Pergamon

0031-9422(95)00146-8

Phytochemistry, Vol. 39, No. 6, pp. 1429–1431, 1995

0031-9422/95 $9.50 + 0.00

OCHROLONE, A PYRENE FROM *COELOGYNE OCHRACEA*

V. Anuradha, N. S. Prakasa Rao and M. Udayabhaskar

Department of Chemistry, Nagarjuna University, Nagarjuna Nagar, India 522510

(*Received* 10 *October* 1994)

Key Word Index—*Coelogyne ochracea*; orchidaceae; ochrolone; pyrene.

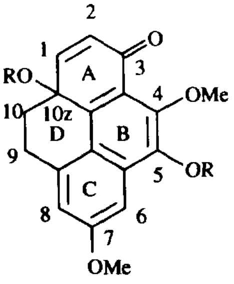
Abstract—From whole plants of *Coelogyne ochracea*, a new pyrene, ochrolone, was isolated. Its structure was elucidated as 5,10*a*-dihydroxy-4,7-dimethoxy-9,10,10*a*-trihydropyrene-3-one on the basis of spectroscopic data. This is the first report of the occurrence of ochrolone from nature and a pyrene from the Orchidaceae.

INTRODUCTION

In the course of our investigations on the chemical constituents of different orchids, we have reported the isolation and characterization of pyrans [1–3], pyrone [4], quinones [5], bibenzyls [6] and a phenanthrene carboxylic acid [7]. In this paper we report the structural elucidation of a new pyrene, ochrolone (**1**), isolated from *Coelogyne ochracea*.

RESULTS AND DISCUSSION

Ochrolone (**1**) gave a positive ferric chloride reaction characteristic of a phenolic hydroxyl group. It showed UV maxima at $\lambda_{\max}^{\mathrm{EtOH}}$ 223, 284, 309 and 321 nm characteristic of a phenanthrene skeleton. IR absorption bands at $\nu_{\max}^{\mathrm{KBr}}$ 3420 and 3380 cm^{-1} supported the presence of hydroxyl groups and an absorption band at $\nu_{\max}^{\mathrm{KBr}}$ 1680 supported the presence of a carbonyl group. The mass spectrum exhibited a $[\mathrm{M}]^+$ at *m/z* 312 ($C_{18}H_{16}O_5$) and other significant ions at *m/z* 297 $[\mathrm{M} - \mathrm{Me}]^+$ *m/z* 272 $[\text{–}\mathrm{CH_2 = CH_2}\text{–}, \mathrm{Me}, +3\mathrm{H}]^+$ and *m/z* 257 $[272 - 15]^+$. The ^{1}H NMR spectrum showed the presence of two aromatic methoxyl groups at δ3.83 (*s*, 3H) and 3.75 (*s*, 3H).



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

Ochrolone formed a diacetate (**2**, $C_{22}H_{20}O_7$) with acetic anhydride and pyridine indicating the presence of two hydroxyl groups. The ^{1}H NMR spectrum of **2** showed acetoxyl signals at δ2.18 (*s*, 3H) and δ2.40 (*s*, 3H) supporting the presence of two hydroxyl groups. The two hydroxyl and two methoxyl groups accounted for the four oxygens in the molecular formula $C_{18}H_{16}O_5$ and the remaining oxygen was allocated to the carbonyl group.

The ^{1}H NMR spectrum of (**1**) showed signals at δ7.82 (1H, *d*, *J* = 8.5 Hz), δ6.75 (1H, *d*, *J* = 8.5 Hz), δ6.48 (1H, *d*, *J* = 2.5 Hz) and δ6.44 (*d*, 1H, *J* = 2.5 Hz). The Ar–CH_2–CH_2–Ar protons at δ2.75 (2H, *m*) and δ2.70 (2H, *m*), along with the above, accounted for all 16 protons.

The absence of proton signals below δ8.2 expected for the bay protons of a phenanthrene nucleus indicated substitution at the 4 and 5 positions. The pair of methylene protons observed at δ2.70 (*m*, 2H) and 2.75 (*m*, 2H) indicated the presence of Ar–CH_2–CH_2–Ar protons. The two methylene groups were allocated to the 4 and 5 positions linking rings A and C in the phenanthrene nucleus, resulting in a 9,10-dihydropyrene nucleus.

