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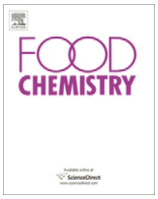

Dendronone, a new phenanthrenequinone from *Dendrobium cariniferum*

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ABSTRACT

The stems of several *Dendrobium* species of the Orchidaceae, used as health foods and nutrients, are rich sources of aromatics, such as bibenzyls, phenanthrenes, fluorenones and simple aromatic acids and esters with antitumour, antioxidant and antimutagenic activities. From the chloroform extract of the whole plant of *Dendrobium cariniferum*, a new phenanthrenequinone, dendronone, was isolated. Its structure was identified as 5-hydroxy-7-methoxy-9,10-dihydro-1,4-phenanthrenequinone, based on extensive spectroscopic studies, including HRESIMS, EIMS, ^{1}H NMR, ^{13}C NMR, DEPT, H–H COSY, HSQC, HMBC and NOESY spectra. In this paper, we described the isolation procedure and the structural elucidation of this new compound, as well as the detection of gigantol and batatasin III by co-chromatography with authentic standards.

1. Introduction

The stems of a number of *Dendrobium* species (Orchidaceae) are used as health foods and nutrients (Bao, Shun, & Chen, 2001). Previous studies on the chemical constituents of the genus led to the isolation of a series of diverse compounds, including alkaloids, fluorenones, sesquiterpenoids, bibenzyls and phenanthrenes; some of these compounds were found to possess antitumour and antimutagenic activities (Chen, Wu, Ko, & Teng, 1994; Fan, Wang, Wang, Qin, & Zhao, 2001; Gong, Fan, Wu, Yang, Hu, & Wang, 2004; Miyazawa et al., 1999; Ye, Zhao, & Qin, 2003). *D. cariniferum* Rchb. f. is distributed in India, Burma, Thailand, Laos, Vietnam and Yunnan Province of south-western China (Delectis Florae Reipublicae Popularis Sinicae Agendae, Academiae Sinicae Edita, 1999). The chemical constituents of this plant have not been studied previously. In the course of our effort to find new natural products from the medicinal plants in Yunnan Province, we isolated and identified a new phenanthrenequinone, named dendronone (**1**) from this plant (see Fig. 1). The isolation and structure elucidation of compound **1** are described herein, as well as the detection of gigantol and batatasin III, by co-chromatography with authentic standards.

2. Materials and methods

2.1. General methods

Mass spectra were determined on an API Qstar Pulsar LC/TOF mass spectrometer (Applied Biosystems, Foster City, CA). NMR spectra were measured on a Bruker DRX-500 spectrometer with TMS as internal standard. Silica gel (200–300 mesh, Qingdao Marine Chemical Co., China) and Sephadex LH-20 (25–100 μm, Pharmacia Fine Chemical Co. Ltd.) were used for column chromatography and silica gel GF$_{254}$ (Qingdao Marine Chemical Co., China) for TLC. Solvents were of industrial purity and distilled prior to use.

2.2. Plant material

The whole plant of *Dendrobium cariniferum* was collected from Lianghe County of Yunnan Province, China in February, 2006 and identified by Dr. Hong Yu, School of Life Science, Yunnan University, where a voucher specimen (No. 0602025) was deposited.

2.3. Extraction and isolation

The air-dried powdered whole plant of *D. cariniferum* (1.3 kg) was extracted with 95% EtOH (six times, each 10 l) at room temperature. The EtOH extract was concentrated *in vacuo* to yield a dark brown residue (50 g, 3.85%). Distilled water (0.5 l) was added to the residue, and the resultant solution was extracted with chloroform, to afford a chloroform extract (26 g, 2%), which was applied to a silica gel column, eluting with petroleum ether, EtOAc, acetone

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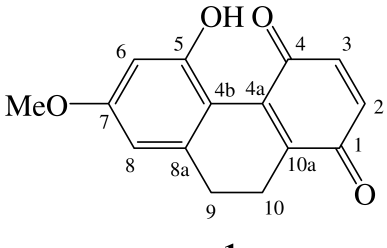

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Fig. 1. Structure of compound **1** isolated from *D. cariniferum*.

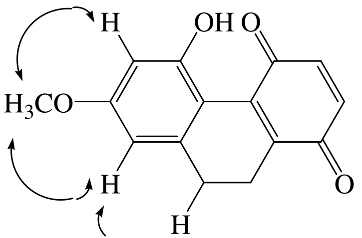

Fig. 2. NOE correlations for **1**.

and MeOH successively, to obtain four fractions. The EtOAc fraction (15 g, 1.15%) was applied to a silica gel column, eluting with petroleum ether containing increasing amounts of EtOAc, to give five fractions (A–E). Fraction B (7 g) was further isolated on column chromatography (silica gel, petroleum ether: EtOAc 4:1; then Sephadex LH-20, MeOH) to yield **1** (9 mg, 0.00069%).

