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A New *ent*-Kaurane Diterpenoid from *Isodon enanderianus*

Zhi NA[1], Bei JIANG[1], Hui YANG[2], Zhong Wen LIN[1], Han Dong SUN[1]*

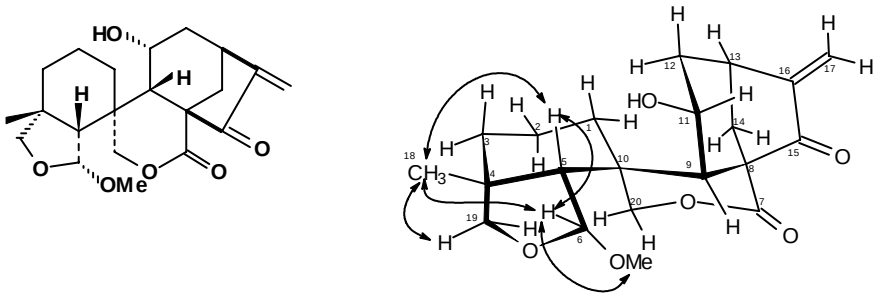
[1]Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204
[2]Chemistry Deparment of the College of Life Science and Chemistry, Yunnan University, Kunming 650091

Abstract: A new spirosecokaurenoid, enanderinanin F **1** and its C-6 epimer, angustifolin were isolated from the aerial parts of *Isodon enanderianus.* The structure of **1** was determined on the basis of spectral data, especially by 2D techniques. The ^{13}C NMR data of angustifolin were revised by 2D NMR.

Keywords: *Isodon enanderianus*, *ent* -kaurane diterpenoid, enanderinanin F, angustifolin.

Isodon enanderianus (Hand. -Mazz.) H. W. Li, has been used in folk medicine as anti-inflammatory and detoxified agent[1]. The *Isodon* genus is known to be rich in *ent*-kaurane diterpenoids, a series of new *ent*-kaurane diterpenoids have been isolated from the dried leaves of *I. enanderianus*[2-4]. In order to find more biologically active substances, we have carefully investigated the chemical constituents of *I. enanderianus* collected in Shiping county of Yunnan province, and as a result, enanderinanin F **1** and angustifolin were isolated from the 70% acetone extract of the aerial parts of the title plant. In this paper, we present the structural elucidation of **1** and revised ^{13}C NMR data of angustifolin.

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



Enanderinanin F **1,** colorless crystals (from MeOH), mp: 240-242°C, $[\alpha]_D^{16.7}$ –94.7 (*c* 0.412, MeOH), was established to have a molecular formula of $C_{21}H_{28}O_6$ by EI mass

([M]$^+$ *m/z* 376), and ^{13}C NMR data including DEPT technique. The ^{13}C NMR of **1** indicated the presence of one methoxy group, one methyl group, eight methylenes (including two oxygenated methylenes), five methines (including two oxygenated methines) and six quaternary carbons (including one olefinic carbon, one ketonic carbon and one lactonic carbonyl). The ^{1}H and ^{13}C NMR spectra (**Table 1**) of **1** were very similar to those of angustifolin[5], so we assumed that **1** has the same skeleton as that of angustifolin, 6, 7-*seco*-*ent*-kaurene (spirolactone), which was verified by 2D NMR experiments. In the HMBC spectrum, the correlations were clearly observed among H-5 with C-6 and C-9, H-6 with C-4, C-10, C-19, H-13 with C-8, C-11, C-15 and C-16, H-19a and H-19b with C-3, C-5 and C-6, H-20a and H-20b with C-7, C-9 and C-10. Meanwhile, according to the cross peaks in HMBC spectrum, one methoxy group and one hydroxy group were obviously located at C-6 and C-11, respectively. The relative configuration of the substituents was revealed by NOE experiments. The significant difference between **1** and angustifolin in ROESY spectra was that there were correlations of H-6 with Me-18 and H-5β in **1**. Thus, the methoxy group at C-6 in **1** was α-orientation. The key correlations in ROESY spectrum were shown in **Figure 1.** Therefore, **1** was determined as 11 α-hydroxy-6α-methoxy-6, 7-*seco*-6, 19-epoxy-7, 20-olide-*ent*-kaur-16-en-15-one.

Enanderinanin F **1** ^{1}H NMR (400.13 MHz, C_5D_5N) δ ppm: 6.89 (*d*, 1H, *J*=3.6 Hz, OH-11α), 6.12 and 5.45 (*s*, each 1H, H_2-17), 5.29 (*ABd*, 1H, *J*=10.5 Hz, H-20a), 5.24 (*d*, 1H, *J*=4.6 Hz, H-6 β), 4.51 (*br d*, 1H, J=3.6 Hz, H-11β), 4.34 (*ABdd*, 1H, *J*=1.9, 10.5 Hz, H-20b), 3.72 and 3.63 (*ABd*, each 1H, *J*=8.1 Hz, H_2-19), 3.70 (*d*,1H, *J*=11.3 Hz, H-14α), 3.10 (*dd*, 1H, *J*=4.5, 9.0 Hz, H-13α), 2.46 (*dd*, 1H, *J*=9.0, 14.5 Hz, H-12α), 2.29 (*d*, 1H, *J*=4.6 Hz, H-5 β), 2.24 (*br s*, 1H, H-9β), 2.19 (*dd*, 1H, *J*=4.5, 11.3 Hz, H-14β), 1.79 (*overlap*, 1H, H-12β), 1.04 (*s*, 3H, Me-18), 3.24 (*s*, 3H, OMe).

Table 1 ^{13}C NMR data of compound **1** and angustifolin (revised) in C_5D_5N (100.6 MHz, δ in ppm)

Carbon	1	Angustifolin	Carbon	1	Angustifolin
1	26.8 (t)	27.0 (t)	12	42.3 (t)	42.4 (t)
2	19.5 (t)	18.8 (t)	13	35.1 (d)	34.7 (d)
3	35.3 (t)	32.8 (t)	14	34.4 (t)	35.0 (t)
4	38.7 (s)	41.8 (s)	15	200.0 (s)	199.4 (s)
5	49.7 (d)	52.2 (d)	16	151.4 (s)	151.4 (s)
6	107.5 (d)	107.3 (d)	17	118.1 (t)	118.2 (t)
7	171.6 (s)	171.5 (s)	18	25.0 (q)	21.6 (q)
8	54.4 (s)	54.5 (s)	19	82.1 (t)	79.6 (t)
9	44.2 (d)	43.4 (d)	20	74.2 (t)	74.1 (t)
10	38.2 (s)	37.7 (s)	OMe	54.4 (q)	55.1 (q)
11	65.6 (d)	65.7 (d)			

References

1. Kunming Institute of Botany, Chinese Academy of Sciences, *Flora Yunnannica*, Science Press, **1977,** vol. 1, p.764.
2. Y. H. Wang, Y. Z. Chen, Z. W. Lin, H. D. Sun, J. S. Fan, *Phytochemistry*, **1998**, *48* (7), 1267.
3. Y. H. Wang, Y. Z. Chen, Z. W. Lin, H. D. Sun, *Chin. Chem. Lett.*, **1998,** *9* (8), 733.
4. K. Zhang, Y. H. Wang, Y. Z. Chen, H. D. Sun, Z. W. Lin, *Acta Scientiarum Naturalium Universitatis Sunyatseni*, **1998,** *37* (2), 49.
5. H. D. Sun, Z. W. Lin, M. Yoshinori, M. Teruyoshi, *Acta Pharmaccutica Sinica* , **1984**, *19*(8), 633.

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