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PARVIFLORIN A PHENANTHROPYRAN FROM *VANDA PARVIFLORA*

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Key Word Index—*Vanda parviflora*; Orchidaceae; parviflorin; phenanthropyran.

Abstract—From the whole plant of *Vanda parviflora*, a new phenanthropyran derivative was isolated. Its structure is elucidated as 2,6-dihydroxy-8-methoxy-9,10-dihydrophenanthropyran on the basis of spectroscopic data. This is the first report of a phenanthropyran with a 2,6,8-substitution pattern.

INTRODUCTION

In the course of our investigation on the chemical constituents of different orchids, we reported the isolation and characterisation of pyrans [1–3], a pyrone [4], quinones [5], bibenzyls [6], a phenanthrene carboxylic acid [7] and a novel pyrene [8]. In this paper we report on the structural elucidation of a new phenanthropyran derivative, parviflorin (**1**), from *Vanda parviflora* R.Br.

RESULTS AND DISCUSSIONS

Parviflorin (**1**) gave a positive ferric chloride reaction characteristic of a phenolic hydroxyl group and analysed for $C_{16}H_{14}O_4$, ($[M]^+$ m/z = 270), and showed UV maxima at λ_{max}^{EtOH} 223, 284, 309 and 321 nm characteristic of a phenanthrene skeleton. IR absorption bands at ν_{max}^{KBr} 3420 and 3380 cm^{-1} supported the presence of phenolic hydroxyl groups.

The ^1H NMR spectrum of **1** showed an aromatic methoxyl group at δ 3.77 (*s*, 3H), two D_2O exchangeable hydroxyl groups at δ 8.20 and 8.79, and a singlet at δ 5.02 (2H) assignable to the methylene protons of a oxymethylene group indicating that **1** was a monomethoxy-dihydroxy-phenanthropyran derivative and accounting for the four oxygen atoms in the molecular formula of **1**.

1 formed a diacetate (**2**) ($C_{20}H_{18}O_6$ $[M]^+$, m/z = 354) with acetic anhydride and pyridine supporting the presence of two hydroxyl groups. The two acetoxyl signals in the ^1H NMR spectrum of **2** at δ 2.27 (*s*, 3H) and 2.23 (*s*, 3H) further supported the presence of two hydroxyl groups.

The singlet signal at δ 2.80 (*br s*, 4H) in the ^1H NMR spectrum of **1** was allocated to the 9 and 10 methylene protons indicating it to be a 9,10-dihydrophenanthropyran derivative. The two doublets at δ 6.06 (*d*, 1H, J = 2.5 Hz) and 6.28 (*d*, 1H, J = 2.5 Hz) were shifted down field and appeared as a broad singlet at δ 6.56 (*br s*, 2H) in the spectrum of **2** indicating the two protons to be *meta* coupled to each other and *ortho* to a phenolic hydroxyl group. The considerable chemical shift difference in the two doublets in **1** indicated different chemical environments for the two protons and thus were assigned to H-1 and H-3 with a hydroxyl group at C-2.

The considerable downfield shift of the H-5 protons in **2** to δ 5.22 indicated that hydroxyl was in close proximity to these protons. Thus, the second hydroxyl group was allocated to C-6. The ^1H NMR spectrum of **1** showed another aromatic signal at δ 6.62 (*s*, 1H) which was shifted downfield and appeared as a broad singlet at δ 6.84 in **2** indicating that the proton is *ortho* to a hydroxyl group and eliminating the other possible structure i.e. 2,6-dihydroxy-7-methoxy-9,10-dihydro-phenanthropyran. Hence, the methoxyl was allocated to C-8 and the signal at δ 6.64 (*s*, 1H) was allocated to H-7. Thus, assigning the structure for **1** as 2,6-dihydroxy-8-methoxy-9,10-dihydrophenanthropyran.

