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A New Bibenzyl Derivative from *Dendrobium moniliforme*

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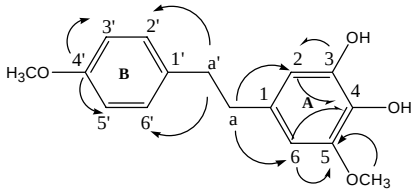
Abstract: A new bibenzyl derivative, 3,4-dihydroxy-4′,5-dimethoxy bibenzyl, was isolated from a orchid *Dendrobium moniliforme*. The structure elucidation and ^{1}H,^{13}C NMR assignments were achieved by spectroscopic method.

Keywords: Orchidaceae, *Dendrobium moniliforme*, 3,4-dihydroxy-4′,5-dimethoxy bibenzyl.

The chinese crude drug "Shihu", derived from the dried or fresh stems of many plants of Genus *Dendrobium*, is usually used to clear heat and for the benefit of eyes. In previous communications[1,2,3] we reported the isolation of some phenolic compounds from *Dendrobium chrysotoxum* Lindl., in this paper, we report the isolation of a new phenolic compound from *Dendrobium moniliforme* (L.) Sw.. The structure of the new compound **1** was established as 3, 4-dihydroxy-4′,5-dimethoxy bibenzyl **(Scheme)** from the spectral evidence.

Scheme The HMBC correlation of compound **1**



The 95% EtOH extract of *D. moniliforme* was partitioned with petroleum ether and acetone, successively. The acetone fraction was further fractionated on silica gel column chromatography to afford the compound **1**. Compound **1** was a viscous solid, UV λ max(MeOH) at 203, 277nm showed characteristic of bibenzyls. EI-MS *m/z*: 274(M^+) and HR-MS *m/z*: 274.1207(calculated 274.1025) suggested the molecular formula to be $C_{16}H_{18}O_4$. The ^{1}H-NMR spectrum of **1** exhibited a 4H signal at δ 2.71 characteristic of methylene protons in a bibenzyl nucleus. Two singlets at δ 3.69(s, 3H) and 3.66(s, 3H) indicated the presence of two aromatic methoxyl groups; two singlets at δ 6.66 and 6.33(disappearing on deuterium exchange) for two normal phenolic hydroxyl protons. In addition, there were six aromatic protons at δ 7.01(d, 2H, J=8.2Hz), 6.78(d, 2H, J=8.2Hz), 6.44(d, 1H, J=1.3Hz) and 6.20(d, 1H, J=1.3Hz). The EI-MS of compound **1** showed two intense peaks at *m/z* 153(44) and 121(base peak) arising by the

cleavage of benzylic linkage. The ion peak at *m/z* 153 required two hydroxyl and one methoxyl groups in ring A and the remaining fragment at *m/z* 121 required the placement of one methoxyl group in ring B. The coupled pattern of the signals at δ 7.01 and 6.78 gave the evidence that the methoxyl group should be located at C-4′.

The ^{13}C NMR spectrum gave fourteen carbon signals. The DEPT spectrum revealed four tertiary carbons, six quaternary carbons, two second carbons and two methoxy carbons, and suggested that C-2′, C-3′ and C-5′, C-6′ had the same δ c value (129.3 and 113.4). The COLOC spectrum showed that the signals at δ_H 2.71 (a,a′-CH_2) was correlated with the signals at δ c129.3(C-2′,6′), 108.7(C-2), 103.6(C-6), and not correlated with the signal at δ c113.4(C-3′,5′). The signal at δ c143.7(C-3) was correlated with the signal at δ_H 6.44(H-2), δ c130.5(C-4) was correlated with the signals at δ_H 6.20(H-6) and 6.44(H-2); δ c146.9(C-5) was correlated with δ_H 3.66(-OCH_3) and δ_H 6.20(ring A). All the above data supported that the methoxyl group(δ_H3.66) should be substituted at C-5 of ring A, and the two hydroxyl groups substituted at C-3 and C-4, respectively. Hence, compound **1** was assigned as 3,4-dihydroxy-4′,5-dimethoxy bibenzyl. The assignment of the position was further confirmed by the HMQC spectrum. ^1H, ^{13}C NMR spectra data of compound **1** are listed in **Table 1**.

Table 1 ^1H and ^{13}C NMR spectra data of compound **1** ($CDCl_3$)

Position	δ_C ppm	$\delta_H$ppm
1	133.4	
2	108.7	6.44(d, 1.3Hz)
3	143.7	
4	130.5	
5	146.9	
6	103.6	6.20(d, 1.3Hz)
1′	133.7	
2′,6′	129.3	7.01(d, 8.2Hz)
3′,5′	113.4	6.78(d, 8.2Hz)
4′	157.3	
5-OCH_3	55.7	3.66(s)
4′-OCH_3	54.9	3.69(s)
a-CH_2	37.6	2.71(m)
a′-CH_2	36.7	2.71(m)

References

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