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OCHROLIDE, A PHENANTHROPYRONE FROM *COELOGYNE OCHRACEA*

M. UDAYA BHASKAR, L. JAGAN MOHAN RAO, N. S. PRAKASA RAO* and P. R. MOHANA RAO†

Department of Chemistry and †Botany, Nagarjuna University, Nagarjuna Nagar-522 510, Andhra Pradesh, India

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Key Word Index—*Coelogyne ochracea*; Orchidaceae; ochrolide; 2,6-dihydroxy 7,8-dimethoxy phenanthro(4,5-*bcd*)pyran-5-one.

Abstract—The structure of ochrolide, 2,6-dihydroxy 7,8-dimethoxyphenanthro(4,5-*bcd*)pyran-5-one, isolated from the orchid *Coelogyne ochracea* has been established from spectroscopic evidence.

INTRODUCTION

Continuing our investigations [1–3] on orchids, we now report the isolation of ochrolide, (2,6-dihydroxy 7,8-dimethoxy phenanthro (4,5-*bcd*) pyran-5-one) (**1**) from the whole plant of the *Coelogyne ochracea*. This is the second report of the isolation of a phenanthropyrone from nature, the first being flacidinin (**2**) [4].

RESULTS AND DISCUSSION

From the acetone extract of the whole plant of *C. ochracea*, **1** ($C_{17}H_{12}O_6$, mp 209–210°, $[M]^+$, *m/z* 312) was separated by chromatographic methods. It gave a positive ferric chloride reaction (IR ν_{max}^{KBr} 3370 cm^{-1}). Compound **1** showed UV absorptions λ_{max}^{MeOH} 220, 249, 264, 285 and 382 nm resembling those of phenanthrene derivatives. The low intensity absorption band at λ_{382} appeared indicative of the presence of a conjugated carbonyl function. The presence of two phenolic hydroxyl groups in the molecule was confirmed by the formation of a dimethyl ether (**3**) ($C_{19}H_{16}O_6$, mp 162–163°, $[M]^+$, *m/z* 340 with $(Me)_2SO_4/K_2CO_3$ in Me_2CO) and a diacetate **4** ($C_{21}H_{16}O_8$, mp 165° with pyridine–Ac_2O). The dimethyl ether **3** is identical in all respects to the product obtained on treatment of coeloginin dimethyl ether (**5**) with DDQ. The dehydro derivative of **5** confirmed the identical substitution pattern in **3**.

The ^1H NMR spectrum of **1** at 270 MHz in acetone-d_6 showed the presence of two methoxyl groups at δ4.02 (3H, *s*) and 4.28 (3H, *s*). The A-ring protons H-1 and H-3 were observed as *meta*-coupled doublets at δ7.06 (1H, *d*, $J = 2$ Hz) and 7.24 (1H, *d*, $J = 2$ Hz). The two double doublets at δ7.64 (1H, *d*, $J = 9.5$ Hz) and 7.96 (1H, *d*, $J = 9.5$ Hz) were assigned to H-9 and H-10 as in **6** and **7** [5, 6].

The absorption band of **1** in the IR spectrum at ν_{max}^{KBr} 1665 cm^{-1} shifted to ν_{max}^{KBr} 1728 cm^{-1} in the corresponding dimethyl ether (**3**) indicating the presence of chelated carbonyl function. Hence, one of the hydroxyls is allocated to C-6 to account for chelation. Coeloginin diacetate (**8**) on treatment with DDQ, yielded the corresponding dehydro diacetate, which was found to be identical with ochrolide diacetate (**4**) by mmp and co-TLC. Hence, the second hydroxyl group was allocated to C-2 and the methoxyl groups to C-7 and C-8. Thus, the structure of ochrolide is proposed as **1**.

EXPERIMENTAL

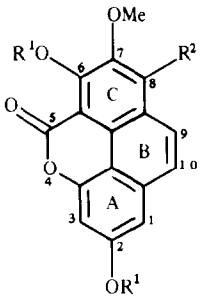
Mps: uncorr. Silica gel (100–200 mesh) was used for CC and silica gel-G for TLC. ^1H NMR spectra were recorded at 270 and 80 MHz.

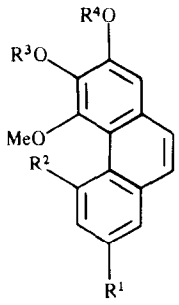
Plant material (2.4 kg) of *C. ochracea* was collected near Sikkim (India). A voucher specimen (No. 82) is deposited at the Department of Botany, Nagarjuna University.

