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# A new *ent*-abietane diterpenoid from *Isodon macrophyllus*

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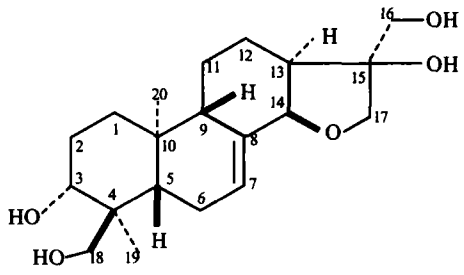
**Abstract**

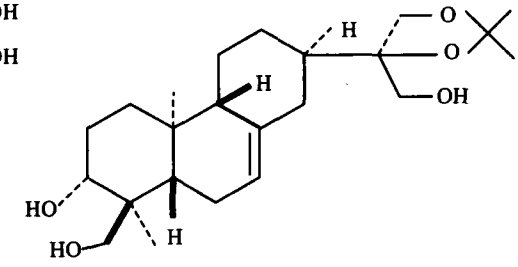
A new *ent*-abietane diterpenoid, named dayecrystal C, was isolated from the EtOAc extract of the dried leaves of *Isodon macrophyllus*. Its structure was determined on the basis of spectroscopic methods.


*Keywords:* *Isodon macrophyllus*; *ent*-Abietane; Diterpenoid; Dayecrystal C

In previous reports [1–4], we have isolated about twenty-six *ent*-kaurene diterpenoids including five new compounds from *Isodon macrophyllus*. Continued study of the extract of *I. macrophyllus* (Migo) C.Y. Wu and H.W. Li collected in Tongbai prefecture of Henan province of China, has resulted in obtaining a new highly oxidized *ent*-abietane diterpenoid, 15(*S*)-3α,15β,16,18-tetrahydroxy-14β,17-epoxy-*ent*-abieta-7(8)-ene(**1**), (dayecrystal C). In this paper, the structural elucidation is presented.



**1**



Maoyecrystal H

Dayecrystal C, a white amorphous powder, $[\alpha_D^{20}]$ −2.0 (*c* 0.4, MeOH), m.p. 140–143 °C, had a molecular formula $C_{20}H_{32}O_5$ based on its HR-ESI-MS (*m/z* 375.2144 $[M+Na]^+$, calcd. 375.2147), suggesting five degrees of

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Table 1
$^{13}C$ (100 MHz) and $^{1}H$ (400 MHz) NMR spectral date of 1 in $C_5D_5N$ ($\delta$ in ppm, $J$ in Hz)

| Position | $\delta_C$ | $\delta_H$ | Position | $\delta_C$ | $\delta_H$ |
|---|---|---|---|---|---|
| 1 | 38.0 (t) | 1.80 (m, 1H) 1.18 (m, 1H) | 11 | 24.3 (t) | 1.24 (m, 1H) 1.00 (dd, $J$ = 12.8, 1H) |
| 2 | 27.9 (t) | 1.93 (m, 2H) | 12 | 24.0 (t) | 1.89 (m, 1H) 1.68 (d, $J$ = 9.6, 1H) |
| 3 | 73.6 (d) | 4.22 (m, 1H) | 13 | 49.8 (d) | 2.31 (m, 1H) |
| 4 | 43.0 (s) | | 14 | 83.3 (d) | 5.10 (d, $J$ = 3.6, 1H) |
| 5 | 42.6 (d) | 1.98 (m, 1H) | 15 | 84.9 (s) | |
| 6 | 23.7 (t) | 1.20 (m, 2H) | 16 | 67.6 (t) | 4.13 (d, $J$ = 10.8, 1H) 4.02 (d, $J$ = 10.8, 1H) |
| 7 | 128.8 (d) | 5.85 (br s, 1H) | 17 | 75.8 (t) | 4.20 (s, 2H) |
| 8 | 135.8 (s) | | 18 | 64.5 (t) | 4.07 (d, $J$ = 10.8, 1H) 3.60 (d, $J$ = 10.8, 1H) |
| 9 | 49.8 (d) | 2.11 (m, 1H) | 19 | 12.9 (q) | 1.12 (s, 3H) |
| 10 | 35.0 (s) | | 20 | 15.4 (q) | 0.84 (s, 3H) |

