CHEMICAL CONSTITUENTS OF *Dendrobium crystallium*

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The important Chinese herb "Shi-Hu" is prepared from the dried stems of several *Dendrobium* species (Orchidaceae) such as *D. nobile, D. candidum, and D. fimbriatum var. oculatum* and used as a tonic to nourish stomach, promote secretion of saliva, and reduce fever [1]. Earlier work on the genus led to the isolation of a series of compounds such as alkaloids, fluorenones, sesquiterpenoids, bibenzyls, and phenanthrenes, and several compounds were found to possess antitumor and antimutagenic activities [2–7]. *D. crystallium* Rchb. f. is distributed in Burma, Thailand, Laos, Cambodia, Vietnam, and the southern part of Yunnan, China [8]. Previously there were no reports on its chemical constituents. In the course of our search for new bioactive natural products from medicinal plants in Yunnan of China, we investigated the plant.

D. crystallium was collected from Simao County of Yunnan, China in November, 2004. The air-dried plants (0.35 kg) were chopped and exhaustively extracted with 95% EtOH. The EtOH extract (10 g) was applied to a silica gel column, eluting with petroleum ether containing increasing amounts of EtOAc to offer four fractions (A-D). Fraction B (4 g) was further subjected to column chromatography (silica gel, petroleum ether/EtOAc 10:1; then Sephadex LH-20, MeOH/H_2O 9:1) to yield **3** (200 mg) and **4** (20 mg). Fraction C (3.6 g) was further subjected to column chromatography (silica gel, $CHCl_3$/acetone 20:1; then Sephadex LH-20, MeOH/H_2O 9:1) to isolate **1** (18 mg) and **2** (6 mg).

Compound 1, $C_{16}H_{18}O_4$, yellow gum. The mass spectrum exhibited peaks for ions at *m*/*z* 274 $[M]^+$, 137 (100), 122, 107, 94, and 77. Based on NMR and mass spectral data, **1** contains two methoxyls and two hydroxyls. The mass spectral fragmentation is consistent with one methoxyl and one hydroxyl on both benzene rings. Comparison of the spectral data with those reported in the literature identified **1** as gigantol [6, 9].

Compound 2, $C_{15}H_{16}O_3$, yellow gum. The mass spectrum exhibited peaks for ions at *m*/*z* 244 $[M]^+$, 137 (100), 107, and 77. The PMR spectrum (CD_3COCD_3, δ, ppm, J/Hz) also showed characteristic signals of bibenzyls at 7.12 (1H, dd, J = 7.7, 7.7, H-5″), 6.73 (1H, d, J = 7.7, H-6″), 6.72 (1H, dd, J= 7.7, 2.4, H-4″), 6.71 (1H, m, H-2″), 6.39 (1H, s, H-4′), 6.30 (2H, s, H-2′,6′), 3.72 (3H, s, 5′-OCH_3), 2.82 (4H, m, 1,2-CH_2). The CNMR and DEPT spectra (CD_3COCD_3, δ, ppm) had signals at 161.9 (C-5′), 159.3 (C-3′), 158.2 (C-3″), 145.2 (C-1′), 144.4 (C-1″), 130.2 (C-5″), 120.5(C-6″), 116.3 (C-2″), 113.7 (C-4″), 108.9 (C-2′), 106.3 (C-6′), 99.9 (C-4′), 55.4 (OCH_3-5′), 38.5 (C-1), 38.2 (C-2). The NMR and mass spectrum indicated that **2** differed from **1** by the lack of a methoxyl in one benzene ring. Comparison of the spectral data with those reported in the literature identified **2** as batatasin III [10].

Compound 3, $C_{15}H_{12}O_5$, yellow amorphous powder. The PMR spectrum (CD_3COCD_3, δ, ppm, J/Hz) showed characteristic signals of flavanones at 7.37 (2H, d, J= 8.3, H-2′, 6′), 6.89 (2H, d, J = 8.3, H-3′, 5′), 5.95 (2H, s, H-6, 8), 5.42 (1H, dd, J = 12.8, 2.6, H-2), 3.16 (1H, dd, J = 17.1, 12.8, 3-Ha), 2.71 (1H, dd, J = 17.1, 2.7, 3-Hb). The CNMR and DEPT spectra (CD_3COCD_3, ppm) had signals at 197.4 (C-4), 168.0 (C-7), 165.1 (C-5), 164.3 (C-9), 158.9 (C-4′), 130.4 (C-1′), 129.0 (C-2′, 6′), 116.3 (C-3′, 5′), 103.0 (C-10), 97.0 (C-6), 96.0 (C-8), 79.9 (C-2), 43.4 (C-3). Comparison of the spectral data with those reported in the literature identified **3** as naringenin [9, 11].

Compound 4, $C_{29}H_{48}O$, white needles, mp 138–140°C. The mass spectrum exhibited peaks for ions at *m*/*z* 412 $[M]^+$(100), 369, 351, 300, 271, 255, 213, 145, 91. Based on the data and a direct comparison with an authentic sample, **4** was identified as stigmasterol [12]. All the compounds were isolated from the plant for the first time.

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