The ^{13}C NMR spectrum of **2** supported the structure. A considerable upfield shift in the ^{13}C NMR spectrum of **2** was observed for C-4a, C-5, C-7 and C-8a. The upfield shift in C-7 to δ 107.8 was due to the combined *ortho* effect of OAc and OMe. The *ortho* effect of the acetoxyl and *para* effect of OMe made the C-5 resonate at δ 116.3. The considerable upfield shift of C-4a to δ 108.6 was attributed to the combined

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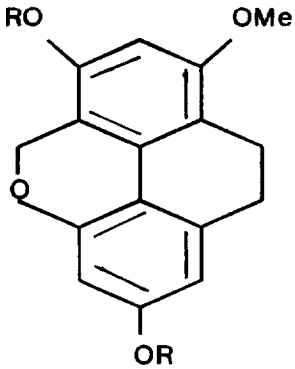

(1) R = H (2) R = Ac

effect of the three substituents at C-2, C-6 and C-8. The upfield shift of C-8a to δ 117.1 was attributed to the combined *para* effect of C-6 acetoxyl and *ortho* effect of C-8 methoxyl groups. The chemical shift difference in C-9 and C-10 carbons was attributed to the different locations of the methoxyl group at C-8 for C-9 and C-10 carbons, respectively, resulting in an upfield shift for C-10, resonating at δ 20.6, and downfield shift for C-9, resonating at δ 29.5.

Thus, the structure 2,6-dihydroxy-8-methoxy-9,10-dihydro-phenanthro-pyran was allocated to **1**, which we have named as parviflorin. Parviflorin is a new natural compound.

EXPERIMENTAL

General. Mps: uncorr.; IR:KBr; UV:EtOH; ^{1}H NMR: 270 MHz, $CDCl_3$.

Plant material. The plant material of *Vanda parviflora* was collected in Ooty during November 1996.

Extraction and isolation. The air dried whole plant was extracted with hexane, Me_2CO and MeOH. Each extract was impregnated with a minimum amount of silica gel and washed with hexane, Et_2O, Me_2CO and MeOH. The Et_2O wash of the three extracts were found to be similar on TLC and were mixed. The combined extract was subjected to CC using hexane, C_6H_6, $CHCl_3$ and MeOH. The C_6H_6 eluate was subjected to phenolic, and non-phenolic sepn and the phenolic part was concd and rechromatographed using hexane, C_6H_6 and Me_2CO mixts. The hexane–C_6H_6 (1:1) mixt. was subjected to PTLC on Silica gel HF 254. The fluorescent band was eluted with Me_2CO, concd and recrystallised from C_6H_6 to yield parviflorin.

Parviflorin (**1**). M.p. 142°, analysed for $C_{16}H_{14}O_4$. UV λ_{max}^{EtOH} nm 223, 284, 309 and 321; IR ν_{max}^{KBr} cm^{-1}: 3420 and 3380, 1620, 860 and 845; ^{1}H NMR ($CDCl_3$): δ 2.80 (4H, *s*, H-9 and H-10), 3.70 (3H, *s*, —OMe), 5.02 (2H, *s*, —O—CH_2—Ar), 8.20, 8.69 (each 1H, *s*, ArOH), 6.03 (1H, *d*, J = 2.3 Hz H-3), 6.28 (*d*, 1H, J = 2.3 Hz, H-1) and 6.62 (*s*, 1H, H-7).

Parviflorin diacetate (**2**). M.p. 121°, analysed for $C_{20}H_{18}O_6$. UV λ_{max}^{EtOH} nm: 220, 282 and 304; IR ν_{max}^{KBr} cm^{-1}: 1225, 1280 and 1765, 1610, 890, 860 and 845; ^{1}H NMR ($CDCl_3$): δ 2.27 (3H, *s*, —OCOMe), 2.33 (3H, *s*, —OCOMe), 2.87 (4H, *s*, H-9, H-10), 3.77 (3H, *s*, —ArOMe), 5.22 (2H, *s*, Ar—OCH_2—Ar) 6.56 (2H, *br s*, H-1 and H-3) 6.62 (*br s*, 1H, H-7); ^{13}C NMR ($CDCl_3$): δ 114.3(C-1), 150.6(C-2), 121.5(C-3), 152.9(C-4), 108.6(C-4a), 128.9(C-4b), 63.1(C-5a), 116.3(C-5), 150.3(C-6), 107.8(C-7), 158.6(C-8), 117.1(C-8a), 29.5(C-9), 20.6(C-10), 135.6(C-10a), 21.6, 20.5(OCOMe), 168.3, 169.5 (OCOMe) 56.4(OMe).

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