

**BIBENZYL, 9,10-DIHYDROPHENANTHRENE,
AND PHENANTHRAQUINONE
FROM *Dendrobium longicornu***

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The stems of a number of *Dendrobium* species (Orchidaceae) have been used as a precious health food and nutrient [1]. Previous studies on the chemical constituents of the genus led to the isolation of a series of diverse compounds such as alkaloids, fluorenones, sesquiterpenoids, bibenzyls, and phenanthrenes, in which some compounds were found to possess antioxidant, antitumor, and antimutagenic activities [2–6]. *D. longicornu* Lindl is distributed in Nepal, Sikkim, Bhutan, India, Vietnam, and the southwestern part of China [7]. Previously, bibenzyls, phenanthrenes, and lignan glycosides were isolated [8]. In the course of our search for bioactive natural products from medicinal plants in Yunnan of China, we isolated eight mono-aromatic compounds from *D. longicornu* [9]. Further investigation on the plant extract led to the isolation of five bibenzyls, two 9,10-dihydrophenanthrenes, and a phenanthraquinone.

The extracts of *D. longicornu* were prepared as described in the previous report [9]. The EtOAc extract (26 g) was applied to a silica gel column, eluting with petroleum ether containing increasing amounts of acetone to obtain six fractions. Fraction 5 (9 g) was purified on column chromatography (silica gel, CHCl₃–acetone 10:1) to afford two subfractions. The first subfraction (4 g) was subjected to repeated column chromatography, first on silica gel (CHCl₃–acetone 20:1) and then on Sephadex LH-20 (MeOH), to obtain **1** (7 mg), **2** (20 mg), **3** (8 mg), and **4** (9 mg). The second subfraction (3 g) was subjected to repeated column chromatography similarly, first on Sephadex LH-20 (MeOH), and then on preparative TLC (petroleum ether–EtOAc 2:1, CHCl₃–MeOH 15:1), to afford **5** (45 mg), **6** (9 mg), and **7** (6 mg). The petroleum ether extract (30 g) was applied to a silica gel column, eluting with petroleum ether containing increasing amounts of EtOAc to obtain seven fractions. Fraction 4 (1 g) was purified on Sephadex LH-20 (MeOH), and then on preparative TLC (petroleum ether–acetone 5:1) to afford **8** (10 mg).

The structures of isolates were identified by a combination of spectroscopic methods (MS, PMR, ¹³C NMR, and 2D NMR) and comparisons with the literature data as 3,4'-dihydroxy-3',4,5-trimethoxybibenzyl (**1**) [10], 3,3'-dihydroxy-4,5-dimethoxybibenzyl (**2**) [11], cannabistilbene II (**3**) [12], batatasin III (**4**) [13], aloifol I (**5**) [11], coelonin (**6**) [14], hircinol (**7**) [15], and ephemeranthoquinone (**8**) [16]. Compounds **1–3** were discovered from the *Dendrobium* genus for the first time, and **6–8** were originally isolated from the plant. Compound **1** was isolated before as a diacetate from the heartwood of *Combretum apiculatum* [10]; this was the first time that the compound was obtained in its original form.

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