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Two New Diterpenoids from *Isodon rubescens*

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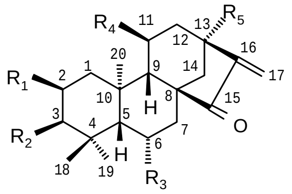
Abstract: Two new diterpenoids taibairubescensin A (**1**) and B (**2**) have been isolated from *Isodon rubescens*. The structures of compound **1** and **2** were elucidated as 2β,3β-diacetoxy-11β,13α-dihydroxy-*ent*-kaur-16-en-15-one (**1**) and 3β,11β-diacetoxy-2β,6α-dihydroxy-*ent*-kaur-16-en-15-one (**2**) on the basis of spectroscopic analysis.

Keywords: *Isodon rubescens*, taibairubescensin A, taibairubescensin B, *ent*-kaurene diterpenoids.

In order to further study on minor diterpenoid constituents of *Isodon rubescens*, we reinvestigated this species, which was collected in Taibai mountain, Shaanxi Province. Two new diterpenoids, taibairubescensins A (**1**) and B (**2**), were isolated. In this paper, we present the structure elucidation of these two new diterpenoids.



1.R_1=R_2=OAc, R_3=H, R_4=R_5=OH
2.R_1=OH, R_2=OAc, R_3=OH R_4=OAc,R_5=H
3.R_1=H, R_2=OH, R_3=H, R_4=R_5=OH
4.R_1=OH, R_2=OAc, R_3=R_4=OH,R_5=H

Taibairubescensin A (**1**), $C_{24}H_{34}O_7$ (FABMS *m/z* 435$[M+1]^+$), an amorphous powder, showed UV and IR absorption bands for the existence of hydroxyl, acetoxyl and a five-membered ring ketone conjugated with an *exo*-methylene functions (240.5nm; 3468, 1740, 1732 and 1649 cm^{-1}). The ^{13}C-NMR (**Table 1**) and DEPT spectra of **1** showed signals for this compound with 5×CH_3, 5×CH_2, 5×CH, 4×C, two olefinic carbons, one ketonic carbon and two ester carbonyl carbons. These data suggested that **1** possessed a basic skeleton of *ent*-kaur-16-en-15-one with two acetoxyls and two hydroxyls. The ^{1}H-, ^{13}C-NMR data of **1** were very similar to those of deacetylisodopharicin A (**3**)[1] except for one more acetyl groups. Comparison of their

^{13}C-NMR data indicated that the difference between **1** and **3** was only in A ring. This ment that two hydroxyls were at C-11β and C-13α, and two acetoxyls were in A ring, respectively, in compound **1**. In the ^{1}H-^{1}H COSY spectrum of **1**, the signal at δ 4.98 (1H, d, *J* = 2.6 Hz, H-3α) showed correlation with the signal at δ 5.24 (1H, ddd, *J* = 12.3, 2.6, 3.9 Hz, H-2α), the latter showed correlation with both signals at δ 1.59 (1H, dd, *J* = 11.9, 3.9 Hz, H-1α) and δ 1.91 (1H, dd, *J* = 11.9, 12.3 Hz, H-1β). Thus two acetoxyl groups should be located at the C-3 and C-2 positions, respectively. The relative configurations were established as 2β-OAc and 3β-OAc by considering the coupling constants of H-2 and H-3. These cases were further confirmed by NOESY spectrum of **1**. Therefore, compound **1** should be elucidated as 2β,3β-diacetoxy-11β,13α-dihydroxy-*ent*-kaur-16-en-15-one.

Taibairubescensin B (**2**), $C_{24}H_{34}O_7$ [HRFABMS(pos.) *m/z*: 435.2364[M+1], calc. 435.2382], an amorphous powder, showed UV and IR absorption bands for the existence of hydroxyl and a five-membered ring ketone conjugated with an *exo*-methylene functions (243.5nm; 3473, 1738, 1648 cm^{-1}). The ^{13}C-NMR (**Table 1**) and DEPT spectra of **2** clearly indicated that the compound **2** was an *ent*-kaurene diterpenoid derivative with two acetoxyl groups and two hydroxyl groups. The ^{13}C-NMR spectrum of **2**, compared with that of Lusanrubescensin D (**4**)[2], differed from that of **4** only in chemical shift at C-11. The chemical shift of the C-11 is δ 65.1 in **4**, but it is δ 68.5 in **2**. This fact indicated that the acetoxyl group at the C-11β position in **2** had replaced the hydroxyl group in **4**. These assignments were further confirmed by ^{1}H-^{1}H COSY and HMBC spectra of **2**. Thus, taibairubescensin B (**2**) was established as 3β,11β-diacetoxy-2β,6α-dihydroxy-*ent*-kaur-16-en-15-one.

Table 1. ^{13}C NMR data* for **1** and **2**

Carbon	**1**	**2**	Carbon	**1**	**2**	Carbon	**1**	**2**	Carbon	**1**	**2**
1	37.9 t	43.2t	7	32.5 t	41.1t	13	75.3 s	37.0d	19	21.3q	22.6q
2	67.5d	65.0d	8	52.8 s	48.4s	14	44.9 t	37.7 t	20	18.3q	19.9q
3	76.6d	80.9d	9	61.9d	62.9d	15	207.3 s	208.7s	OAc	170.4s	171.9s
4	38.1s	38.4s	10	39.6 s	39.4s	16	151.9 s	149.1s		170.6s	169.8s
5	48.6d	48.4d	11	66.7d	68.5d	17	113.7 t	113.7t		20.9q	21.1q
6	17.6 t	65.8d	12	48.2 t	37..3t	18	27.8q	28.2q		21.0q	21.6q

*Recorded in $CDCl_3$; chemical shift values reported as δ values (ppm) from TMS at 100.6MHz .

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