Chinese Chemical Letters Vol. 11, No. 11, pp. 995–996, 2000

Two New *ent*-Kaurane Diterpenoids from *Isodon adenantha*

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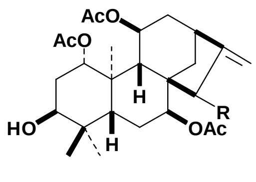
Abstract: Two new *ent*-kaurane diterpenoids, adenanthins B (**1**) and C (**2**), were isolated from the EtOAc extract of *Isodon adenantha*. Their structures were elucidated by spectroscopic evidences.

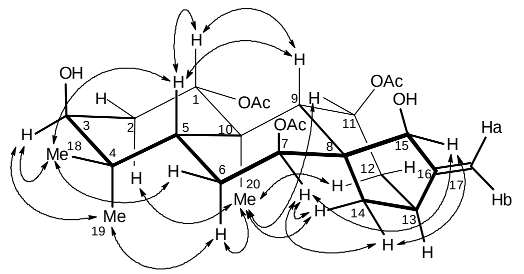
Keywords: *Isodon adenantha*, Labiatae, *ent*-kaurane diterpenoids, adenanthins B (**1**) and C (**2**).

As a medicinal herb locally used for the treatment of enteritis and dysentery in Yunnan province[2], *Isodon adenantha* (Diels) Hara has been previously studied, which led to the isolation of several *ent*-kaurane diterpenoids including a new one[3-5]. In continuation of our research on the bio-active constituents from *Isodon* species[6], two new *ent*-kaurane diterpenoids, adenanthins B (**1**) and C (**2**), were isolated from *I. adenantha* collected in Dali, Yunnan. In this paper, we report the structural elucidation of these new compounds by spectral analysis.

Figure 1 Key ROESY correlations of compound **1**



1 R = β-OH
2 R = =O



Adenanthin B (**1**), colorless crystals, possessed a molecular formula of $C_{26}H_{38}O_8$ deduced by the negative FABMS molecular ion peak at *m/z* 479 combining with analysis of its ^{1}H and ^{13}C NMR spectral data. The IR, MS and NMR of **1** indicated the presence of three acetoxyl groups, three methyl groups, five methylenes (including one *exo*-methylene group), eight methines (including five oxygenated methines) and four quaternary carbons. Considering the structures of the compounds isolated from this plant, **1** was suggested to have an *ent*-kaurene skeleton. This conclusion was verified by 2D-NMR experiments. In the HMBC spectrum, the correlations were clearly observed among Me-20 (with C-1, C-5, C-9 and C-10), H-5 (with C-3, C-4, C-6, C-7, C-10 and Me-18, 19), H-11 (with C-8, C-10, C-12 and C-13) and H-15 (with C-7, C-14 and C-16). Meanwhile, according to the cross peaks in HMBC spectrum, three acetoxyl groups were

obviously located at C-1, C-7 and C-11, respectively. Moreover, inspection of MS and NMR spectra of **1** suggested the presence of two hydroxyl groups at C-3 and C-15. The relative configurations of the substituents were revealed by NOE experiment, and the key correlations in ROESY spectrum were shown in **Figure 1**. Thus, **1** was elucidated as 3β,15β-dihydroxy- 1α,7β,11β-triacetoxy-*ent*-kaur-16-en.

Using the same methods mention-above, **2** was determined as 3β-hydroxy-1α,7β,11β- triacetoxy-*ent*-kaur-16-en-15-one.

Adenanthin B (**1**) ^{1}H NMR (400.13 MHz, C_5D_5N) δ: 6.45 (1H, *br s*, OH-3), 5.90 (1H, *t*, *J* = 3.8 Hz, H-11α), 5.83 (1H, *dd*, *J* = 5.1, 10.6 Hz, H-1β), 5.23 (1H, *s*, H-17a), 5.18 (1H, *br s*, H-7α), 4.95 (1H, *d*, *J* = 2.5 Hz, H-17b), 4.43 (1H, *dd*, *J* = 2.5, 11.1 Hz, H-15α), 3.71 (1H, *t*, *J* = 2.5 Hz, H-3α), 3.37 (1H, *d*, *J* = 11.1 Hz, OH-15), 2.62 (1H, *br s*, H-9β), 2.58 (1H, *dd*, *J* = 1.8, 12.4 Hz, H-5β), 2.50 (1H, *m*, H-13α), 2.12 (2H, *overlap*, H_2-2), 1.98 (2H, *overlap*, H_2-12), 1.75 (1H, *overlap*, H-14α), 1.72 and 1.75 (each 1H, *overlap*, H-6α and 6β), 1.28, 1.12 and 0.90 (each 3H, *s*, Me-20, 18, 19), 1.21 (1H, *dd*, *J* = 4.4, 11.9 Hz, H-14β), 2.19, 2.10 and 1.84 (each 3H, *s*, 3×OAc).

Adenanthin C (**2**) ^{1}H NMR (400.13 MHz, C_5D_5N) δ: 6.46 (1H, *br s*, OH-3), 5.92 (1H, *t*, *J* = 4.3 Hz, H-11α), 5.77 (1H, *dd*, *J* = 4.4, 11.0 Hz, H-1β), 5.87 (1H, *s*, H-17a), 5.42 (1H, *br s*, H-7α), 5.10 (1H, *s*, H-17b), 3.69 (1H, *br s*, H-3α), 2.59 (1H, *s*, H-9β), 2.73 (1H, *dd*, *J* = 5.2, 9.3 Hz, H-5β), 2.88 (1H, *m*, H-13α), 2.29 (2H, *overlap*, H_2-2), 2.11 (2H, *overlap*, H_2-12), 2.15 (1H, *overlap*, H-14α), 2.18 (2H, *overlap*, H_2-6), 1.35, 1.11 and 0.89 (each 3H, *s*, Me-20, 18, 19), 1.55 (1H, *br d*, *J* = 10.6 Hz, H-14β), 2.15, 2.15 and 1.69 (each 3H, *s*, 3×OAc).

Table 1. ^{13}C NMR Data for Adenanthins B (**1**) and C (**2**) in C_5D_5N (100.6 MHz, δ in ppm)

C	1	2	C	1	2
C-1	80.3 (d)	80.5 (d)	C-14	35.4 (t)	36.3 (t)
C-2	33.7 (t)	33.6 (t)	C-15	81.4 (d)	204.7 (s)
C-3	75.2 (d)	73.0 (d)	C-16	158.3 (s)	151.6 (s)
C-4	37.7 (s)	38.0 (s)	C-17	105.7 (t)	112.6 (t)
C-5	39.1 (d)	39.5 (d)	C-18	28.8 (q)	29.3 (q)
C-6	24.8 (t)	25.0 (t)	C-19	22.2 (q)	22.5 (q)
C-7	78.7 (d)	75.6 (d)	C-20	14.2 (q)	15.1 (q)
C-8	48.0 (s)	51.0 (s)	OAc	170.7 (s)	170.7 (s)
C-9	50.2 (d)	56.3 (d)		170.4 (s)	170.5 (s)
C-10	43.0 (s)	44.0 (s)		169.0 (s)	169.6 (s)
C-11	70.6 (d)	70.2 (d)		21.9 (q)	22.2 (q)
C-12	40.2 (t)	39.3 (t)		21.5 (q)	21.9 (q)
C-13	38.6 (d)	37.0 (d)		21.3 (q)	21.4 (q)

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Received 30 May 2000