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CHEMICAL CONSTITUENTS OF *Dendrobium thyrsiflorum*

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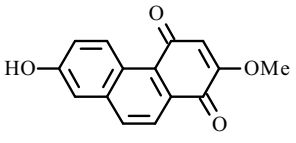
The stems of several *Dendrobium* species (Orchidaceae) are used in traditional Chinese medicine as a tonic to nourish the stomach, promote the production of body fluid, and reduce fever [1]. *D. thyrsiflorum* Rchb. f. is distributed in India, Burma, Thailand, Laos, Vietnam, and Yunnan of southwestern China [2]. Previous investigation on the constituents of *D. thyrsiflorum* has isolated a series of aromatic compounds such as coumarins, bibenzyls, phenanthrenes, fluorenones, and flavonoids [3–6]. Some of the compounds were found to possess significant cytotoxic activities against Hela, K-562, and MCF-7 cell lines [6], and the polysaccharide was found to enhance the immune function in mice [7]. To find further active principles from *D. thyrsiflorum*, we investigated the plant.

D. thyrsiflorum was collected from Simao County of Yunnan, China in February, 2003. The air-dried whole plants (2 kg) were chopped and exhaustively extracted with 95% EtOH. Water (0.8 L) was added to the EtOH extract (200 g), and the resulting solution was extracted with petroleum ether, EtOAc, and *n*-BuOH successively (four times, each 0.5 L). The petroleum ether extract (25 g) was separated on a silica gel column, eluting with petroleum ether containing increasing amounts of EtOAc to obtain 7 fractions. Fraction C (7.5 g) was subjected to repeated column chromatography (silica gel, petroleum ether–EtOAc 6:1; then Sephadex LH-20, MeOH–$CHCl_3$ 2:3) to afford **1** (40 mg), **2** (1.2 g), **3** (0.8 g) and **4** (6 mg). Fraction D (3 g) was chromatographed over silica gel ($CHCl_3$–Me_2CO 10:1) to furnish **5** (5 mg) and **6** (4 mg).

Compound **2**, $C_{11}H_{10}O_4$, white amorphous powder. The mass spectrum exhibited peaks for ions at *m/z* 206 (M^+, 85), 191, 163, 107, and 69. The PMR spectrum ($CDCl_3$, δ, ppm, J/Hz) displayed signals of four aromatic protons at 7.61 (1H, d, J = 9.4), 6.84 (1H, s), 6.82 (1H, s), and 6.26 (1H, d, J = 9.4), and two methoxyls at 3.93 and 3.92 (each 3H, s). The ^{13}C NMR and DEPT spectra ($CDCl_3$, ppm) showed signals at 160.5, 151.9, 149.0, 145.4, 142.4, 112.5, 110.5, 107.0, 99.0, 55.4, and 55.3. By comparison of the spectral data with those reported in the literature, we identified **2** as scoparone [8].

Compound **3**, $C_{10}H_6O_4$, white amorphous powder. The mass spectrum exhibited peaks for ions at *m/z* 190 (M^+, 96), 162, 161, 104, and 76. The PMR spectrum ($CDCl_3$, δ, ppm, J/Hz) displayed signals of four aromatic protons at 7.58 (1H, d, J = 9.5), 6.82 (1H, s), 6.81 (1H, s), and 6.27 (1H, d, J = 9.5), and a methylenedioxy group at 6.06 (2H, s). The ^{13}C NMR and DEPT spectra ($CDCl_3$, ppm) showed signals at 160.3, 150.3, 150.3, 143.9, 142.5, 112.4, 111.7, 104.0, 101.4, and 97.4. By comparison of the spectral data with those reported in the literature, we identified **3** as ayapin [8].

Compound **4**, $C_{14}H_{10}O_5$, white amorphous powder. The mass spectrum exhibited peaks for ions at *m/z* 258 (M^+, 92), 243, 215, 187, and 129. The PMR spectrum [$(CD_3)_2CO$, δ, ppm, J/Hz] displayed signals of four aromatic protons at 6.90 (1H, d, J = 8.9, H-3), 6.82 (1H, d, J = 1.9, H-6), 6.80 (1H, d, J = 1.9, H-8), and 6.63 (1H, d, J = 8.9, H-2), and a methoxyl at 4.14 (3H, s). The ^{13}C NMR and DEPT spectra [$(CD_3)_2CO$, δ, ppm] showed signals at 195.0 (C-9), 161.5 (C-7), 154.0 (C-5), 153.0 (C-1), 144.6 (C-4), 137.5 (C-8a), 128.8 (C-3), 124.5 (C-4a), 119.8 (C-4b), 119.4 (C-2), 116.2 (C-9a), 106.0 (C-6), 105.7 (C-8), 57.6 (5-OMe). By comparison of the spectral data with those reported in the literature, we identified **4** as dendroflorin [9].



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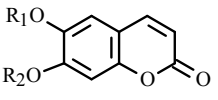

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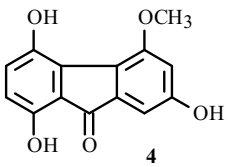
2: $R_1 = R_2 = CH_3$
3: $R_1R_2 = CH_2$



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Compounds **1**, **5**, and **6** were identified as densiflorol B, stigmasterol, and hexadecanoic acid 2,3-dihydroxypropyl ester, respectively, based on comparison of the PMR, ^{13}C NMR, and EI-MS spectra with those of authentic samples [5, 10, 11]. Compounds **1** and **5** were isolated from *D. thyrsiflorum* for the first time.

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