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COELONIN, A 9,10-DIHYDROPHENANTHRENE FROM THE ORCHIDS *COELOGYNE OCHRACEA* AND *COELOGYNE ELATA*

PRIYALAL MAJUMDER, SWAPNA LAHA and NABANITA DATTA

Department of Chemistry, University College of Science, Calcutta 700009, India

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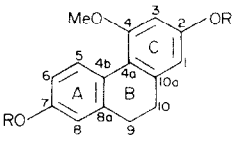
Key Word Index—*Coelogyne*; Orchidaceae; orchid; coelonin; 9,10-dihydrophenanthrene.

Abstract—2,7-Dihydroxy-4-methoxy-9,10-dihydrophenanthrene was isolated and identified from the whole plant of *Coelogyne ochracea* and *C. elata*.

The isolation of physiologically active alkaloids like dendrobine and a number of its structural analogues from the orchids of the genus *Dendrobium* [1] prompted us to investigate chemically a series of high-altitude Himalayan orchids. In this communication we report the structure elucidation of a new phenolic compound, coelonin, isolated from two such orchids, *Coelogyne ochracea* and *C. elata*.

Coelonin, $C_{15}H_{14}O_3$ ($M^{\cdot+}$ 242) was isolated as an amorphous solid in extremely poor yield from the $CHCl_3$ and MeOH extracts of *C. ochracea* and *C. elata*. The UV spectrum of coelonin shows resemblance to those of 9,10-dihydrophenanthrenes [2]. It responds to colour reactions characteristic of a phenolic compound. This is supported by its IR spectrum showing absorption for hydroxyl group (ν_{max} 3620 cm^{-1}) and usual bands for aromatic nucleus. The ^1H NMR spectrum of coelonin shows a four-proton singlet at δ 2.60 which is typical [2, 3] of the four equivalent protons of the 9- and 10-methylene groups of 9,10-dihydrophenanthrenes. The spectrum also displays signals for an aromatic methoxyl (δ 3.75), two exchangeable protons at δ 4.83 and five aromatic protons at δ 8.02 (1H, *d*, $J = 8$ Hz), 6.67 (1H, *dd*, $J_1 = 8$ Hz and $J_2 = 3$ Hz), 6.51 (1H, *d*, $J = 3$ Hz), 6.33 (1H, *d*, $J = 3$ Hz) and 6.30 (1H, *d*, $J = 3$ Hz). The downfield aromatic proton is reminiscent [4, 5] of the H-4 or H-5 of a 9,10-dihydrophenanthrene and its appearance as a clear doublet having a coupling constant of 8 Hz implies that it must have an *ortho* aromatic proton with the *meta* position being substituted. The chemical shifts and the splitting patterns of the remaining four aromatic protons when considered along with the above observation and the presence of two phenolic hydroxyl groups and an aromatic methoxyl nicely fit in with structure **1a** for coelonin. In the alternative 4,7-dihydroxy-2-methoxy-9,10-dihydrophenanthrene formulation the two phenolic OH protons would be expected to resonate at different fields, as is observed in structurally similar compounds [6].



1a R=H
1b R=Ac
1c R=Me

Table 1. Carbon chemical shifts of diacetylcoelonin

Carbon atoms	*Chemical shifts (δ ppm)	Carbon atoms	*Chemical shifts (δ ppm)
C-1	113.4(*d*)	C-8	120.3†(*d*)
C-2	149.9(*s*)	C-8a	135.8(*s*)
C-3	104.0(*d*)	C-9	30.0‡(*t*)
C-4	157.5(*s*)	C-10	29.4‡(*t*)
C-4a	120.2(*s*)	C-10a	135.8(*s*)
C-4b	134.7(*s*)	-OMe	55.6(*q*)
		O ‖	
C-5	129.4(*d*)	-O-C-Me	169.3(*s*)
C-6	120.5†(*d*)	O ‖	
C-7	149.9(*s*)	-O-C-Me	21.0(*q*)

*Chemical shifts of the carbons were measured with $\delta^{TMS} = \delta^{CDCl_3} + 76.9$ ppm and the letters in parentheses indicate the multiplicity of the signals in SFORD.

†,‡Chemical shifts are interchangeable.

Structure **1a** for coelonin is also corroborated by the ^{1}H NMR spectra of diacetylcoelonin, $C_{19}H_{18}O_5$ ($M^{\cdot+}$ 326), mp 128° and coelonin dimethyl ether, $C_{17}H_{18}O_3$ ($M^{\cdot+}$ 270). While the chemical shift of the most downfield proton of coelonin remains practically unchanged in diacetylcoelonin, the remaining four aromatic protons of the former are all shifted downfield by ~0.25 ppm in the latter, indicating that each of them is *ortho* to a phenolic hydroxyl group in coelonin. The appearance of the two acetyl methyl protons as a sharp six-proton singlet [2] (δ 2.23) instead of two three-proton singlets [6] suggests the equivalent nature of the two acetyl functions as in **1b**. This is again in accord [6, 7] with the chemical shifts of the three aromatic methoxyl groups of dimethyl coelonin (**1c**), two of which appear as a six-proton singlet at δ 3.76 while the third has a different chemical shift (δ 3.79).