Dendronone (**1**) was obtained as a reddish gum. EIMS: *m*/*z* (%): 256 (M^+, 100%), 239 (23), 213 (24), 201 (25), 174 (20), 115 (22); ^1H NMR (CD_3OD, 500 MHz): δ 6.84 (1H, d, $J = 10.1$, H-3), 6.71 (1H, d, $J = 10.1$, H-2), 6.37 (1H, d, $J = 2.0$, H-6), 6.35 (1H, d, $J = 2.0$, H-8), 3.76 (3H, s, 7-OMe, 2.63 (2H, m, H-9), 2.58 (2H, m, H-10); ^{13}C NMR (CD_3OD, 125 MHz): δ 186.1 (C-4), 185.7 (C-1), 159.4 (C-7); 159.1 (C-5), 143.5 (8a), 141.3 (C-4a), 140.2 (10a), 137.6 (C-3), 135.5 (C-2), 112.9 (C-4b), 107.9 (C-8), 99.1 (C-6), 56.2 (7-OMe), 28.9 (C-10), 20.5 (C-9); HRESIMS: *m*/*z* 257.0816 $[M + H]^+$, $C_{15}H_{13}O_4$ requires 257.0813.

3. Results and discussion

The 95% ethanol extract of *D. cariniferum* was partitioned with chloroform to yield a chloroform extract, which was applied to a silica gel column, eluted with petroleum ether, EtOAc, acetone and MeOH. The EtOAc fraction was analysed on TLC to allow the detection of gigantol and batatasin III by co-TLC with authentic standards, which were previously isolated from *Bulbophyllum odoratissimum* by our group (Chen, Xu, Yu, Qing, Zhang, Wang, Liu & Wang, 2008). Gigantol and batatasin III are the two most common bibenzyls in Orchidaceae plants (Juneja, Sharma, & Tandon, 1987; Leong, Kang, Harrison, & Powell, 1997). The EtOAc fraction was further subjected to a succession of chromatographic procedures, including silica gel chromatography and gel permeation chromatography, using Sephadex LH-20, to afford the isolation of the new compound. Its structure was established by analysis of spectral data including 2D NMR and HRESIMS.

Compound **1** had the molecular formula $C_{15}H_{12}O_4$ by HRESIMS at *m*/*z* 257.0816 $[M + H]^+$ (calcd for $C_{15}H_{13}O_4$, 257.0813). The ^1H NMR, ^{13}C NMR and DEPT spectra suggested the presence of a 1,2,3,5-tetrasubstituted benzene ring [δ 6.37 (1H, d, $J = 2.0$, H-6) and 6.35 (1H, d, $J = 2.0$, H-8); δ 99.0 (C-6) and 107.8 (C-8)], a pair of *ortho*-coupled aromatic protons [δ 6.71 (1H, d, $J = 10.1$, H-2) and 6.84 (1H, d, $J = 10.1$, H-3); δ 135.5 (C-2) and 137.7 (C-3)], a methoxy group [δ 3.76 (3H, s, 7-OMe) and 56.2], and two methylenes [δ 2.63 (2H, m, H-9) and 2.58 (2H, m, H-10); δ 20.5 (C-9) and 28.9 (C-10)]. Besides, signals for mutually coupled olefinic protons (H-2 and H-3) and two carbonyl groups, characteristic of a quinone unit [(δ 186.1 (C-4) and 185.7 (C-1)], were observed, suggesting compound **1** should be a 9,10-dihydrophenanthraquinone-type metabolite (Bae et al., 2004).

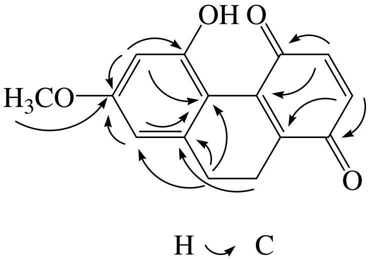

Fig. 3. HMBC correlations from H to C for **1**.

The structure of **1** was further elucidated by 2D NMR techniques, including H–H COSY, HSQC, HMBC and NOESY. The arrangement of atom orders was in a good agreement using ^1H NMR, ^{13}C NMR and COSY and DEPT analysis. The HSQC experiment indicated the cross peaks between protons and the attached carbons, e.g., C-2 and H-2, C-3 and H-3, and C-6 and H-6. The NOE correlations methoxy/H-6 and H-8, and H-8/H-9 as shown in Fig. 2, revealed the location of the remaining hydroxyl group to be at C-5, which was further supported by the correlations in the HMBC spectrum (see Fig. 3). Thus, the structure of **1** was identified as 5-hydroxy-7-methoxy-9,10-dihydro-1,4-phenanthrenequinone.

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