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AMOENUMIN, A 9,10-DIHYDRO-5H-PHENANTHRO-(4,5-*b,c,d*)-PYRAN FROM *DENDROBIUM AMOENUM*

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Key Word Index—*Dendrobium amoenum*; Orchidaceae; amoenumin; 9,10-dihydro-5H-phenanthro-(4,5-*b,c,d*)-pyran.

Abstract—The structure of a 9,10-dihydro-5H-phenanthro-(4,5-*b,c,d*)-pyran, amoenumin, from the orchid *Dendrobium amoenum* has been established on the basis of spectral data.

INTRODUCTION

A number of physiologically active alkaloids such as dendrobine and its structural analogues have been isolated from the genus *Dendrobium* [1–4]. The species from *Coelogyne*, *Pholidota* and *Otochilus* yielded a number of 9,10-dihydro-5H-phenanthro-(4,5-*b,c,d*)-pyrans [5–9]. The present paper deals with the structural elucidation of amoenumin (**1**) from the orchid *Dendrobium amoenum*. This is the first report of a 9,10-dihydrophenanthropyran from *Dendrobium*.

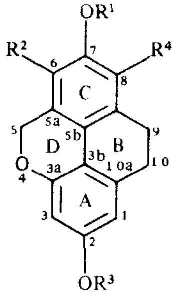
RESULTS AND DISCUSSION

Amoenumin (**1**), $C_{16}H_{14}O_4$ ($M^+ = m/z$ 270) was isolated from the whole plant of *D. amoenum*. It gave a positive ferric reaction (IR $\nu_{\max}^{\mathrm{KBr}}$ 3000 cm^{-1}) and a UV spectrum ($\lambda_{\max}^{\mathrm{MeOH}}$ 218, 284 and 304 nm) similar to those of 9,10-dihydrophenanthrenes [5–12]. The presence of two phenolic hydroxyl groups in the molecule was confirmed by the formation of a diacetyl derivative, $C_{20}H_{18}O_6$ ($M^+ = m/z$ 354), with acetic anhydride–pyridine and a dimethyl ether, $C_{18}H_{18}O_4$ ($M^+ = m/z$ 298), with dimethylsulphate–potassium carbonate in acetone.

The 100 MHz ^{1}H NMR spectrum of amoenumin (**1**) in $CDCl_3$ displayed two one proton broad singlets at δ4.98 and 5.52 for two phenolic hydroxyl groups, a three proton singlet at δ3.78 for an aromatic methoxyl group, a four proton singlet at δ2.80 for the 9,10 methylene protons of a 9,10-dihydrophenanthrene and a two proton singlet at δ5.19 for oxymethylene protons [5].

The spectrum also revealed the presence of three aromatic protons, two of which appeared as a singlet at δ6.31 for H-1 and H-3 [5–11]. However, these two protons appeared as a pair of doublets ($J = 3$ Hz) at δ6.12 and 6.22 when the spectrum was recorded in CD_3OD. The third one resonated as a singlet at δ6.72 in $CDCl_3$ and δ6.62 in CD_3OD. The ^{1}H NMR spectrum of amoenumin diacetate (**2**) is essentially similar to that of amoenumin (**1**) except that the signals for the phenolic hydroxyl groups of the latter are replaced by two acetyl signals at δ2.29 and 2.35 in the former. Furthermore the signal for H-1 and H-3 in amoenumin (**1**) is shifted downfield by $\Delta\delta \sim 0.25$ to δ6.56 in **2**. This is similar to that imbricatin acetate and locates one of the hydroxyls on C-2 [13–15]. The third aromatic proton at δ6.72 in amoenumin (**1**) is shifted downfield by $\Delta\delta \sim 0.13$ in **2** to δ6.85 indicating the absence of a proton *ortho* to a phenolic hydroxyl group [13–15].

The ^{13}C NMR spectral data of the acetate **2** is useful in the assignment of the second hydroxyl group. The chemical shifts of the carbons in **2** were determined by SEFT and are in excellent agreement with the calculated values using the known additivity parameters of the functional groups on the reported carbon chemical shifts of the parent 9,10-dihydrophenanthrene. The carbon chemical shifts of ring A carbons in **2** are essentially similar to flavidin diacetate (**4**), flavidinin acetate (**5**), imbricatin diacetate (**6**), and coelogin (**7**) supporting the assignment of one of the hydroxyl groups in amoenumin (**1**) to C-2 (Table 1).



	R^1	R^2	R^3	R^4
1	Me	OH	H	H
2	Me	OAc	Ac	H
3	Me	OMe	Me	H
4	Ac	H	Ac	H
5	Me	H	Ac	H
6	Ac	OMe	Ac	H
7	Me	OH	H	OMe

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The oxymethylene carbon in **2** appeared at δ63.6 as in **6** and **7** with a substituent at C-6 whereas the other compounds without a C-6 substituent showed the same carbon at δ67.5. The ring C trisubstituted compound coelogin (**7**) showed an upfield shift for both C-9 and oxymethylene groups [5] whereas **2** showed an upfield shift only for the oxymethylene carbon in support of the allocation of the second hydroxyl to C-6. Thus the two phenolic hydroxyls are allocated to C-2 and C-6 and the methoxyl to C-7.