Air-dried and finely powdered whole plant was successively extracted with hexane, Me_2CO and MeOH. The Me_2CO fr. was chromatographed on silica gel using C_6H_6 and C_6H_6–Me_2CO mixts. Ochrolide (**1**) was obtained from the C_6H_6–Me_2CO (9:1) column fr. after prep. TLC and recrystallized from C_6H_6 to give colourless needles, yield 20 mg. Mp 209–211° (Found C, 65.36; H 3.89; $C_{17}H_{12}O_6$ requires C, 65.39; H, 3.87%), MS, *m/z* 312 ($[M]^+$, 95), 297 ($[M-15]^+$, 40), 269 ($[M-15-28]^+$, 45). UV λ_{max}^{MeOH} 220, 249, 264, 285 and 382 nm; IR ν_{max}^{KBr} 3370, 1665, 1637, 1468, 1402, 1255, 1156, 1055, 990, 760 and 685 cm^{-1}; ^1H NMR δ(CD_3)$_2$CO; 4.02 (3H, *s*; ArOMe), 4.28 (3H, *s*; ArOMe), 7.06 and 7.24 (each 1H, *d*, $J = 2$ Hz; H-1 and H-3), 7.64 and 7.96 (each 1H, *d*, $J = 9.5$ Hz, H-9 and H-10).

Methylation of **1** (Me_2SO_4, Me_2CO, K_2CO_3, 3 hr) yielded 2,6,7,8-tetramethyoxyphenanthro (4,5-*bcd*)pyran-5-one (**3**), mp 162–163° (Found C, 67.00; H, 4.76; $C_{19}H_{16}O_6$ requires C, 67.05, H, 4.74%). IR ν_{max}^{KBr} 2910, 1728, 1631, 1592, 1463, 1355, 1157, 1048 and 830 cm^{-1}, ^1H NMR δ ($CDCl_3$): 3.94, 4.00, 4.12 and 4.23 (each 3H, *s*, OMe's), 7.09 and 7.14 (each 1H, *d*, $J = 2H_2$, H-1 and H-3), 7.69 and 8.03 (each 1H, *d*, $J = 9H_2$, H-9 and H-10). Acetylation of **1** (pyridine–Ac_2O, 24 hr) at room temp. yielded 2,6-diacetoxy 7,8-dimethoxy phenanthro(4,5-*bcd*)pyran-5-one (**4**), mp 165° (found C, 63.60, H, 4.09; $C_{21}H_{16}O_8$ requires C, 63.64; H, 4.07%). Dehydrogenation of coeloginin diMe ether (**5**) with DDQ; **5** (10 mg) in dry C_6H_6 (2 ml) with DDQ (14 mg) was refluxed for 25 min. and filtered. The soln was absorbed on silica gel and transferred onto a column of silica gel and eluted with hexane, C_6H_6 and C_6H_6–Me_2CO (19:1); **3** was obtained from the latter fr. and crystallized from MeOH to give colourless needles, yield 7 mg, mp 163°.

* Author to whom correspondence should be addressed.





1 R^1 = H, R^2 = OMe
2 R^1 = R^2 = H
3 R^1 = Me, R^2 = OMe
4 R^1 = Ac, R^2 = OMe
5 R^1 = Me, R^2 = OMe; 9,10-dihydro
8 R^1 = Ac, R^2 = OMe; 9,10-dihydro

6 R^1 = R^3 = H, R^2 = OH, R^4 = Me
7 R^2 = R^4 = H, R^1 = OH, R^3 = Me

Dehydrogenation of coeloginin diacetate (**8**) with DDQ; **8** (10 mg) in dry C_6H_6 (2 ml) with DDQ (14 mg) was refluxed for 3 hr and filtered. The dehydro derivative was purified as described above. Ochrolide diacetate (**4**) was obtained from the C_6H_6–Me_2CO (19:1) column fr. and crystallized from MeOH to give colourless needles, yield 8 mg, mp 165°.

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REFERENCES

1. Veerraju, P., Prakasa Rao, N. S., Jagan Mohan Rao, L., Jagannadha Rao, K. V. and Mohana Rao, P. R. (1989) *Phytochemistry* **28**, 950.
2. Veerraju, P., Prakasa Rao, N. S., Jagan Mohan Rao, L., Jagannadha Rao, K. V. and Mohana Rao, P. R. (1989) *Phytochemistry* (in press).
3. Udaya Bhaskar, M., Jagan Mohan Rao, L., Prakasa Rao, N. S. and Mohana Rao, P. R. (1990) *Phytochemistry* (in press).
4. Majumder, P. and Maiti, D. C. (1989) *Phytochemistry* **28**, 887.
5. Majumder, P., Kar, A. and Shoolery, J. N. (1985) *Phytochemistry* **24**, 2083.
6. Bhandari, S. R., Kapadi, A. H., Majumder, P., Joarder, M. and Shoolery, J. N. (1985) *Phytochemistry* **24**, 901.