The MS of coelonin showing only significant peaks at *m/z* 242 ($M^{\cdot+}$) and 227 (M-15) is also consistent with the assigned structure.

Further confirmation of the structure of coelonin was made by a ^{13}C NMR spectral analysis of its diacetyl derivative. The chemical shifts of the carbon atoms of the latter (Table 1), except that of C-5, are in excellent agreement with the values for **1b** calculated using the known additivity parameters [8] on the reported carbon shifts of the parent 9,10-dihydrophenanthrene [8]. C-5 shows a downfield shift of about 4 ppm from the calculated value, which finds analogy in a similar downfield shift of C-5 of 2,7-diacetoxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene recently studied [9] by us. An interchange of the acetoxy and methoxy functions in ring C of **1b** would result in an upfield shift of C-1 by ~4 ppm.

Coelonin is thus a new addition to the growing list of naturally occurring 9,10-dihydrophenanthrenes. In view of the phytoalexin-like activity [10] of the related orchinol [6], coelonin holds out promise of having similar biological activity.

EXPERIMENTAL

Si gel (60–100 mesh) was used for CC and Si gel G for TLC. All analytical samples were dried over P_2O_5 for 24 hr *in vacuo* and were tested for purity by TLC and MS. The UV spectra were recorded in 95% EtOH and the IR spectra in KBr discs. ^{13}C NMR spectrum was run in $CDCl_3$ in a Varian CFT 20 instrument.

Isolation of **1a**. Air-dried finely powdered whole plants of *Coelogyne ochracea* (1 kg) were successively extracted with $CHCl_3$ and MeOH in a Soxhlet for 50 hr. After removal of solvent the combined residue was taken in EtOAc and chromatographed. The petrol–EtOAc (5:1) eluate on evaporation gave a crude residue of phenolic mass which was taken in Et_2O and extracted with 1 N NaOH solution. The aq. alkaline solution was acidified with HCl in the cold. The liberated solid was extracted with ether, washed, dried and evaporated. The crude solid on repeated chromatography afforded pure **1a** as an amorphous powder (yield 0.002%). The same procedure was employed with *C. elata* for the isolation of **1a** (yield 0.003%). (Calc. for $C_{15}H_{14}O_3$: C, 74.38; H, 5.78. Found: C, 74.29; H, 5.69%.) λ_{max} 214, 270*inf*, 280 and 295*sh* (log ε 4.90, 4.34, 4.44 and 4.13) nm; ν_{max} 3620 (OH), 1530, 920, 840 cm^{-1}; $\delta_{(ppm)}$: 2.60 (4H, *s*, 9-H$_2$ and 10-H$_2$), 3.75 (3H, *s*, Ar-OMe), 4.83 (2H, *br* signal, disappears on deuteration; OH) 6.30 (1H, *d*, J = 3 Hz; H-3), 6.33 (1H, *d*, J = 3 Hz; H-1), 6.51 (1H, *d*, J = 3 Hz; H-8), 6.67 (1H, *dd*, J_1 = 8 Hz and J_2 = 3 Hz; H-6), 8.02 (1H, *d*, J = 8 Hz; H-5); *m/z* (relative abundance): 242 ($M^{\cdot+}$, 100), 227 (6.5) and 199 (11.0).

Acetylation of **1a**. Acetylation of **1a** (0.15 g) with Ac_2O (2 ml) and pyridine (1 ml) followed by chromatography of the product gave **1b** (0.145 g), mp 128°, crystallized from MeOH. (Calc. for $C_{19}H_{18}O_5$: C, 69.93; H, 5.52. Found: C, 69.85; H, 5.45%.) λ_{max} 215, 274*inf*, 293 and 301*sh* (log ε 4.86, 4.25, 4.13 and 4.03) nm; ν_{max} 1760 and 1250 (OAc), 1600, 1590 and 830 cm^{-1}; $\delta_{(ppm)}$: 2.23 (6H, *s*, OAc), 2.69 (4H, *s*, 9-H$_2$ and 10-H$_2$), 3.78 (3H, *s*; Ar-OMe), 6.55 (2H, *br* signal; H-1 and H-3), 6.89 (1H, *d*, J = 3 Hz; H-8), 6.90 (1H, *dd*, J_1 = 8 Hz and J_2 = 3 Hz; H-6) and 8.15 (1H, *d*, J = 8 Hz; H-5); *m/z* (relative abundance) 326 ($M^{\cdot+}$, 14.6), 284 (20.2), 242 (100), 227 (5.8), 199 (10.8) and 43 (14.3).

