A new menthane-type monoterpeno from *Pleurotus eryngii*

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[ABSTRACT] A new menthane-type monoterpeno, pleurolactone (1), was isolated from the culture broth of the fungus *Pleurotus eryngii*, along with five known compounds 1, 2-dihydroxymint lactone (2), (22E, 24R)-ergosta-5, 7, 22-trien-3β-ol (3), (22E, 24R)-ergosta-7, 22-dien-3β-β, 5α, 6β-triol (4), (22E, 24R)-ergosta-7, 22-dien-3β-β, 5α, 6β-triol (5) and cerebroside B (6). Their structures were identified by extensive spectroscopic analyses.

[KEY WORDS] *Pleurotus eryngii*, Menthane-type monoterpeno; Pleurolactone


1 Introduction

*Pleurotus eryngii* (DC.) Quél. (Pleurotaceae) (King oystar), the largest species of the oyster mushroom genus, is well known for its good taste. Its original distribution is located in Northern Africa, Southern Europe, and Central Asia[1], and in the 1990s, it was introduced into China. The previous chemical investigation on *P. eryngii* revealed several polysaccharides with various biological activities[2], such as hepatoprotective, hypolipidemic[3], antioxidant[4], antitumor and immunomodulating functions[5]. However, little attention was paid on its small-molecular constituents. As a part of efforts to discover structurally diverse and biologically significant metabolites from higher fungi[6-9], the investigation was paid on its small-molecular constituents. As a part of efforts to discover structurally diverse and biologically significant metabolites from higher fungi[6-9], the investigation led to the isolation of a new menthane-type monoterpeno, named pleurolactone (1), along with five known compounds 1, 2-dihydroxymint lactone (2)[10], (22E, 24R)-ergosta-5, 7, 22-trien-3β-ol (3)[11], (22E, 24R)-ergosta-7, 22-diene-3β, 5α, 6β-triol (4)[12], (22E, 24R)-ergosta-7, 22-dien-3β-ol (5)[13], and cerebroside B (6)[14].

The structure of 1 was elucidated by extensive spectroscopic analyses, while the known compounds were identified by comparison with the NMR data in the literature. All these compounds were isolated from this fungus for the first time.

2 Materials and Methods

The fungus *P. eryngii* was collected in Kunming, and identified by Prof. YANG Zhu-Liang, Kunming Institute of Botany. The culture medium consisted of potato (peeled, 200 g), glucose (20 g), KH2PO4 (3 g), and MgSO4 (3 g) in deionized water (1 L). The pH was adjusted to 6.5 before autoclaving, and the fermentation was carried out in a shaker (150 r/min) at 25 °C for 25 days. The culture broth (20 L) was extracted with EtOAc three times, and the organic layer was concentrated under reduced pressure to give a crude extract (19 g). This residue was subjected to column chromatography (CC) over silica gel using a petroleum ether/acetone gradient (1 : 0 → 0 : 1) to afford fractions A–F. Fraction C was separated by CC over Sephadex LH-20 (CHCl3/MeOH, 1 : 1) to obtain two subfractions, C-1 and C-2. Subfraction C-1 was purified by CC over silica gel using a petroleum ether/acetone gradient (1 : 0 → 0 : 1) to afford fractions A–F. Fraction C was separated by CC over Sephadex LH-20 (CHCl3/MeOH, 1 : 1) to obtain two subfractions, C-1 and C-2. Subfraction C-1 was purified by CC over silica gel using a petroleum ether/acetone gradient (1 : 0 → 0 : 1) to afford fractions A–F. Fraction C was separated by CC over Sephadex LH-20 (CHCl3/MeOH, 1 : 1) to obtain two subfractions, C-1 and C-2. Subfraction C-1 was purified by CC over silica gel using a petroleum ether/acetone gradient (1 : 0 → 0 : 1) to afford fractions A–F. Fraction C was separated by CC over silica gel using a petroleum ether/acetone gradient (1 : 0 → 0 : 1) to afford fractions A–F. Fraction C was separated by CC over silica gel using a petroleum ether/acetone gradient (1 : 0 → 0 : 1) to afford fractions A–F. Fraction C was separated by CC over silica gel using a petroleum ether/acetone gradient (1 : 0 → 0 : 1) to afford fractions A–F. Fraction C was separated by CC over silica gel using a petroleum ether/acetone gradient (1 : 0 → 0 : 1) to afford fractions A–F.
tion D, by repeated CC.

