224). The NMR (**Table 1**) and IR data of **2** were similar to those of **1** except for a hydroxy-bearing quaternary carbon (δ 74.5) in **2** instead of a methine (δ 36.2, CH) in **1**. The downfield shift of the H-14 methyl singlet (δ 1.32) and an oxygen-bearing quaternary carbon (δ 74.5) obviously required an β-orientated hydroxyl at C-10[4]. Therefore, the structure of **2** was determined to be 3β-angeloyloxy-10β-hydroxy-8-oxo-eremophil-6 (7)-en-12-oic acid.

Compound **3**, a colorless gum, $[\alpha]_D^{20}$ +80 (c 0.20, $CHCl_3$). The molecular formula, $C_{18}H_{26}O_4$, was determined by HRESIMS *m/z* 329.1709 $[M+Na]^+$ (calcd. 329.1723), ^{13}C NMR and DEPT NMR. The NMR data of **3** were similar to those of **2** except for the signals of H-11, C-11 and C-12 were missing and the presence of a methyl singlet at δ 2.34 in **3** instead of the methyl doublet at δ 1.25 (d, *J*=7.0 Hz) in **2**. These data suggested that the methyl (δ 2.34) was located at C-7. The ^1H-^1H COSY and HMBC experiments supported the structure of **3**.

Acknowledgments

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