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BRIEF COMMUNICATIONS

CHEMICAL CONSTITUENTS OF *Dendrobium aurantiacum* VAR. *denneanum*

Ying Liu,[1] Jin-He Jiang,[1] Yan Zhang,[2] and Ye-Gao Chen[1]*

UDC 547.68

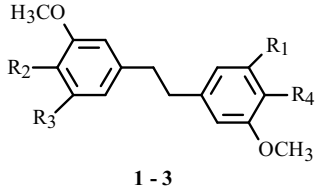
Dendrobium aurantiacum Rchb. f. var. *denneanum* (Kerr.) Z. H. Tsi (= *D. denneanum* Kerr; *D. clavatum* Lindl; *D. chryseum* auct. non Rolfe) is distributed in southwestern China, India, Burma, Laos, Thailand, and other parts of South Asia [1]. Previously phenanthrenes, bibenzyls, fluorenones, flavonoids, coumarin, and esters of aromatic acids were isolated from the plant [2–5]. Pharmacological experiments showed that polysaccharides from the plant possessed tumor inhibitory and blood glucose reducing effect *in vivo* [6, 7]. In the course of our search for bioactive natural products from medicinal plants in Yunnan of China, we investigated the plant.

D. aurantiacum var. *denneanum* was collected from Wenshan County of Yunnan, China in July, 2005. The air-dried powdered whole plants (2.5 kg) were extracted with 95% EtOH at room temperature. The EtOH extract (150 g) was added with H_2O and then extracted with petroleum ether, $CHCl_3$, EtOAc, and *n*-BuOH successively. Evaporation of the respective solvent gave the petroleum ether (37 g), $CHCl_3$ (17 g), EtOAc (14 g), and *n*-BuOH (60 g) extracts.

The petroleum ether fraction (37 g) was applied to a silica gel column, eluting with petroleum ether containing increasing amounts of EtOAc to yield five fractions. Fraction 2 (1 g) was isolated on a silica gel column (petroleum ether/EtOAc 5:1) and then on preparative TLC (silica gel, petroleum ether/acetone 4:1) to yield **3** (7 mg). Fraction 3 (4 g) was crystallized from EtOAc to obtain **8** (1.2 g).

The $CHCl_3$ extract (17 g) was subjected to a silica gel column, eluting with petroleum ether containing increasing amounts of EtOAc to obtain four fractions. Fraction 1 (2.5 g) was purified on a silica gel column (petroleum ether/EtOAc 4:1) and then on preparative TLC (silica gel, $CHCl_3$/acetone 10:1) to yield **1** (13 mg) and **2** (5 mg). Fraction 2 (1.5 g) was purified on a Sephadex LH-20 chromatograph (MeOH) and then on preparative TLC (silica gel, $CHCl_3$/acetone 10:1) to afford **6** (6 mg).

The EtOAc extract (14 g) was separated on a silica gel column, eluting with petroleum ether containing increasing amounts of EtOAc to obtain four fractions. Fraction 2 (2 g) was purified on preparative TLC (silica gel, $CHCl_3$/MeOH 10:1) to yield **7** (17 mg). Fraction 3 (8 g) was subjected to repeated chromatography (silica gel, petroleum ether/acetone 1:1) and then on Sephadex LH-20 (MeOH) to afford **4** (19 mg) and **5** (7 mg).



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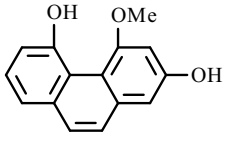

4

1: $R_1 = R_2 = H$, $R_3 = R_4 = OH$
2: $R_1 = OMe$, $R_2 = R_4 = OH$, $R_3 = H$
3: $R_1 = R_4 = OMe$, $R_2 = OH$, $R_3 = H$

1) Department of Chemistry, Yunnan Normal University, Kunming 650092, China, fax: +86 871 5516061, e-mail: ygchen48@gmail.com; 2) Department of Chemistry, Kunming Medical College, Kunming 650031, China. Published in Khimiya Prirodnykh Soedinenii, No. 4, pp. 447–448, July–August, 2009. Original article submitted November 27, 2007.

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The purified compounds were measured on a Bruker DRX-500 spectrometer to obtain PMR (500 MHz) and ^{13}C NMR (125 MHz) spectra. Compounds **1**, **4**, and **8** were identified as gigantol, moscatin, and stigmasterol, respectively, based on co-TLC and comparison of PMR, ^{13}C NMR, and EIMS with those of authentic samples [8, 9].

Compound **2**, $C_{17}H_{20}O_5$, colorless gum. The mass spectrum exhibited peaks for ions at *m/z* 304 $[M]^+$ (54), 137 (100), 122, 107, 94, and 77. The PMR spectrum ($CDCl_3$, δ, ppm, J/Hz) showed characteristic signals of bibenzyls at 6.84 (1H, d, J = 8.0, H-5″), 6.67 (1H, dd, J = 8.0, 1.9, H-6″), 6.62 (1H, d, J = 1.9, H-2″), 6.36 (2H, s, H-2′, 6′), 3.82, 3.81, 3.80 (9H, s, 3′, 3″, 5′-OMe), and 2.81 (4H, t, 1,2-CH_2). The ^{13}C NMR and DEPT spectra ($CDCl_3$, δ, ppm) had signals at 147.8 (C-3′, 5′), 147.3 (C-3″), 144.7 (C-4″), 134.6 (C-4′), 133.9 (C-1″), 133.8 (C-1′), 122.0 (C-6″), 115.2 (C-5″), 112.0 (C-2″), 106.3 (C-2′, 6′), 57.2 (3′-OCH_3), 56.8 (5′-OCH_3), 54.7 (3″-OCH_3), 39.3 (C-2), and 38.8 (C-1). Based on NMR and mass spectral data, **2** contained three methoxyls and two hydroxyls. The mass spectral fragmentation is consistent with one methoxyl and one hydroxyl on a benzene ring and a hydroxyl group and two methoxyls on another benzene ring. By comparison of the spectral data with those reported in the literature, **2** was identified as moscatilin [10].

