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THE STILBENOIDS FROM *DENDROBIUM PLICATILE*

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Key Word Index—*Dendrobium plicatile*; Orchidaceae; stilbenoid; phenanthrene; bibenzyl; biphenanthrene; phenols.

Abstract—Seven stilbenoids were isolated from stems of *Dendrobium plicatile* and their structures were elucidated on the basis of spectroscopic data. Six of them were known compounds, 3-methoxy-3′,5-dihydroxybibenzyl, 3,3′,4′-trimethoxy-5-hydroxybibenzyl, 2-methoxy-4,7-dihydroxy-9,10-dihydrophenanthrene, 2,4-dimethoxy-3,7-dihydroxyphenanthrene, 3,4-dimethoxy-2,7-dihydroxy-9,10-dihydrophenanthrene and ephemeranthoquionone. The seventh, 2,2′-dimethoxy-4,4′,7,7′-tetrahydroxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene, was a new dimer. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The chinese crude drug 'Shi Hu' is prepared from the dried stems of *Dendrobium* species, and has been used as a tonic and an antipyretic. *Dendrobium plicatile* Lindl. is also used as a source of 'Shi Hu' in Japan, but no detailed study on its constituents has been reported. In this paper, we report on the isolation of a new phenanthrene dimer along with six known stilbenoids from *D. plicatile*.

RESULTS AND DISCUSSION

The ethyl acetate-soluble portion of a methanolic extract of *D. plicatile* was repeatedly chromatographed over silica gel and LH-20 to give six stilbenoids.

Compounds **1–6** were identified as 3-methoxy-3′,5-dihydroxybibenzyl (batatasin) [1], 3,3′,4′-trimethoxy-5-hydroxybibenzyl (3-*O*-methylgigantol) [2], 2-methoxy-4,7-dihydroxy-9,10-dihydrophenanthrene (lusianthridin) [3], 2,4-dimethoxy-3,7-dihydroxyphenanthrene (ephemeranthol B) [2], 2,7-dihydroxy-3,4-dimethoxy-9,10-dihydrophenanthrene (erianthridin) [2] and ephemeranthoquionone [2], respectively, based on the spectral data.

Compound **7** showed UV absorption maxima at 280 and 300 nm, suggesting that the compound was a dihydrophenanthrene. The IR spectrum showed absorptions at 3300 (OH), 1590 and 1450 cm^{-1} (benzenoids). The mass spectrum of **7** exhibited a molecular ion peak at m/z 482 $[M]^+$ and a significant peak at m/z 241 corresponding to the fragment $[M/2]^+$, suggesting that **7** was a bidihydrophenanthrene. The ^1H NMR spectrum also confirmed the dimeric structure formed by the symmetrical coupling of two dihydrophenanthrenes, since there was no doubling up of the signals from the two moieties present: i.e. a singlet at δ 6.48 due to H-3,3′, a doublet at δ 8.19 ($J = 9$ Hz) due to *ortho*-coupled H-5,5′, a doublet of doublets at δ 6.64 ($J = 9$ and 2.5 Hz) due to *ortho*- and *meta*-coupled H-6,6′ and a doublet at δ 6.58 ($J = 2.5$ Hz) due to *meta*-coupled H-8,8′. Additionally, the ^1H NMR spectrum showed signals for two methoxyl groups at δ 3.65 and multiplets at δ 2.50 and 2.31 assignable to H-9,9′ and H-10,10′. NOE enhancement was used to determine the assignment of signals and the position of the functional groups. Irradiation of the methoxyl signal only enhanced the signal for H-3,3′ (12%). Furthermore, irradiation of H-9,9′ at δ 2.50 caused enhancement of the signal due to H-8,8′ (8.8%), while irradiation of H-10,10′ at δ 2.31 gave no enhancement.

Thus, the methoxyl groups were located at C-2,2′ and the two phenanthrene moieties were linked at C-1 and C-1′. From the above findings, the structure of **7** was established as 2,2′-dimethoxy-4,4′,7,7′-tetrahydroxy-9,9′,10,10′-tetrahydro-1,1′-biphenanthrene, i.e. a dimer of lusianthridin.

EXPERIMENTAL

IR: KBR; UV: MeOH; ^1H NMR: 500 MHz; MeOH-d_4 with TMS as int. standard; MS: EI; CC; Merck silica gel, Sephadex LH-20 and Cosmosil C18.

Plant materials. The crude drug 'Shi Hu' was purchased from Tochimoto-Tenkaido Co. (collected in Guangxi Province, China) and identified by Dr K. Yoneda, Faculty of Pharmaceutical Sciences, Osaka University. A voucher specimen is deposited in our laboratory.

Extraction and isolation. The crude drug (4.8 kg)

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was extracted with MeOH at room temp. After evapn of solvent, the residue was diluted with H_2O and partitioned successively with EtOAc and *n*-BuOH. A part (28 g) of the EtOAc extract (99 g) was subjected to CC on silica gel using CH_2Cl_2–MeOH with increasing amounts of MeOH to give 4 frs. Fr. 4 was repeatedly subjected to CC on silica gel and LH-20 to give: **1** (2 mg), **2** (3 mg), **3** (13 mg), **4** (2 mg), **5** (1 mg), **6** (5 mg) and **7** (2 mg).

Compound **7**. Powder. IR ν_{max} cm^{-1}: 3300, 1590, 1450; UV λ_{max} nm (log ε): 272 sh (4.30), 280 (4.34), 300 (4.19), 312 (4, 04); MS *m/z* (rel. int.): 482 (100), 241 (21.5), 227 (6.7), 107 (5.7); ^{1}H NMR δ: 2.31 (4H, *m*, H-10,10′), 2.50 (4H, *m*, H-9,9′), 3.65 (6H, *s*, MeO), 6.48 (2H, *s*, H-3,3′), 6.58 (2H, *d*, $J = 2.5$ Hz, H-8,8′), 6.64 (2H, *dd*, $J = 9$, 2.5 Hz, H-6,6′), 8.19 (2H, *d*, $J = 9$ Hz, H-5,5′).

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