The ^{1}H NMR spectrum of amoenumin dimethyl ether (**3**) showed three methoxyl signals at δ3.80, 3.84 and 3.88. Two aromatic protons appeared as a singlet at δ6.40. The melting point (101°) of **3** is similar to imbricatin dimethyl ether (**9**) supporting the allocation of the three functional groups to C-2, C-6 and C-7. Unfortunately, an authentic sample of imbricatin dimethyl ether is not available for direct comparison.

EXPERIMENTAL

Mps: uncorr. CC: silica gel (100–200 mesh). TLC: silica gel G. ^{1}H NMR: 100 MHz and 90 MHz; ^{13}C NMR: 67.89 MHz.

Isolation of amoenumin (**1**). Air-dried and powdered whole plant of *Dendrobium amoenum* was extracted with hexane, Me_2CO and MeOH successively. The Me_2CO extract was concd and subjected to CC. The earlier fractions of the C_6H_6–Me_2CO (9:1) elute on evapn gave amoenumin (**1**) which was crystallized from MeOH. Mp 120°. [Found C, 71,12; H, 5.21 $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%]. MS m/z: 270 $[M]^+$(100), 269 (23.8), 255 (41.2), 237 (7.5), 225 (6.0), 209 (10.2), 197 (8.4), 181 (12.2), 169 (6.3), 152 (16.9), 139 (11.1), 128 (6.5), 115 (11.8); UV λ_{max}^{MeOH} nm: 218, 284 and 304; IR ν_{max}^{KBr} cm^{-1}: 3300, 2995, 1625, 1445, 1385, 1360, 1310, 1265, 1140, 1020, 855, 745 and 725; ^{1}H NMR ($CDCl_3$) δ2.8 (4H, *s*, H_2-9 and H_2-10) 4.98 and 5.52 (each 1H, *s*, –OH) 3.78 (3H, *s*, –OMe) 5.19 (2H, *s*, oxymethylene) 6.31 (2H, *ms*, H-1 and H-3) and 6.72 (1H, *s*, H-8).

Table 1. ^{13}C NMR data for compounds **2**, **4**–**7**

C	**2**	**4**	**5**	**6**	**7**
1	114.4	114.3	114.1	114.1	108.9
2	151.2	150.6	149.8	150.6	154.9
3	108.3	108.2	107.8	107.8	101.3
3a	153.5	153.2	152.5	152.9	156.2
3b	116.7	116.6	117.3	116.3	112.2
5(–OCH_2)	63.6	67.8	68.2	63.1	63.2
5a	125.2	129.9	129.9	122.2	117.3
5b	122.2	123.7	119.3	124.5	122.9
6	142.7	115.5	108.0	145.2	142.9
7	145.8	149.8	159.4	142.2	136.6
8	121.9	120.2	112.7	121.5	149.1
8_a	129.3	135.7	134.9	128.9	109.8
9	26.9	27.2	27.5	26.4	20.6
10	27.7	27.1	27.5	27.1	27.4
10_a	136.0	134.6	134.9	135.6	138.4
–OCO–Me	21.0	20.9	20.9	20.6	
	20.7			20.3	—
–O$\underline{\text{C}}$O–Me	169.2	169.3	169.4	168.9	
	169.0			168.7	
–OMe	61.4	—	55.3	60.98	60.1
					61.3

δ values are in ppm downfield from TMS. TMS = $CDCl_3$ + 76.9 ppm.

Amoenumin diacetate (**2**). Amoenumin on acetylation with Ac_2O–pyridine and crystallization from MeOH yielded a white solid mp 121°. [Found C, 67.82; H, 5.11 $C_{20}H_{18}O_6$ requires C, 67.8; H, 5.12%]. MS m/z: 354 $[M]^+$(10.7), 312 (14.1), 271 (12.9), 270 (59.1), 269 (13.6), 255 (9.5), 239 (3.0), 225 (3.5), 209 (3.3), 197 (6.3), 181 (4.1), 165 (2.8), 152 (7.1), 139 (5.9), 128 (2.1), 115 (7.2); UV λ_{max}^{MeOH} nm: 209, 268 sh, 276, 300 and 310 (sh); IR ν_{max}^{KBr} cm^{-1}: 2995, 2860, 1770, 1620, 1500, 1430, 1385, 1290, 1210, 1150, 1130, 1010, 910, 850, 740 and 710; ^{1}H NMR ($CDCl_3$): δ2.29 (3H, *s*, –OAc), 2.35 (3H, *s*, –OAc), 2.88 (4H, *s*, H_2-9 and H_2-10), 3.79 (3H, *s*, –OMe), 5.24 (2H, *s*, oxymethylene), 6.56 (2H, *s*, H-1) and H-3) and 6.85 (1H, *s*, H-8).

Methylation of amoenumin. Amoenumin on methylation with Me_2SO_4 and dry K_2CO_3 in dry Me_2CO under reflux for 24 hr afforded amoenumin dimethyl ether (**3**) which was crystallized from MeOH. Mp 101° (imbricatin dimethyl ether, Lit [9] mp 101°). [Found C, 72.44; H, 6.09 $C_{18}H_{18}O_4$ requires C, 72.46; H, 6.08%]. ^{1}H NMR ($CDCl_3$): δ2.85 (4H, *s*, H_2-9 and H_2-10), 3.80, 3.84 and 3.88 (each 3H, *s*, OMe), 5.24 (2H, *s*, oxymethylene), 6.4 (2H, *s*, H-1 and H-3) and 6.7 (1H, *s*, H-8).

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