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.

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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.

Dayecrystal C, a white amorphous powder, [α] D 20 2.2 (c 0.4, MeOH), m.p. 140–143 °C, had a molecular formula C20H32O5 based on its HR - ESI - MS ( m/z 375.2144 [M + Na] + , calcd. 375.2147 ), suggesting five degrees of

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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 \(^{13}\text{C}\) 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-15\(\beta\) and OH-16, and the formation of an O-bridge between C-14 and C-17 was established by the \(^1\text{H}, \ ^{13}\text{C}\) long-range correlations of H\(_2\)-17/C-14 and H-14/C-17 in the HMBC spectrum (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-abietaene diterpenoids from the genus \textit{Isodon}), H-5, H-9, H-13 and Me-20 have the \(\beta\), \(\beta\), \(\alpha\) and \(\alpha\) orientation, respectively [6]. Thus, compound 1 has the orientation of OH-3\(\alpha\), H-14\(\alpha\) and OH-15\(\beta\), which was determined by the

### Table 1

\(^{13}\text{C}\) (100 MHz) and \(^1\text{H}\) (400 MHz) NMR spectral data of 1 in \(\text{C}_6\text{D}_6\)N (\(\delta\) in ppm, \(J\) in Hz)

<table>
<thead>
<tr>
<th>Position</th>
<th>(\delta_C)</th>
<th>(\delta_H)</th>
<th>Position</th>
<th>(\delta_C)</th>
<th>(\delta_H)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>38.0 (t)</td>
<td>1.80 (m, 1H)</td>
<td>11</td>
<td>24.3 (t)</td>
<td>1.24 (m, 1H)</td>
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<tr>
<td>2</td>
<td>27.9 (t)</td>
<td>1.93 (m, 2H)</td>
<td>12</td>
<td>24.0 (t)</td>
<td>1.89 (m, 1H)</td>
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<tr>
<td>3</td>
<td>73.6 (d)</td>
<td>4.22 (m, 1H)</td>
<td>13</td>
<td>49.8 (d)</td>
<td>2.31 (m, 1H)</td>
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<tr>
<td>4</td>
<td>43.0 (s)</td>
<td></td>
<td>14</td>
<td>83.3 (d)</td>
<td>5.10 (d, (J=3.6), 1H)</td>
</tr>
<tr>
<td>5</td>
<td>42.6 (d)</td>
<td>1.98 (m, 1H)</td>
<td>15</td>
<td>84.9 (s)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>23.7 (t)</td>
<td>1.20 (m, 2H)</td>
<td>16</td>
<td>67.6 (t)</td>
<td>4.13 (d, (J=10.8), 1H)</td>
</tr>
<tr>
<td>7</td>
<td>128.8 (d)</td>
<td>5.85 (br s, 1H)</td>
<td>17</td>
<td>75.8 (t)</td>
<td>4.20 (s, 2H)</td>
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<tr>
<td>8</td>
<td>135.8 (s)</td>
<td></td>
<td>18</td>
<td>64.5 (t)</td>
<td>4.07 (d, (J=10.8), 1H)</td>
</tr>
<tr>
<td>9</td>
<td>49.8 (d)</td>
<td>2.11 (m, 1H)</td>
<td>19</td>
<td>12.9 (q)</td>
<td>1.12 (s, 3H)</td>
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<tr>
<td>10</td>
<td>35.0 (s)</td>
<td></td>
<td>20</td>
<td>15.4 (q)</td>
<td>0.84 (s, 3H)</td>
</tr>
</tbody>
</table>

![Fig. 1. Key HMBC correlations of compound 1.](image1)

![Fig. 2. Key NOESY correlations of compound 1.](image2)
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(5)-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, [α]_{D}^{20} = -2.0 (c 0.4, MeOH), m.p. 140-143 °C, IR ν_{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).

References