Phenols and a triterpene from *Dendrobium aurantiacum* var. *denneanum* (Orchidaceae)

Li Yang a,b, Zhengtao Wang a,b,*, Luoshan Xu b

a Key Laboratory of Standardization of Chinese Medicines of Ministry of Education, Institute of Chinese Materia Medica, Shanghai University of Traditional Chinese Medicine, 1200 Cailun Road, Zhangjiang Hi-tech Park, Shanghai 201203, PR China

b Department of Pharmacognosy, China Pharmaceutical University, 1 Shennong Road, Nanjing 210038, PR China

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1. Subject and source

*Dendrobium aurantiacum* Rchb.f. var. *denneanum* (Kerr.) Z. H. Tsi (Fam. Orchidaceae), locally known as “Shihu” or “Huangcao” in China, is widely distributed in South China, Burma, Laos, Thailand and other parts of South Asia. The aerial parts of this plant were collected from Yunnan Province, P.R. China in March 2004. A voucher specimen of this collection (DQ-YN0403-01) has been deposited at Herbarium of China Pharmaceutical University, Nanjing, P.R. China.

2. Previous work

Bibenzyls, phenanthrenes, benzoquinone, coumarin, cinnamic acid derivatives, β-sitosterol and daucosterol (Ma et al., 1998; Zheng et al., 2000) have been isolated previously from *D. aurantiacum* Rchb.f. var. *denneanum* (Kerr.) Z. H. Tsi.

3. Present study

Powdered air-dried stems (10 kg) of *D. aurantiacum* var. *denneanum* were extracted exhaustively with 95% EtOH under reflux. After evaporation of EtOH in vacuo, the aqueous residue was successively extracted with EtOAc and n-BuOH. The EtOAc fraction (430 g) was subjected to silica gel column chromatography using a solvent mixture of petrol—EtOAc with increasing polarity to yield 15 fractions.

Fraction 4 (24.2 g) from the eluate of petrol—EtOAc (95:5) was chromatographed on silica gel column with petrol—acetone gradient system to yield 9 subfractions. Prep. TLC (cyclohexane—acetone, 9:1) of subfractions 9/1 (0.3 g) afforded taraxerol (1, 8 mg) (Wang and Wang, 1996), and coumarin (2, 3.7 g) (Zheng et al., 2000) was isolated from subfractions 9/3 (8.6 g) as a precipitate followed by crystallization from cyclohexane—acetone. Further silica gel column
chromatography (petrol–CH$_2$Cl$_2$, 9:1) of subfraction 9/6 (10.5 g) yielded n-octacosyl ferulate (11, 3.2 g) (Talapatra et al., 1989) and defuscin (12, 2.3 g) (Wandjii et al., 1990), respectively.

Fraction 9 (13.3 g) from the eluate of petrol–EtOAc (8:2) was also subjected to silica gel column chromatography with CH$_2$Cl$_2$–acetone gradient system to provide 8 subfractions. Further Sephadex LH-20 column chromatography with CH$_2$Cl$_2$–MeOH (1:1) of subfractions 8/3 (2.1 g) and 8/4 (1.3 g) gave moscatilin (3, 20 mg) (Majumder and Sen, 1987), chrysotobibenzyl (4, 45 mg) (Ma et al., 1994) and chrysotoxin (5, 9 mg) (Ma et al., 1996), respectively. Repeated column chromatography on silica gel with petrol–acetone (8:2) of subfraction 8/6 (6.2 g) yielded gigantol (6, 2.8 g) (Leslie and Jamieson, 1982).

Fraction 11 (9.6 g) was applied on a reverse-phase C$_{18}$-ODS column with MeOH–H$_2$O gradient system, and 6 subfractions were collected. Further C$_{18}$-ODS column chromatography (MeOH–H$_2$O, 8:2) and prep. TLC (CH$_2$Cl$_2$–MeOH, 9:1) of subfraction 6/2 (1.6 g) afforded kaempferol (7, 12 mg) (Ulubelen et al., 1980) and naringenin (8, 15 mg) (Shen et al., 1993). Subfractions 6/4 (1.2 g) was chromatographed on Sephadex LH-20 column with MeOH–CH$_2$Cl$_2$ (7:3) to provide dengibsin (9, 30 mg) (Talapatra et al., 1985) and dendroflorin (10, 11 mg) (Zhang et al., 2004).

The compounds were identified conclusively by UV, IR, MS, $^1$HNMR and $^{13}$C NMR analysis. The experimental data were in good agreement with those published in literatures.
4. Chemotaxonomic significance

Among the compounds presented in this study are the first reports on the occurrence of gigantol (6), naringenin (8), dengibisin (9) and dendroflorin (10) from *D. aurantiacum* var. *denneanum* and the first report on the isolation of tarraxerol (1) and kaempferol (7) from the genus *Dendrobium* (DNP, 2005), although the latter in glycosidic form has been reported as a constituent of some *Dendrobium* species by Williams (1979).

The remaining compounds, coumarin (2), moscatilin (3), chrysotobibenzyl (4), chrysotoxin (5), n-octacosyl ferulate (11) and defuscin (12) were previously isolated from *D. aurantiacum* var. *denneanum* and other *Dendrobium* species (Ma et al., 1998; Zheng et al., 2000; DNP, 2005).

However, the compounds we obtained from *D. aurantiacum* var. *denneanum* include the chemotypes of triterpene, coumarin, cinnamic acid derivates, bibenzyl, flavone and fluorenone, the biosynthesis of which except triterpene are all proposed to follow cinnamic acid pathway. Our phytochemistry study of *D. aurantiacum* var. *denneanum* is also in agreement with other reports on the chemical composition of *Dendrobium* species showing that bibenzyls are the most characteristic compounds for the genus *Dendrobium*. More than 20 bibenzyls have been reported from this genus (DNP, 2005). Furthermore, fluorenone is another type of compound that is characteristic for the genus *Dendrobium*, as in other plant sources to date are few (Wu et al., 1994). In Wu’s paper, 1-hydroxy-2,5,8-trimethyl-9H-fluoren-9-one was isolated from *Trypterigium wilfordii* (Celastraceae), but this compound was methyl substituted, whereas the fluorenones in the genus *Dendrobium* are hydroxyl or methoxyl substituted derivatives. The significance of fluorenone derivatives as chemotaxonomic marker for the genus *Dendrobium* requires further investigation.

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References