Compound **3**, $C_{18}H_{22}O_5$, colorless powder. The mass spectrum exhibited peaks for ions at *m/z* 318 $[M]^+$ (15), 181 (100), and 137 (43). The PMR spectrum ($(CD_3)_2CO$, δ, ppm, J/Hz) also showed characteristic signals of bibenzyls at 6.79 (1H, d, J= 8.0, H-5″), 6.73 (1H, d, J = 8.0, H-6″), 6.67 (1H, s, H-2″), 6.51 (2H, s, H-2′, 6), 3.78 (9H, s, 3 × OCH_3), 3.68 (3H, s, OCH_3), and 2.82 (4H, s, 2 × CH_2). The ^{13}C NMR and DEPT spectra ($(CD_3)_2CO$, δ, ppm) had signals at 154.2 (C-3′, 5′), 148.1 (C-3″), 145.7 (C-4″), 138.5 (C-1′), 137.5 (C-4′), 134.1 (C-1″), 121.7 (C-6″), 115.6 (C-5″), 113.0 (C-2″), 106.6 (C-2′, 6′), 60.5 (3″-OCH_3), 56.4 (3′, 5′-OCH_3), 56.2 (4′-OCH_3), 39.3 (C-1), and 38.3 (C-2). Based on NMR and mass spectral data, **3** contained four methoxyls and one hydroxyl. The mass spectral fragmentation is consistent with one methoxyl and one hydroxyl on a benzene ring and three methoxyls on another benzene ring. By comparison of the spectral data with those reported in the literature, **3** was identified as crepidatin [11].

Compound **5**, $C_7H_6O_2$, white powder. The mass spectrum exhibited peaks for ions at *m/z* 122 $[M]^+$, 121 (100), and 93. The PMR spectrum ($(CD_3)_2CO$, δ, ppm, J/Hz) showed an aldehyde proton at δ 9.87 (1H, s) and four 1,4-disubstitued aromatic protons at 7.82 (2H, d, J = 8.7) and 7.04 (2H, d, J = 8.7). The ^{13}C NMR and DEPT spectra [$(CD_3)_2CO$, δ, ppm] had signals at 191.9 (CHO), 164.9 (C-4), 133.7 (C-2, 6), and 117.6 (C-3, 5). Based on NMR and mass spectral data and comparison of the spectral data with those reported in the literature, **5** was identified as *p*-hydroxybenzaldehyde [12].

Compound **6**, $C_9H_6O_2$, white powder. The mass spectrum exhibited peaks for ions at *m/z* 146 $[M]^+$ (90), 118 (100), 90 (48), 89 (58), and 63 (54). The PMR spectrum ($(CD_3)_2CO$, δ, ppm, J/Hz) showed six aromatic protons at δ 7.97 (1H, d, J = 9.6, H-4), 7.67 (1H, m, H-7), 7.61 (1H, m, H-5), 7.34 (2H, m, H-6, 8), and 6.44 (1H, d, J = 9.6, H-3). The ^{13}C NMR and DEPT spectra ($(CD_3)_2CO$, δ, ppm) had signals at δ 160.6 (C-2), 155.1 (C-8a), 144.5 (C-4), 132.6 (C-5), 129.2 (C-7), 125.2 (C-6), 120.0 (C-4a), 117.3 (C-8), and 117.2 (C-3). Based on NMR and mass spectral data and comparison of the spectral data with those reported in the literature, **6** was identified as coumarin [13].

Compound **7**, $C_{15}H_{10}O_6$, yellow powder. The mass spectrum exhibited peaks for ions at *m/z* 286 $[M]^+$, 270, 153, 152, 109, and 43. The PMR spectrum ($(CD_3)_2CO$, δ, ppm, J/Hz) showed six aromatic protons at δ 7.48 (1H, s, H-2′), 7.44 (1H, d, J = 8.4, H-6′), 6.99 (1H, d, J = 8.4, H-5′), 6.60 (1H, s, H-3), 6.54 (1H, s, H-8), and 6.25 (1H, s, H-6). The ^{13}C NMR and DEPT spectra ($(CD_3)_2CO$, δ, ppm) had signals at δ 184.1 (C-4), 166.5 (C-7), 163.9 (C-5′), 159.7 (C-5), 151.6 (C-4′), 147.7 (C-2), 124.2 (C-1′), 120.9 (C-6′), 117.6 (C-3′), 116.7 (C-9), 115.0 (C-2′), 105.9 (C-10), 104.8 (C-3), 100.9 (C-6), and 95.9 (C-8). Based on NMR and mass spectral data and comparison of the spectral data with those reported in literature, **7** was identified as luteolin [14]. Luteolin was isolated from the genus for the first time, and crepidatin and *p*-hydroxybenzaldehyde were not reported from the plant before.

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