3 Results

Compound 1 was isolated as a colorless oil with the molecular formula C$_{10}$H$_{14}$O$_{4}$ deduced from the [M + Na]$^+$ peak at m/z 221.078 8 (Calcd. 221.078 9) in HRESI-MS. The IR spectrum displayed absorption bands for hydroxyl (3440 cm$^{-1}$), carbonyl (1760 cm$^{-1}$) and alkene (1630 cm$^{-1}$) functional groups. The $^{13}$C NMR (DEPT) spectra revealed the presence of ten carbons, including one methyl (δ$_{C}$ 26.4), three methylenes (δ$_{C}$ 19.1, 31.8, and 119.9), three methines (δ$_{C}$ 39.7, 77.5 and 82.6), and three quaternary carbons (δ$_{C}$ 71.7, 136.8, and 170.6). The $^1$H NMR spectrum indicated the existence of two olefinic protons (δ$_{H}$ 6.26, d, J = 3.4 Hz, and 5.52, d, J = 3.4 Hz), belonging to an sp$^2$ methylene. The above resonances suggested that compound 1 had a similar structure with the known compound 1, 2-dihydroxymintlactone (2)$^{[10]}$, which was also obtained from the same fungus in this investigation, except for the double bond C$_{4}$=C$_{8}$ in 2 migrating to C$_{8}$=C$_{10}$ in 1. The elucidation was further supported by HMBC correlations from H-10 to C-9, C-8, and C-4. The relative stereochemistry of compound 1 was determined by the ROESY spectrum, in which the correlations of H-2 with H-7, and H-3 with the 2-OH and H-4 were detected. Therefore, compound 1 was elucidated as shown in Fig. 1.

Pleurotlactone (1): colorless oil; $[\alpha]_{D}^{24}$ +85.5 (c 0.02, MeOH); UV (MeOH) $\lambda_{\text{max}}$ (log $\varepsilon$) 213 (2.95) nm; IR (KBr) $\nu_{\text{max}}$ 3440, 1760, 1630 cm$^{-1}$; $^1$H and $^{13}$C NMR data, see Table 1; ESI-MS (positive) m/z 221 [M + Na]$^+$, 419 [2M + Na]$^+$; HRESI-MS (positive) m/z 221.078 8 (Calcd. for C$_{10}$H$_{14}$O$_{4}$Na, 221.078 9).

1, 2-Dihydroxymintlactone (2): colorless oil; $^1$H and $^{13}$C NMR data, see Table 1. The data were in accordance to those in the literature$^{[10]}$.

![Fig. 1 Structures of compounds 1–6](image)

Table 1 $^1$H and $^{13}$C NMR spectroscopic data for compounds 1 and 2 in CDCl$_3$

<table>
<thead>
<tr>
<th>Position</th>
<th>$\delta_{C}$ (mult.)</th>
<th>$\delta_{H}$ (mult., $J$ in Hz)</th>
<th>$\delta_{C}$ (mult.)</th>
<th>$\delta_{H}$ (mult., $J$ in Hz)</th>
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<tbody>
<tr>
<td>1</td>
<td>71.7 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>2</td>
<td>77.5 (d)</td>
<td>3.18 (d, 7.9)</td>
<td>72.5 (s)</td>
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<td>3</td>
<td>82.6 (d)</td>
<td>4.62 (t, 7.9)</td>
<td>84.0 (d)</td>
<td>4.85 (d, 8.5)</td>
</tr>
<tr>
<td>4</td>
<td>39.7 (d)</td>
<td>3.29 (m)</td>
<td>120.6 (s)</td>
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<tr>
<td>5a</td>
<td>19.1 (t)</td>
<td>2.18 (m)</td>
<td>21.3 (t)</td>
<td>2.60 (m)</td>
</tr>
<tr>
<td>5b</td>
<td></td>
<td>1.84 (m)</td>
<td></td>
<td>2.58 (m)</td>
</tr>
<tr>
<td>6a</td>
<td>31.8 (t)</td>
<td>1.70 (dt, 13.8, 4.0)</td>
<td>36.3 (t)</td>
<td>2.09 (dt, 13.8, 3.7)</td>
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<tr>
<td>6b</td>
<td></td>
<td>1.43 (dt, 13.8, 4.4)</td>
<td></td>
<td>1.42 (dt, 13.8, 9.3)</td>
</tr>
<tr>
<td>7</td>
<td>26.4 (q)</td>
<td>1.26 (s)</td>
<td>25.9 (q)</td>
<td>1.33 (s)</td>
</tr>
<tr>
<td>8</td>
<td>136.8 (s)</td>
<td></td>
<td>160.1 (s)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>170.6 (s)</td>
<td></td>
<td>175.1 (s)</td>
<td></td>
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<tr>
<td>10a</td>
<td>119.9 (t)</td>
<td>6.26 (d, 3.4)</td>
<td>8.3 (q)</td>
<td>1.82 (s)</td>
</tr>
<tr>
<td>10b</td>
<td></td>
<td>5.52 (d, 3.4)</td>
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</table>

(22E, 24R)-Ergosta-5, 7, 22-trien-3ß-ol (3): colorless needles; $^1$H NMR (400 MHz CDCl$_3$): 5.57 (1H, m), 5.38 (1H,
杏鲍菇中一个新的薄荷烷型单萜

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【摘 要】 对侧耳属真菌杏鲍菇（Pleurotus eryngii）的发酵液进行了系统的化学成分研究，经过一系列的正相反相硅胶柱色谱和高效液相色谱等现代分离技术，分离得到了 2 个薄荷烷型单萜，3 个麦角甾醇和 1 个脑苷酯 B，并通过 MS, IR, NMR 等光谱方法确定了这些化合物的结构，其中侧耳内酯 (1) 为一个新的薄荷烷型单萜。

【关键词】 杏鲍菇；薄荷烷型单萜；侧耳内酯

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