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### **A new perylenequinone from the fruit bodies of *Bulgaria inquinans***

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## Note

# A new perylenequinone from the fruit bodies of *Bulgaria inquinans*

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A new perylenequinone, 4,9-dihydroxy-1,2,11,12-tetrahydroperylene-3,10-quinone (**1**), together with three known compounds, have been isolated from the ethanolic extract of the fruit bodies of *Bulgaria inquinans*, and their structures elucidated on the basis of the spectral data and comparison with the literature.

**Keywords:** Fungus; *Bulgaria inquinans*; Perylenequinone; Anthracenedione; Ergosterol

## 1. Introduction

*Bulgaria inquinans* is a wood-inhabiting Ascomycete growing on freshly felled oak widely distributed in the North of China, which has activities of antibacteria [1] and photosensitivity [2]. Several benzofluoranthrene derivatives, one dihydroxyperylenequinone [2] and three azaphionones [1] have been isolated from the fruit bodies. In the present investigation, we obtained compounds **1–4** from the fruit bodies, including a new perylenequinone, 4,9-dihydroxy-1,2,11,12-tetrahydroperylene-3,10-quinone (**1**), and the three known compounds, ergosterol peroxide (5 $\alpha$ ,8 $\alpha$ -epidioxyergosta-6,22*E*-dien-3 $\beta$ -ol, **2**), 5 $\alpha$ ,8 $\alpha$ -epidioxyergosta-6,9(11),22*E*-trien-3 $\beta$ -ol (**3**) and 1,3,5,7-tetrahydroxy-9,10-anthracenedione (**4**). Compounds **2**, **3** and **4** were isolated from *B. inquinans* for the first time.

## 2. Results and discussion

Compound **1** was obtained as yellow needles, mp > 300°C. HREI-MS showed an ion peak at *m/z* 318.0890, compatible with the molecular formula C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>. Compound **1** showed ten carbon signals in the <sup>13</sup>C NMR spectrum; along with the molecular formula and the <sup>1</sup>H NMR spectrum, it could be concluded that the molecule was symmetrical.

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The EI-MS spectrum showed  $[M]^+$  at  $m/z$  318 and the fragment peaks at  $m/z$  290 ( $[M-28]^+$ ) and  $m/z$  262 ( $[M-56]^+$ ), which implied the successive loss of carbonyl group from the parent molecular ion. Furthermore, NMR spectra of **1** showed a remarkable downfield shift of phenyl hydroxyl ( $\delta_H$  13.20) and carbonyl groups ( $\delta_C$  203.8), which indicated that the carbonyl groups were associated with the hydroxyl groups. The  $^1H$  NMR spectrum displayed two *ortho* methylene signals at  $\delta$  3.46 (2H, t,  $J = 7.0$  Hz, H-1) and 3.04 (2H, t,  $J = 7.0$  Hz, H-2). Two *ortho* aromatic protons were also observed at  $\delta$  7.31 (1H, d,  $J = 9.3$  Hz, H-5) and 8.71 (1H, d,  $J = 9.3$  Hz, H-6) in the  $^1H$  NMR spectrum. The  $^{13}C$  NMR spectrum of **1** had ten carbon signals among which, except for one carbonyl mentioned above, seven were aromatic carbons ( $\delta$  162.4, 119.0, 131.9, 111.2, 121.9, 128.9, and 130.2) and two were methylene carbons ( $\delta$  24.7, 36.6).

In the  $^1H$ - $^1H$  COSY spectrum, the signal at  $\delta$  7.31 (H-5) was coupled to  $\delta$  8.71 (H-6). At the same time, the coupling between H-1 ( $\delta$  3.46) and H-2 ( $\delta$  3.04) was also observed. In the HSQC spectrum, the signals at  $\delta_H$  8.71, 7.31, 3.46 and 3.04 were correlated with  $\delta$  131.9 (C-6), 119.0 (C-5), 24.7 (C-1) and 36.6 (C-2), respectively. In the HMBC experiment (figure 1), the signal of H-1 at  $\delta$  3.46 showed long-range correlations with three carbon signals at  $\delta$  203.8 (C-3), 128.9 (C-12b), and 130.2 (C-3b). The signal of H-2 at  $\delta$  3.04 showed long-range correlations with  $\delta$  203.8 (C-3) and 130.2 (C-3b). Those correlating cross-peaks above led to moiety A. The other moiety (B) was revealed by the correlating signals of H-6 at  $\delta$  8.71 with  $\delta$  162.4 (C-4) and 130.2 (C-3b), as well as H-5 at  $\delta$  7.31 with 121.9 (C-6a). Thus, the connection of the two moieties would be indicated as shown in figure 1. Because of its symmetrical character mentioned above, the structure of **1** was established as 4,9-dihydroxy-1,2,11,12-tetrahydroperylene-3,10-quinone (figure 1). The complete  $^1H$  NMR and  $^{13}C$  NMR signal assignments of **1** are presented in table 1.

Recently, perylene quinones have been drawing more and more attention for their photosensitization activity [3]. Much perylenequinone derivatives have been isolated from many fungi [4,5] whereas up to now, tetrahydroperylenequinone has not been reported.

