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TWO NEW FLUORENONES FROM *DENDROBIUM CHRYSOTOXUM*

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Two new fluorenones have been isolated from the orchid *Dendrobium chrysotoxum* Lindl. and their structures established as 2,4,7-trihydroxy-5-methoxy-9-fluorenone and 2,4,7-trihydroxy-1,5-dimethoxy-9-fluorenone.

Keywords: Orchidaceae; *Dendrobium chrysotoxum* Lindl.; Fluorenones

INTRODUCTION

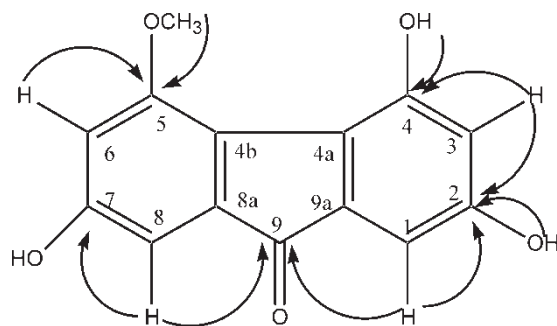
In continuation of our work on the orchid *Dendrobium chrysotoxum* Lindl. [1–3], two new fluorenones, 2,4,7-trihydroxy-5-methoxy-9-fluorenone (**1**) and 2,4,7-trihydroxy-1,5-dimethoxy-9-fluorenone (**2**), were isolated from the stem of *Dendrobium chrysotoxum*. Their structures were established as **1** and **2** from following spectroscopic evidence.

RESULTS AND DISCUSSION

The structures of compounds **1** and **2** were determined largely by interpretation of 400 MHz NMR spectral data, making use especially of HMBC and HMQC enhancement results. Both 2,5,7-trihydroxy-4-methoxy-9-fluorenone (**1**), C₁₄H₁₀O₅, and 2,4,7-dihydroxy-1,5-dimethoxy-9-fluorenone (**2**), C₁₅H₁₂O₆, showed typical fluorenone UV absorptions similar to those of fluorenones derivatives [1]; for compound **1** at λ_{max} 276 and 345 nm, and (**2**) at 270, 276 and 338 nm.

The ¹H and ¹³C NMR spectra of 2,4,7-trihydroxy-5-methoxy-9-fluorenone (**1**) revealed one carbonyl, twelve aromatic carbons and four aromatic protons. By comparing the chemical shifts with those of related compounds [1], compound **1** is seen to possess a fluorenone skeleton having three hydroxyl and one methoxyl groups. The spectrum also displayed four

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FIGURE 1 Key HMBC correlations of **1**.

aromatic protons, appearing as two pairs of *meta*-related doublets at δ 6.76 (d, $J = 2.0$) and δ 6.74 (d, $J = 2.0$), and δ 6.64 (d, $J = 2.2$) and δ 6.39 (d, $J = 2.2$). The assignment was further confirmed by HMQC and HMBC spectra. In the HMBC spectrum, both the protons at δ 6.64 and δ 6.76 showed long-range correlation with the carbonyl signal at δ 193.3 (C-9), indicating that these two protons must be located at C-1 (106.3) and C-8 (105.3) (Fig. 1). As the signals at δ 6.64, δ 6.39 and δ 6.76, δ 6.74 are *meta*-related, the protons at δ 6.39 and δ 6.74 should be located at C-3 (106.0) and C-6 (109.9), respectively. Both the methoxyl at δ_{H} 4.09 (δ_{C} 57.4) and H-6 at δ 6.39 correlated with the signal at 152.6 (C-5), so the methoxyl must be located at C-5 and the three hydroxyl groups should be located in the other positions, at C-2 (159.6), C-4 (152.6) and C-7 (160.0). Based on the foregoing evidence, the structure of compound **1** was deduced to be 2,4,7-trihydroxy-5-methoxy-9-fluorenone.

The ^1H NMR spectra of compound **2** showed signals for two aromatic methoxyl groups (δ 4.10, 3.81, each 3H, s), three aromatic protons, one of which was single (δ 6.42, 1H, s), two others appeared as one set of *meta*-related doublets at δ 6.77 (1H, d, $J = 2.0$) and δ 6.74 (1H, d, $J = 2.0$). The ^1H and ^{13}C NMR data of **2** are similar to those of **1** except for the HMBC chemical shift of C-1 (δ_{C} 142.9). In the HMBC spectrum, a 3-bond correlation of methoxyl protons at δ 3.91 (3H) with the carbon at δ_{C} 142.9 established the methoxyl to be at C-1 (Fig. 2). Based on the above evidence, the structure of **2** was deduced to be 2,4,7-trihydroxy-1,5-dimethoxy-9-fluorenone. The ^1H and ^{13}C NMR spectral data of **1** and **2** are shown in Table I.