unsaturation. The IR spectrum of **1** displayed two strong absorptions at 3447 and 3306 $cm^{-1}$ (OH) and a weak band at 1629 $cm^{-1}$ corresponding to a double bond. In the $^{13}C$ NMR and DEPT spectrum of **1** (Table 1) showed the presence of two methyl groups, eight methylene groups, five methine groups, three quaternary carbons, two olefinic carbons, suggesting a tricyclic diterpene skeleton. Comparison of the spectroscopic data of compound **1** with those of maoyecrystal H [5] revealed a close similarity between two compounds except for C-14, C-15, C-16 and C-17. The 15, 16-*O*-isopropylidene in maoyecrystal H was replaced by OH-15β and OH-16, and the formation of an O-bridge between C-14 and C-17 was established by the $^{1}H$, $^{13}C$ long-range correlations of $H_2$-17/C-14 and H-14/C-17 in the HMBC spretrum (Fig. 1) in compound **1**. Two olefinic C-atoms at $\delta_C$ 128.8 (d) and $\delta_C$ 135.8 (s), together with the olefinic proton at $\delta_H$ 5.85 (br s, 1H), which was correlated with C-5 (42.6, d) in the HMBC spectrum, indicated the presence of a C=C bond between C-7 and C-8.

The relative configuration of **1** was deduced by NOESY experiments (Fig. 2). In this group of compounds (*ent*-abietane diterpenoids from the genus *Isodon*), H-5, H-9, H-13 and Me-20 have the β, β, α and α orientation, respectively [6]. Thus, compound **1** has the orientation of OH-3α, H-14α and OH-15β, which was determined by the

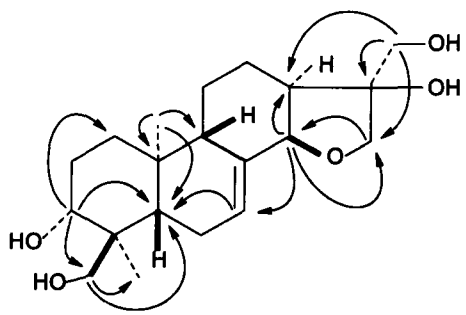


Fig. 1. Key HMBC correlations of compound **1**.

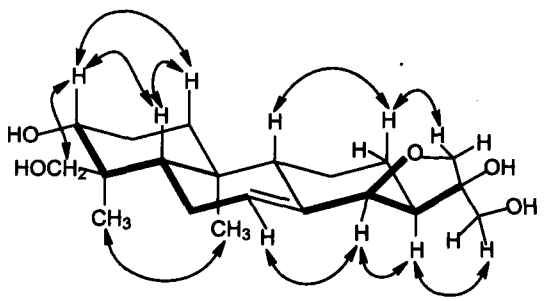


Fig. 2. Key NOESY correlations of compound **1**.

NOE correlations of H-3 with H-1, H-5, H-18, and H-14 with H-7, H-13, and H-13 with H-16. Therefore, compound **1** was assigned as 15(*S*)-3α,15β,16,18-tetrahydroxy-14β,17-epoxy-*ent*-abieta-7(8)-ene and named dayecrystal C.

Dayecrystal C (**1**): $C_{20}H_{32}O_5$, white amorphous powder, $[\alpha_D^{20}]$ −2.0 (*c* 0.4, MeOH), m.p. 140–143 °C, IR $\nu^{KBr}$ $cm^{-1}$: 3447, 3306, 2993, 2936, 2882, 1629, 1469, 1447, 1383, 1344, 1279, 1267, 1066, 1030, 1008, 956, 914. HR-ESI-MS *m/z*: 375.2144 $[M + Na]^+$ (calcd. 375.2147).

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