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Two New *ent*-Kaurenoids from *Cacalia pilgeriana*

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Abstract: Two new *ent*-kaurenoids, 19-acetyl-*ent*-3β, 17-dihydroxykaur-15-ene (**1**), 19-acetyl-*ent*-3β-hydroxykaur-15-en-17-al (**2**) were isolated from *Cacalia pilgeriana*. Their structures were elucidated by spectroscopic methods.

Keywords: *Cacalia pilgeriana*, Compositae, *ent*-kaurenoids.

Phytochemically, the genus *Cacalia* was characterized by containing sesquiterpenes[1-3], only Nasr reported a series of kaurenoid diterpenes from *Cacalia bulbifera*[4]. In this paper, we describe the structural elucidation of two new *ent*-kaurenoids isolated from the methanol extract of the roots of *Cacalia pilgeriana* (Diels) Ling.

Compound **1** was obtained as colorless crystal from acetone, mp. 157-158℃, $[\alpha]_D^{23}$ -55 (*c* 3.4, CH_3OH). The molecular formula $C_{22}H_{34}O_4$ was yielded based on the EI-MS at *m/z* 362 ($[M]^+$), which was also confirmed by HRESI-MS at *m/z* 345.2425 $[M-H_2O+H]^+$ (calcd. 345.2424) and 327.2299 $[M-2H_2O+H]^+$ (calcd. 327.2319). The ^1H NMR spectrum of **1** showed the signals for three tertiary methyls (δ 1.03, 1.13 and 2.07, s, each 3H), two oxygenated methylenes (δ 4.12 and 4.33, d, each 1H, J = 11.2 Hz; δ 4.55, s, 2H), an oxygenated methine (δ 3.28, dd, 1H, J = 11.2, 5.2 Hz) and an olefinic methine (δ 5.48, s, 1H). Furthermore, the ^{13}C NMR and DEPT spectra showed 22 signals for $3\times CH_3$, $9\times CH_2$ (two of which were oxygenated), $5\times CH$ (one was oxygenated), $5\times C$ (one was carbonyl). The NMR spectral data of **1** were similar to those of *ent*-3β, 19-dihydroxykaur-16-ene and its diacetated derivative[5], the differences were only that the olefinic bond in **1** was located at C-15 (16), and a hydroxylmethyl group at C-17. This was confirmed by the correlation of H-15 with C-17, and H-17 with C-15 in the HMBC spectrum. The acetyl group located at C-19 which was deduced by the presence of the HMBC cross peak of H-19 with CH_3CO (δ_C 171.18). The chemical shift of H-3 (δ 3.28, dd, J = 11.2, 5.2 Hz) showed the hydroxyl group was α-orientation[6]. Thus, compound **1** was determined as 19-acetyl-*ent*-3β, 17-dihydroxykaur-15-ene.

Compound **2**, colorless gum, $[\alpha]_D^{23}$ -82 (*c* 0.1, CH_3OH), has the molecular formula $C_{22}H_{32}O_4$ deduced from its HRESI-MS at *m/z* 361.2369 $[M+H]^+$ (calcd. 361.2373). Its NMR spectral data were very similar to those of **1** except for the presence of a –CHO in

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2 (C-17: δ_H, 9.72, s, 1H; δ_C, 189.35) instead of the $-CH_2OH$ in **1** (C-17: δ_H, 4.55, s, 2H; δ_C, 75.02). Therefore, compound **2** was elucidated as 19-acetyl-*ent*-3β-hydroxykaur-15-en-17-al.

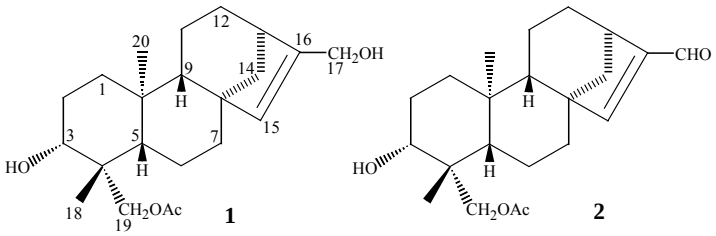

Table 1 ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) and DEPT data of **1**, **2** ($CDCl_3$, TMS, δ ppm)

No.	**1** δ_H	**2** δ_H	**1** δ_C	DEPT	**2** δ_C	DEPT
1			39.15	CH_2	38.38	CH_2
2			25.30	CH_2	25.06	CH_2
3	3.28 (dd, 11.2, 5.2)	3.27 (dd, 11.2, 6.0)	79.17	CH	79.04	CH
4			42.27	C	42.23	C
5			55.49	CH	55.43	CH
6			19.44	CH_2	19.18	CH_2
7			43.45	CH_2	42.75	CH_2
8			48.95	C	46.84	C
9			48.06	CH	46.64	CH
10			38.99	C	38.81	C
11			18.78	CH_2	18.62	CH_2
12			27.18	CH_2	27.21	CH_2
13	2.64 (m)	3.04 (m)	41.58	CH	40.80	CH
14			38.77	CH_2	37.90	CH_2
15	5.48 (s)	6.55 (s)	140.35	CH	139.99	CH
16			141.31	C	148.83	C
17	4.55 (s)	9.72 (s)	75.02	CH_2	189.35	CH
18	1.13 (s)	1.14 (s)	22.39	CH_3	22.49	CH_3
19	4.12 (d, 11.2), 4.33 (d, 11.2)	4.11 (d, 11.7), 4.32 (d, 11.7)	65.34	CH_2	65.20	CH_2
20	1.03 (s)	1.06 (s)	17.81	CH_3	17.84	CH_3
OAc			171.18	C	171.05	C
	2.07 (s)	2.07 (s)	21.10	CH_3	21.10	CH_3

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