The ^{1}H NMR signals at δ7.82 (*s*, 1H, *J* = 8.5 Hz) and δ6.75 (*s*, 1H, *J* = 8.5 Hz) indicated *ortho*-coupled protons. The large difference in the chemical shift positions indicated an α,β-unsaturated carbonyl system in the molecule. The downfield shift of the β-proton at δ7.82 in **1** to δ8.2 in **2** supported the presence of a hydroxyl group *ortho* to the β-proton. This is possible in a pyrene nucleus only if the 10*a*-position in ring A is reduced and occupied by a hydroxyl group. Hence, one of the hydroxyl groups was allocated to 10*a* which is a tertiary hydroxyl and this assignment was supported by the upfield signal at δ2.18 in the acetate. The carbonyl group was allocated to C-3 in order to account for the large chemical shift difference in *ortho*-coupled doublet. The allocation of hydroxyl to 10*a* is also supported by the shift of the β-proton owing to acetylation. It is further supported by the downfield shift of the methylene protons signal at $\delta 2.70$ (*m*, 2H) in **1** to $\delta 2.80$ (*m*, 2H) in **2**.

The proton signals at $\delta 6.48$ (*d*, 1H, $J = 2.5$ Hz) and $\delta 6.44$ (*d*, 1H, $J = 2.5$ Hz) indicated the presence of *meta*-coupled protons in one of the rings and this is possible only in ring-C. The downfield shift of the signal at $\delta 6.44$ to 6.8 in **2** indicated a hydroxyl *ortho* or in close proximity to this proton. Thus, $\delta 6.48$ is assigned to H-8 and $\delta 6.44$ is assigned to H-6 with a hydroxyl at C-5 and a methoxyl at C-7. The remaining methoxyl is allocated to C-4 as all the protons are accounted for, except for the methoxyl signal. The allocation of one methoxyl and one hydroxyl group to the 4 and 5 positions is also supported by the absence of any other *ortho*-coupled signals in the ^{1}H NMR spectrum.

The formation of the fragment ion *m*/*z* 272 (100) and the other significant ions also supported the structure (Scheme 1). Thus, the structure of ochrolone is 5,10*a*-dihydroxy-4,7-dimethoxy-9,10,10*a*-trihydropyrene-3-one and is the first report of its occurence in nature.

EXPERIMENTAL

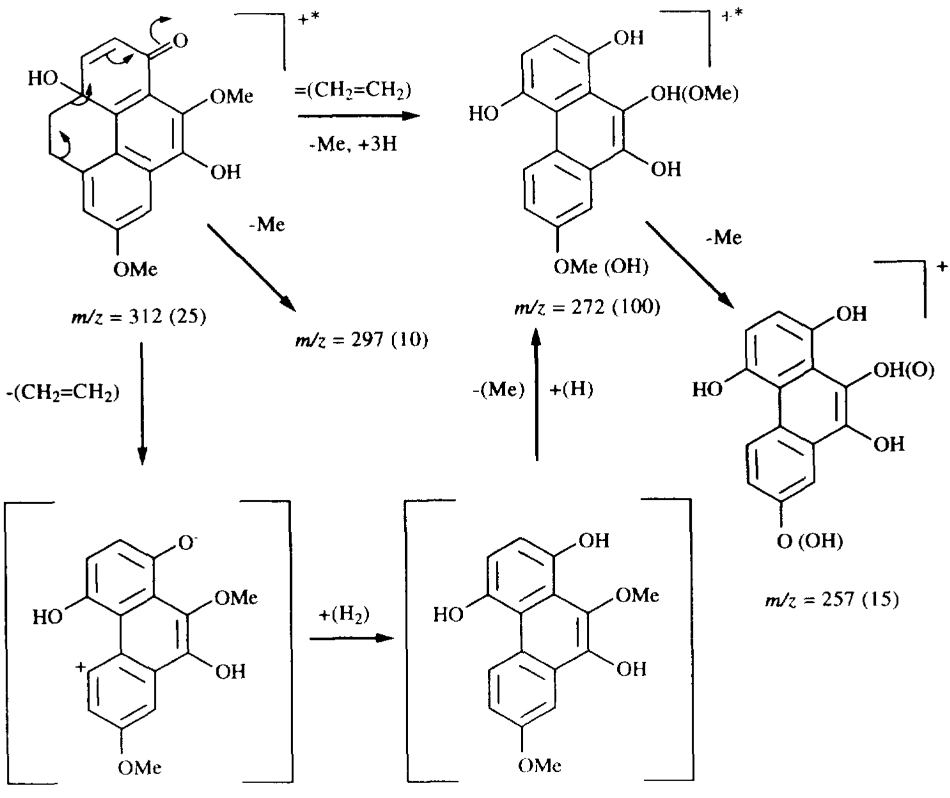
Mps: uncorr. IR: KBr. UV: EtOH. ^{1}H NMR: 270 MHz $(CD_3)_2CO$ (ochrolone); $(CD_3)_2CO$ (ochrolone diacetate) with TMS as int. standard. CC and TLC: silica gel.

