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TESSALLATIN A PHENANTHROPYRAN FROM *VANDA TESSALATA*

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Key Word Index—*Vanda tessalata*; *Orchidaceae*; tessalatin; phenanthropyran.

Abstract—From the whole plant of *Vanda tessalata*, a new phenanthropyran derivative was isolated. Its structure was elucidated as 3,7-dihydroxy-2-methoxy-9,10-dihydrophenanthropyran on the basis of spectroscopic data. This is the first report of a phenanthropyran with a 2,3,7-substitution pattern. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In the course of our investigations on the chemical constituents of different orchids we have reported on the isolation and characterization of pyrans [1–4], a pyrone [5], quinones [6], bibenzyls [7], a phenanthrene carboxylic acid [8] and a novel pyrene [9]. In this paper we report on the structural elucidation of a new phenanthropyran derivative tessalatin (**1**) from *Vanda tessalata* R. Br.

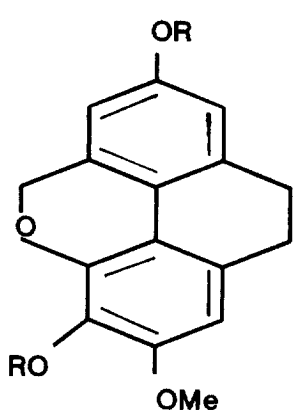
RESULTS AND DISCUSSION

Tessalatin (**1**) gave a positive ferric chloride reaction characteristic of a phenolic hydroxyl group ($C_{16}H_{14}O_4$; $[M]^+$, $m/z = 270$). It showed UV maxima at λ_{max}^{EtOH} 223, 284, and 309 nm characteristic of a phenanthrene skeleton. The 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 3.78 (*s*, 3H), two D_2O exchangeable hydroxyl groups at δ 8.43 and 7.56, and a singlet at δ 5.19 (2H) assignable to the methylene protons of an 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 2.26 (*s*, 3H) and 2.30 (*s*, 3H) further supported the presence of two hydroxyl groups. The singlet signal at δ 2.84 (*br s*, 4H) in **1** was allocated to the 9 and 10 methylene protons indicating it to be a 9,10-dihydro-phenanthropyran derivative. The two doublets at δ 6.27 (*d*, 1H, $J = 2.3$ Hz) and 6.30 (*d*, 1H, $J = 2.3$ Hz) in **1** were shifted downfield and appeared as a broad singlet at δ 6.48 (*br s*, 2H) in **2** indicating the two protons to be *meta* coupled to each other and *ortho* to a phenolic hydroxyl group. The small chemical shift difference in the two doublets in **1** and **2** indicated a similar chemical environment for the two protons and thus they were assigned to H-6 and H-8 with a hydroxyl group at C-7.

The absence of a considerable downfield shift of the 9,10-protons in **2** indicated that the hydroxyl was not in close proximity to the 9,10-protons. Thus, the hydroxyl group was allocated to C-3. The ^1H NMR spectrum of **1** showed another aromatic signal at δ 6.68 (*s*, 1H) which appeared at δ 6.69 in **2** indicating that the proton was not *ortho* to a hydroxyl group and eliminating the other possible structure, i.e. 2,7-dihydroxy-3-methoxy-9,10-dihydro-phenanthropyran.



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

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Hence, the methoxyl was allocated to C-2 and the signal at δ 6.69 (*s*, 1H) was allocated to H-1. Thus, the structure of **1** is 3,7-dihydroxy-2-methoxy-9,10-dihydro-phenanthropyran.

The ^{13}C NMR spectrum of **2** supported the structure. A slight upfield shift was observed for C-4, C-4a, and C-4b. The upfield shift in C-4 to δ 143.9 was due to the *ortho* acetoxyl at C-3. The combined effect of the two acetoxyls at C-3 and C-7 made C-4b resonate at δ 120.4. The considerable upfield shift of C-4a to δ 111.0 was attributed to the *para* methoxyl group at C-2. The chemical shift difference in C-9 and C-10 was in agreement with the C-7 acetoxyl effect on C-9 and the C-2 methoxyl effect on C-10 resulting in C-9 resonating at δ 26.8 and C-10 at δ 21.5.

Thus, the structure 3,7-dihydroxy-2-methoxy-9,10-dihydro-phenanthropyran was assigned to **1** and was named as tessalatin. Tessalatin is a new natural compound.

EXPERIMENTAL

General. Mps: uncorr.; IR: KBr; UV EtOH; ^1H NMR: 270 MHz, $CDCl_3$; ^{13}C NMR: $CDCl_3$ with TMS; CC and TLC: silica gel.

Plant material. The plant material of *Vanda tessalata* was collected in Araku valley during April 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, CH_2Cl_2 and MeOH. The CH_2Cl_2 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 C_6H_6–Me_2CO (19 : 1) mixt. was subjected to PTLC using HF 254 silica gel. The fluorescent band was eluted with Me_2CO, concd and recrystallised from EtOAc–MeOH to give tessalatin.

Tessalatin (**1**). Mp 125°, analysed for $C_{16}H_{14}O_4$. UV λ_{max}^{EtOH} nm,: 225, 284 and 309; IR ν_{max}^{KBr} cm^{-1}: 3420, 3380, 1620, 860 and 845; ^1H NMR ($CDCl_3$): δ 2.84 (4H, *s*, H-9 and H-10), 3.78 (3H, *s*, -OMe), 5.19 (2H, *s*, -O-CH_2-Ar), 8.43, 7.56 (each 1H, *s*, ArOH), 6.27 (1H, *d*, J = 2.3 Hz H-8) and 6.30 (*d*, 1H, J = 2.3 Hz, H-6), 6.68 (*s*, 1H, H-1).

Tessalatin diacetate (**2**). Mp 167°, analysed for $C_{20}H_{18}O_6$. UV λ_{max}^{EtOH} nm,: 222, 269, 284, 302 and 315; IR ν_{max}^{KBr} cm^{-1}: 2940, 2845, 1756, 1450, 1410 and 1275; ^1H NMR ($CDCl_3$): δ 2.26 (3H, *s*, -OCOMe), 2.30 (3H, *s*, -OCOMe), 2.83 (4H, *s*, H-9, H-10), 3.79 (3H, *s*, -ArOMe), 5.18 (2H, *s*, Ar-OCH_2-Ar), 6.48 (2H, *br s*, H-6 and H-8), 6.69 (1H, *s*, H-1); ^{13}C NMR ($CDCl_3$): δ 108.1 (C-1), 152.4 (C-2), 122.3 (C-3), 143.9 (C-4), 111.0 (C-4a), 120.4 (C-4b), 64.0 (C-5a), 131.5 (C-5), 119.3 (C-6), 150.2 (C-7), 119.2 (C-8), 137.5 (C-8a), 26.8 (C-9), 21.5 (C-10), 135.0 (C-10a), 20.6, 20.3 (OCOMe), 168.9, 168.7 (OCOMe), 60.9 (OMe).

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