Methylation of **1a**. **1a** (0.05 g) was refluxed with Me_2SO_4 (1 ml) in dry Me_2CO (10 ml) in the presence of dry K_2CO_3 (1 g) for 8 hr. The product was worked-up in the usual manner and chromatographed to give **1c** (0.04 g) as a homogeneous glassy solid. (Calc. for $C_{17}H_{18}O_3$: C, 75.55; H, 6.66. Found : C, 75.41; H, 6.54%.) $\delta_{(ppm)}$ 2.77 (4H, *s*; 9-H$_2$ and 10-H$_2$), 3.76 (6H, *s*; Ar-OMe), 3.79 (3H, *s*; Ar-OMe), 6.46 (2H, *br* signal; H-1 and H-3), 6.70 (1H, *d*, J = 3 Hz; H-8), 6.81 (1H, *dd*, J_1 = 9 Hz and J_2 = 3 Hz; H-6) and 8.2 (1H, *d*, J = 9 Hz; H-5); *m/z* (relative abundance) 270 (M^+, 100), 255 (8.0) and 227 (11.0).

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A CHALCONE GLYCOSIDE FROM *ACACIA DEALBATA*

FILIPPO IMPERATO

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università di Catania, Catania, Italy

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Key Word Index—*Acacia dealbata*; Leguminosae; flowers; 4,2',4',6'-tetrahydroxychalcone 2'-[*O*-rhamnosyl-(1→4)-xyloside].

Abstract—A new yellow pigment isolated from the flowers of *Acacia dealbata* has been shown to be chalcononaringenin 2'-[*O*-rhamnosyl-(1→4)-xyloside] by chemical and spectroscopic methods.

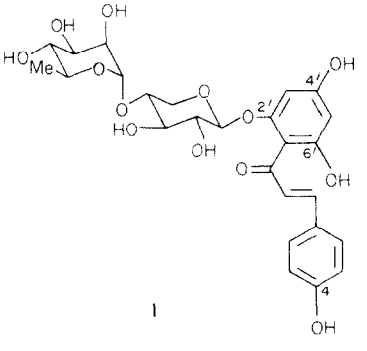
Recent work ([1]; Imperato, F., unpublished) has shown that anthochlor pigments contribute to the yellow colour of the flowers of *Acacia dealbata* and four such pigments have been found.

From an EtOH extract of the flowers of *A. dealbata*, another anthochlor has now been isolated by means of a combination of prep. PC and prep. TLC on Si gel. The UV spectrum of this pigment showed λ_{max}^{MeOH} 348 nm and bathochromic shifts with $AlCl_3$ (56 nm), $AlCl_3$/HCl (52 nm), NaOAc (39 nm) and NaOMe (62 nm; with increase in peak intensity). These spectral properties [2] and colour reactions (brown to orange in UV + NH_3) are consistent with those of a polyhydroxychalcone with free hydroxyl groups at positions 4 and 2'.

Total acid hydrolysis of the isolated pigment gave 1 mol each of naringenin, xylose and rhamnose. Methylation gave a methyl ether which on acid hydrolysis isomerized to flavanone since it gave naringenin trimethyl ether (identified after alkaline degradation to di-*O*-methylphloroglucinol and *p*-methoxycinnamic acid), 2,3-di-*O*-methyl-xylose and 2,3,4-tri-*O*-methyl-rhamnose.

Thus, the isolated pigment must be 4, 2', 4', 6'-tetrahydroxychalcone 2'-[*O*-rhamnosyl-(1→4)-side] (**1**) which is a new natural product. This structure was confirmed as follows. When heated in NaOAc solution [3], this chalcone isomerized to the corresponding flavanone (λ_{max}^{MeOH} 277 nm) which was identified as naringenin 5-*O*-rhamnoxyloside by UV spectral analysis with shift reagents [2], total acid hydrolysis (which gave naringenin, xylose and rhamnose) and controlled acid hydrolysis to give an intermediate which was further degraded into naringenin and xylose and identified as naringenin 5-*O*-xyloside by UV spectral analysis with shift reagents [2] and co-PC with an authentic sample.

4-*O*-Rhamnosyl-xylose is reported for the first time in association with chalcones. This disaccharide has been found only twice before in flavonoid glycosides; it has been found attached in the 3-position of kaempferol in *Euonymus alatus* [4] and in the 7-position of 6-hydroxyluteolin in *Pityrodia coerulea* [5]. Moreover,



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