Plant material was collected near Sikkim at an altitude of 4000–7000 ft during May and June.

Air-dried whole plants were extracted with hexane, Me_2CO and MeOH. The Me_2CO extract was subjected to CC and elution with C_6H_6–Me_2CO mixts. The C_6H_6–Me_2CO (9:1) fr. yielded a mixt. of three compounds, which was rechromatographed, when the C_6H_6–Me_2CO (9:1) fr. yielded a mixt. of two compounds. This mixt. on prep. TLC and multiple development using C_6H_6–Me_2CO (49:1) was separated into two bands. The less polar band on recrystallization from ETOAc yielded ochrolic acid. The more polar band on recrystallization from $CHCl_3$ yielded ochrolone.

Ochrolone (**1**). Mp 212°. Analysed for $C_{18}H_{16}O_5$. UV λ_{max}^{EtOH} nm: 220, 249, 285, 382. IR ν_{max}^{KBr} cm^{-1}: 3420, 3380, 1680. ^{1}H NMR $(CD_3)_2CO$: $\delta 3.83$ (3H, *s*, OMe), 3.75 (3H, *s*, OMe), 2.70 (*m*, 2H, H-10), 2.75 (*m*, 2H, H-9), 6.48 (1H, *d*, $J = 2.5$ Hz, H-8), 6.44 (1H, *d*, $J = 2.5$ Hz, H-6), 7.82 (1H, *d*, $J = 8$ Hz, H-1), 6.75 (1H, *d*, $J = 8.5$ Hz, H-2). MS *m*/*z* (rel. int.): 312 (40) $[M]^+$, 297 (30), 272 (100), 257 (20).

Ochrolone diacetate (**2**). Mp 182°. Analysed for $C_{22}H_{20}O_7$. ^{1}H NMR $(CD_3)_2CO$: $\delta 3.83$ (3H, *s*, OMe), 3.75 (3H, *s*, OMe), 2.18 (3H, *s*, OAc-10*a*) 2.40 (3H, *s*, OAc-5), 2.80 (*m*, 2H, H-10), 2.75 (*m*, 2H, H-9), 8.20 (1H, *s*, $J = 8.5$ Hz, H-1), 6.75 (1H, *s*, $J = 8.5$ Hz, H-2), 6.48 (1H, *d*, 1H, $J = 2.5$ Hz, H-8), 6.80 (1H, *d*, $J = 8.5$ Hz, H-6).



Scheme 1. Mass spectral fragmentation of compound **1**.

Acknowledgements—This research was supported by grants from UGC and CSIR, New Delhi. ^{1}H NMR and mass spectra were obtained through the generosity of the Sophisticated Instruments Facility, IISc (Bangalore) and IICT (Hyderbad), respectively.

REFERENCES

1. Veerraju, P., Prakasa Rao, N. S., Jagan Mohana Rao, L., Jaganadha Rao, K. V. J. and Mohana Rao, P. R. (1989) *Phytochemistry* **28**, 950.
2. Anuradha, V. and Prakasa Rao, N. S. (1994) *Phytochemistry* **35**, 273.
3. Anuradha, V. and Prakasa Rao, N. S. (1994) *Phytochemistry* (in press).
4. Udaya Bhaskar, M., Jagan Mohana Rao, L., Prakasa Rao, N. S., Jaganadha Rao, K. V. J. and Mohana Rao, P. R. (1989) *Phytochemistry* **28**, 3545.
5. Udaya Bhaskar, M., Jagan Mohana Rao, L., Prakasa Rao, N. S., Jaganadha Rao, K. V. J. and Mohana Rao, P. R. (1991) *J. Nat. Prod.* **54**, 386.
6. Veerraju, P., Prakasa Rao, N. S., Jagan Mohana Rao, L., Jaganadha Rao, K. V. J. and Mohana Rao, P. R. (1989) *Phytochemistry* **28**, 3031.
7. Anuradha, V., Prakasa Rao, N. S. and Udaya Bhaskar, M. (1994) *Phytochemistry* (in press).