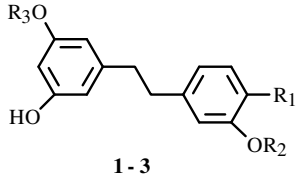
CHEMICAL CONSTITUENTS OF *Dendrobium cariniferum*

Ying Liu, Jin-He Jiang, Ben-LinYin, and Ye-Gao Chen*

UDC 547.568

Considerable studies have been done on plants of the *Dendrobium* species (Orchidaceae), which are used as a tonic to nourish stomach, promote secretion of saliva, and reduce fever [1], and which yielded alkaloids, fluorenones, sesquiterpenoids, bibenzyls, and phenanthrenes with antitumor, antiplatelet aggregation, antioxidant, and antimutagenic activities [2–8]. *D. cariniferum* Rchb. f. is distributed in India, Burma, Thailand, Laos, Vietnam, and Yunnan of southwestern China [9]. Previously there was no report on its chemical constituents. In the course of our search for bioactive natural products from medicinal plants in Yunnan of China, we investigated the plant.

D. cariniferum was collected from Lianghe County of Yunnan, China in February, 2006. The air-dried whole plants (1.3 kg) were chopped and exhaustively extracted with 95% EtOH. Water was added to the EtOH extract (50 g), and it was then extracted with chloroform to afford chloroform extract (26 g), which was applied to a silica gel column, eluting with petroleum ether, EtOAc, acetone, and MeOH successively to obtain four elutions. The petroleum ether elution (4 g) was crystallized to yield **4** (0.8 g). The EtOAc elution (15 g) was subjected to a silica gel column, eluting with petroleum ether containing increasing amounts of EtOAc to offer five fractions (A-E). Fraction B (7 g) was further separated on column chromatography (silica gel, petroleum ether–EtOAc 4:1; then Sephadex LH-20, MeOH) to yield **1** (25 mg) and **2** (14 mg). Fraction C (2 g) was subjected to Sephadex LH-20 chromatography (MeOH) and then to PTLC (silica gel, $CHCl_3$–MeOH 20:1) to offer **3** (24 mg). Fraction D (3 g) was purified on Sephadex LH-20 chromatography (MeOH) and then crystallized to afford **5** (86 mg).



1 - 3

1: R_1 = OH, R_2 = R_3 = Me
2: R_1 = R_2 = H, R_3 = Me
3: R_1 = R_2 = R_3 = H

Compounds **1**, **2**, **4**, and **5** were identified as gigantol (**1**), batatasin III (**2**), stigmasterol (**4**), and daucosterol (**5**) based on co-TLC and comparison of ^{1}H NMR, ^{13}C NMR, and EI-MS with those of authentic samples [10].

Compound **3**, $C_{14}H_{14}O_3$, colorless gum. The mass spectrum exhibited peaks for ions at *m*/*z* 230 $[M]^+$ (100), 212, 123, 107, 77. The ^{1}H NMR spectrum (CD_3COCD_3, δ, ppm, J/Hz) showed characteristic signals of bibenzyls at 8.21 (s, 3′-OH), 8.09 (2H, s, 3,5-OH), 7.10 (1H, dd, J = 7.7, 7.8, H-5′), 6.74 (1H, m, H-2′), 6.72 (1H, m, H-6′), 6.66 (1H, m, H-4′), 6.25 (2H, d, J = 2.0, H-2, H-6), 6.21 (1H, dd, J = 2.1, 2.1, H-4), 2.78 (2H, m, 7′-CH_2), 2.72 (2H, m, 7-CH_2). The ^{13}C NMR and DEPT spectra (CD_3COCD_3, δ, ppm) had signals at 158.8 (C-3, 5), 157.8 (C-3′), 144.6 (C-1), 143.9 (C-1′), 129.5 (C-5′), 119.9 (C-6′), 115.7 (C-2′), 113.1 (C-4′), 107.3 (C-2, 6), 100.7 (C-4), 38.0 (C-7), 37.7 (C-7′). Based on NMR and mass spectral data, **3** contained three hydroxyls. The mass spectral fragmentation is consistent with two hydroxyls on a benzene ring and a hydroxyl group on another benzene ring. By comparison of the spectral data with those reported in literature, **3** was identified as 3,3′,5-trihydroxybibenzyl [11]. All the compounds were isolated from the plant for the first time.

Department of Chemistry, Yunnan Normal University, Kunming 650092, China, fax: +86 871 5516061, e-mail: ygchen48@gmail.com. Published in Khimiya Prirodnykh Soedinenii, No. 2, p. 204, March–April, 2009. Original article submitted September 3, 2007.

0009-3130/09/4502-0237

ACKNOWLEDGMENT

This investigation was supported by a grant (No. 2005DFA30670) for international collaborative research by the Ministry of Science and Technology, China, and a grant (No. 2003C0033M) for scientific research from Yunnan Province, China.

REFERENCES

1. Jiangsu New Medical College, *Dictionary of Chinese Herb Medicine,* Shanghai Scientific and Technologic Press, Shanghai (1986), p. 586.
2. C. K. Ho and C. C. Chen, *Cancer Invest*., **21**, 729 (2003).
3. Q. H. Ye, G. W. Qin, and W. M. Zhao, *Phytochemistry*, **61**, 885 (2002).
4. M. Ono, Y. Ito, C. Masuoka, H. Koga, and T. Nohara, *Food Sci. Technol. Int.,* **1**, 115 (1995).
5. C. C. Chen, L. G. Wu, F. N. Ko, and C. M. Teng, *J. Nat. Prod.,* **57**, 1271 (1994).
6. K. K. Chen and A. L. Chen, *J. Biol. Chem.,* **111**, 653 (1935).
7. W. M. Zhao, Q. H. Ye, X. J. Tan, H. L. Jiang, X. Y. Li, K. X. Chen, and A. D. Kinghorn, *J. Nat. Prod*., **64**, 1196 (2001).
8. Y. H. Lee, J. D. Park, N. I. Baek, S. I. Kim, and B. Z. Ahn, *Planta Med.,* **61**, 178 (1995).
9. Delectis Florae Reipublicae Popularis Sinicae Agendae, Academiae Sinicae Edita, *Flora Reipublicae Popularis Sinicae*, Science Press, Beijing, **19**, 131 (1999).
10. Y. P. Li, Y. M. Zhang, Y. Liu, and Y. G. Chen, *Chem. Nat. Compd*., **43**, 698 (2007).
11. Y. Hernandez-Romero, J. I. Rojas, R. Castillo, A. Rojas, and Ra. Mata, *J. Nat. Prod.*, **67**, 160 (2004).