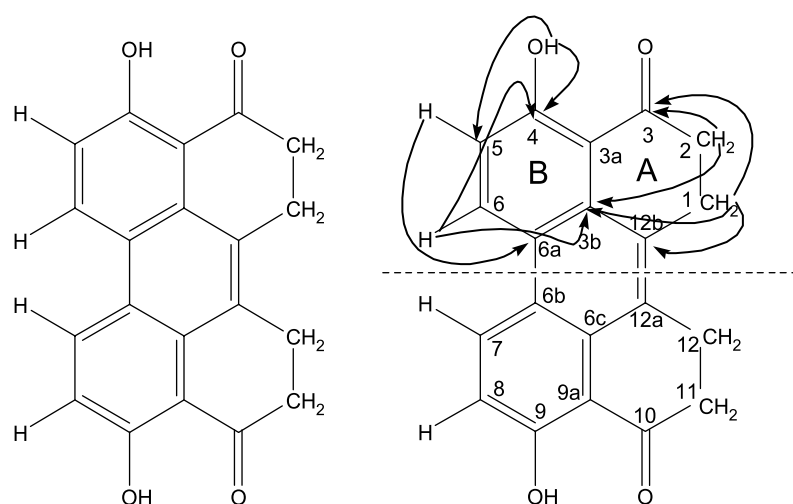


Figure 1. The structure and the important HMBC correlations of compound **1**.

Table 1.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data of compound **1** (in  $\text{CDCl}_3$ ).

Carbon no.	$^{13}\text{C}$	$^1\text{H}$	$^1\text{H}-^1\text{H}$ COSY	HMBC
1, 12	24.7	3.46 (4H, t, $J = 7.0$ Hz)	H-2 (H-11)	C-3, C-12b, C-3b
2, 11	36.6	3.04 (4H, t, $J = 7.0$ Hz)	H-1 (H-12)	C-3, C-12b, C-3b
3, 10	203.8			
4, 9	162.4			
5, 8	119.0	7.31 (2H, d, $J = 9.3$ Hz)	H-6 (H-7)	C-6a
6, 7	131.9	8.71 (2H, d, $J = 9.3$ Hz)	H-5 (H-8)	C-4, C-3b
3a, 9a	111.2			
6a, 6b	121.9			
12a, 12b	128.9			
3b, 6c	130.2			
4,9-OH		13.20 (2H, s)		C-4, C-5

### 3. Experimental

#### 3.1 General experimental procedures

Melting point was measured on a Yamaco-hot-stage and is uncorrected. NMR spectra were recorded on a Bruker-ARX-300 spectrometer, using TMS as an internal standard. EI-MS was performed on a VG-5050E mass spectrometer. ESI-MS was performed on a Finnigan LCQ mass spectrometer. HRMS was performed on a Qstar LCQ mass spectrometer. The HPLC system used a Shimadzu CTP-6A equipped with a UV detector and a Shimadzu SPD-6A column (Shimadzu Shim-pack Prep-ODS, i.d.  $2.5 \times 21.6$  cm). Silica gel for chromatography was produced by Qingdao Ocean Chemical Group Co., China and Sephadex LH-20 was from Pharmacia. The boiling point range of light petroleum ether was  $60-90^\circ\text{C}$ . All other chemicals and reagents were analytical grade.

#### 3.2 Plant material

The fungus was collected at Chang Bai Mountain, Jilin Province, China, in August 2002 and identified by Jilin Provincial Institute of Traditional Chinese Medicine. A voucher specimen (No. 20020801) has been deposited in the Research Department of Natural Medicine, Shenyang Pharmaceutical University.

#### 3.3 Extraction and isolation

The air-dried fruit bodies (7.0 kg) of *Bulgaria inquinans* were extracted with 70% EtOH, the extract was concentrated *in vacuo*, and the extract (1800.0 g) was partitioned with light petroleum ether,  $\text{CHCl}_3$ , EtOAc and n-BuOH successively. The petroleum ether fraction (60.0 g) was subjected to column chromatography on silica gel eluted with petroleum ether/EtOAc by a gradient method. Subfraction 3 (eluted with petroleum ether/EtOAc [100:4], 300.0 mg) was rechromatographed on a silica gel column eluted with petroleum ether/EtOAc (200:7) to give **1** (40.0 mg). Subfraction 10 (eluted with petroleum ether/EtOAc [100:8], 500.0 mg) was separated by semi-preparative HPLC on an ODS column with 93% MeOH as mobile phase, to yield **2** (10.0 mg) and **3** (15.0 mg). The EtOAc fraction (20.0 g) was chromatographed on a silica gel column with gradient elution of  $\text{CHCl}_3/\text{MeOH}$  mixture.

Subfraction 3 (eluted with CHCl<sub>3</sub>/MeOH [100:2], 200.0 mg) was purified on Sephadex LH-20 to give **4** (20.0 mg).

**3.3.1 4,9-Dihydroxy-1,2,11,12-tetrahydroperylene-3,10-quinone (1).** Yellow needles (CHCl<sub>3</sub>/MeOH), mp > 300°C. HREI-MS: [M]<sup>+</sup> *m/z* 318.0890 (calcd for C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>, 318.0892). EI-MS *m/z* (rel. int. %): 318 ([M]<sup>+</sup>, 100), 290 ([M-CO]<sup>+</sup>, 4.41), 262 ([M-2CO]<sup>+</sup>, 5.91), 234 ([M-3CO]<sup>+</sup>, 3.32) and 206 ([M-4CO]<sup>+</sup>, 1.58). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) data: see table 1.

**3.3.2 Compounds 2, 3 and 4.** Identified as ergosterol peroxide (5α,8α-epidioxyergosta-6,22*E*-dien-3β-ol, **2**) [6,7], 5α,8α-epidioxyergosta-6,9(11),22*E*-trien-3β-ol (**3**) [8] and 1,3,5,7-tetrahydroxy-9,10-anthracenedione (**4**) [9] by comparison of their spectral data with reported data from the literature.

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