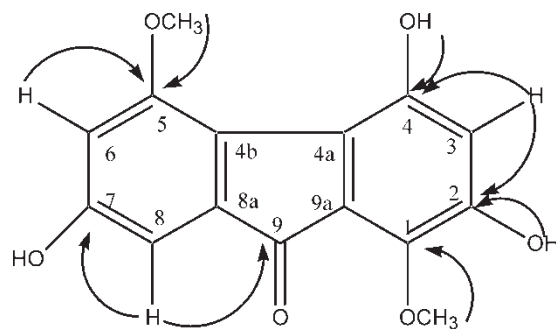
EXPERIMENTAL

General Experimental Procedures

Melting points were determined on a WRX-1 S apparatus and are uncorrected, IR spectra were recorded on a Nicolet Impact 410 as KBr pellets, NMR spectra were taken at 400 MHz, 100 MHz NMR on a Bruker AFC-300, 400 with TMS as internal standard, and mass spectra were performed on a HP5989A mass spectrometer operated at 70 eV. UV spectra were performed on a UV-2501 in MeOH; Column chromatography was carried out on silica gel columns (100–200 mesh) and Sephadex LH-20 (Pharmacia); TLC was conducted on silica gel G using CHCl_3 –MeOH (9:1) and CHCl_3 –acetone (4:1) as solvents.

Plant Material

Plant material was collected at Xishuangbanna (Yunnan Province, China), the plant was identified as *Dendrobium chrysotoxum* Lindl by Dr Xu Hong and the voucher specimen is deposited in the Herbarium of China Pharmaceutical University, Nanjing, China.

FIGURE 2 Key HMBC correlations of **2**.

Extraction and Isolation

Air-dried stems of *Dendrobium chrysotoxum* (12 kg) were powdered and extracted with CHCl_3 three times, then refluxed with 95% EtOH for a further 8 h. After removal of the solvent by evaporation, the resultant residue (400 g) was chromatographed over silica gel and eluted with CHCl_3 -MeOH (100:5) to yield a mixture (20 g), which was further chromatographed on silica gel columns using gradient elution with CHCl_3 -MeOH (100 : 3 \rightarrow 100 : 8) to give fraction I-VI. Fraction III (100:5) and fraction V (100:6) were rechromatographed on Sephadex LH-20 with CHCl_3 -MeOH (1:1), yielding **1** (30 mg) and **2** (10 mg), which were then recrystallized from CHCl_3 -MeOH.

2,4,7-Trihydroxy-5-methoxy-9-fluorenone (**1**)

Dark red needles were obtained from CHCl_3 -MeOH, mp 279–280.4°C; EIMS m/z (%): 258 $[\text{M}]^+$ (100), 243 (88), 215(62), HR-EIMS m/z 258.0547, calcd. for $\text{C}_{14}\text{H}_{10}\text{O}_5$ 258.0458; IR ν_{max} (KBr) (cm^{-1}): 3340 (Ar-OH), 1670, 1621, 1472, 1311; UV λ_{max} (MeOH) (nm): 345, 276; for ^1H and ^{13}C NMR spectral data of **1** see Table I.

TABLE I ^1H and ^{13}C NMR spectral data of compounds **1** and **2** (400 MHz for ^1H , 100 MHz for ^{13}C acetone- d_6); δ (ppm), J (Hz)

C	1			2		
	^1H	^{13}C	HMBC	^1H	^{13}C	HMBC
1	6.76 (1H, d, $J = 2.0$)	106.3	C-2, 3, 9, 4a	–	142.9	–
2	–	159.7	–	–	153.2	–
3	6.74 (1H, d, $J = 2.0$)	106.0	C-1, 2, 4	6.42 (1H, s)	111.3	C-1, 2, 4, 4a
4	–	152.6	–	–	148.5	–
4a	–	123.7	–	–	123.5	–
4b	–	119.9	–	–	118.8	–
5	–	152.5	–	–	153.2	–
6	6.39 (1H, d, $J = 2.2$)	109.9	C-5, 7, 8, 4b	6.74 (1H, d, $J = 2.0$)	106.5	C-5, 7, 8, 4b
7	–	160.0	–	–	160.0	–
8	6.64 (1H, d, $J = 2.2$)	105.3	C-6, 7, 9, 4b	6.77 (1H, d, $J = 2.0$)	106.1	C-6, 9
8a	–	137.1	–	–	137.8	–
9	–	193.3	–	–	191.4	–
9a	–	130.0	–	–	125.8	–
–OCH ₃	4.09 (3H, s)	57.4	C-5	4.10 (3H, s)	62.3	C-5
	–	–	–	3.91 (3H, s)	57.9	C-1

2,4,7-Trihydroxy-1,5-dimethoxy-9-fluorenone (2)

Dark red needles from CHCl_3 -MeOH, mp 245.4–246.5°C; EIMS m/z (%): 288 [M^+] (100), 273, 245, 227, HR-EIMS m/z 288.06049, calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_6$ 288.0575; IR ν_{max} (KBr) (cm^{-1}): 3402(Ar-OH), 3296 (Ar-OH), 1696, 1618, 1495, 1294; UV λ_{max} (MeOH) (nm): 338.00, 276.60, 270.20; for ^1H and ^{13}C NMR spectral data of **2** see Table I.

Acknowledgements

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References

- [1] Ma, G.X., Wang, Z.T., Xu, L.S. and Xu, G.J. (1998), *J. Chin. Pharm. Sci.* **7**, 142–146.
- [2] Ma, G.X., Xu, G.J., Xu, L.S., Wang, Z.T. and Kickuchi, T. (1994), *Acta Pharm. Sin.* **29**, 763–766.
- [3] Ma, G.X., Xu, G.J., Xu, L.S., Wang, Z.T. and Kickuchi, T. (1996), *Acta Pharm. Sin.* **31**, 222–225.