Coelogin and Coeloginin: Two Novel 9,10-Dihydrophenanthrene Derivatives from the Orchid *Coelogyne cristata* †

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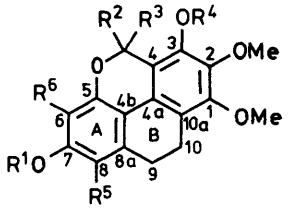
Coelogin and coeloginin, two novel 9,10-dihydrophenanthrene derivatives of the high altitude Himalayan orchid *Coelogyne cristata*, have been shown to have the phenanthro[4,5-*bcd*]pyran structures (1a) and (1b), respectively, from spectral and chemical evidence.

THE isolation of physiologically active alkaloids such as dendrobine and a number of its structural analogues from the orchids of the *Dendrobium* genus [1] prompted us to investigate chemically a series of Indian orchids, an area which still remains practically unexplored. In this paper we report the structure elucidation of two novel phenolic compounds, designated coelogin and coeloginin, isolated from the light petroleum and chloroform extracts of *Coelogyne cristata*, a high altitude Himalayan orchid.

Coelogin (1a), $C_{17}H_{16}O_5$ ($M^{\cdot+}$ 300), m.p. 151 °C, shows u.v. absorptions resembling those of substituted 9,10-dihydrophenanthrenes.[2] Coeloginin (1b), $C_{17}H_{14}O_6$ ($M^{\cdot+}$ 314), m.p. 198 °C, on the other hand, shows a different u.v. spectrum presumably because of the presence of a carbonyl function conjugated with the above chromophoric system. Addition of alkali induced considerable bathochromic shifts in both the spectra showing the phenolic character of the compounds. This was supported by the i.r. spectra of both coelogin and coeloginin. The spectrum of coeloginin exhibits an additional band at 1 650 cm^{-1} indicating the presence of a chelated carbonyl function.

The ^1H n.m.r. spectra of coelogin and coeloginin diacetate (1f) (coeloginin itself is sparingly soluble in $CDCl_3$) show a four-proton singlet, at δ 2.80 and 2.98, respectively, typical of the four equivalent protons of the 9- and 10-methylene groups of 9,10-dihydrophenanthrene derivatives.[2,3] The other common features of the two spectra are the signals from two aromatic methoxy-groups and two *meta*-coupled aromatic protons. The spectrum of coelogin, however, shows an additional two proton singlet at δ 5.19, assigned to the methylene protons of a benzyl phenyl ether system, and displays the signals for two phenolic protons at δ 4.95 and 5.72 which are replaced in the spectrum of coeloginin diacetate by the two acetate methyl signals at δ 2.39 and 2.24.

Both coelogin and coeloginin form dimethyl diethers and diacetyl derivatives confirming the presence of two phenolic hydroxy-groups in each compound. The spectral features of these derivatives are very similar to those of their respective parent compounds except, notably, that (i) the carbonyl absorption at 1 650 cm^{-1} in the i.r. spectrum of coeloginin has been displaced to 1 720 cm^{-1} in that of coeloginin diacetate, the acetoxy-carbonyl band appearing at 1 762 cm^{-1}; and (ii) the carbonyl absorption of coeloginin dimethyl diether appears at $\nu_{max.}$ 1 725 cm^{-1}. These observations indicate the chelated character of the carbonyl function in coeloginin. Another important feature is that the two-proton singlet appearing at δ 5.19 in the ^1H n.m.r. spectrum of coelogin is shifted upfield by 0.27 p.p.m. in coelogin diacetate, while it remains practically unaltered in the spectrum of coelogin dimethyl diether. Such an upfield shift of the methylene protons of the benzyl phenyl ether system suggests that one acetoxy-group in coelogin diacetate (and hence one hydroxy-group in coelogin itself) is *ortho* to the methylene group, since only in this orientation would the above methylene protons be within the shielding cone of the acetoxy-carbonyl function.



(1)

a; $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$
b; $R^1 = R^4 = R^5 = R^6 = H$; $R^2, R^3 = O$
c; $R^1 = R^4 = Me$; $R^2 = R^3 = R^5 = R^6 = H$
d; $R^1 = R^4 = Me$; $R^2, R^3 = O$; $R^5 = R^6 = H$
e; $R^1 = R^4 = Ac$; $R^2 = R^3 = R^5 = R^6 = H$
f; $R^1 = R^4 = Ac$; $R^2, R^3 = O$; $R^5 = R^6 = H$
g; $R^1 = R^2 = R^3 = R^4 = R^6 = H$; $R^5 = CHO$
h; $R^1 = R^2 = R^3 = R^4 = R^5 = H$; $R^6 = CHO$

For ease of comparison of spectral results the phenanthrene numbering system used for compounds (2)—(4) has also been used for compounds (1) and (5). In naming compounds (1) and (5) however the systematic numbering system has been adopted

The foregoing evidence led to the postulation of structures (1a) and (1b) for coelogin and coeloginin, respectively. These structural assignments are also consistent with their mass spectra, both of which show a significant (M − 15) peak as well as their respective molecular ion peaks. Coeloginin showed, in addition, another intense

† A preliminary account of this work was presented in the 4th Asian Symposium on Medicinal Plants and Spices held at Bangkok, 1980, Abstracts, p. 78.

peak at *m/e* 271 (M − 15 − 28), presumably due to the expulsion of CO from the lactone moiety.

The ^{13}C n.m.r. spectra of coelogin (1a) and coeloginin diacetate (1f) provide further evidence in support of the above structural assignments. Using the simple additivity parameters for the functional groups,[4] the carbon shifts in each case, calculated on the basis of the parent 9,10-dihydrophenanthrene,[4] give excellent agreement for nearly all the carbon atoms. While the downfield shifts of *ca.* 5—8 p.p.m. for C-1, C-2, and C-3 from the calculated values are common for polysubstituted aromatic compounds bearing adjacent oxygen functions,[5] the upfield shift of C-4a by *ca.* 5 p.p.m. is presumably due to the γ-heteroatom [6] in the oxymethylene or lactone bridge.

Coeloginin dimethyl diether (1d) on reduction ($LiAlH_4$) afforded coelogin dimethyl diether (1c). This reaction obviously proceeds by the reduction of the lactone to the lactol which is then reduced to the diether.[7] On the other hand, on passing air through an ethanolic solution of coelogin for 50 h it was partially (<10%) converted into coeloginin. Similarly the diether (1c) can also be oxidised to give compound (1d). These experiments thus prove that coeloginin is an oxo-derivative of coelogin, the methyleneoxy function of the latter being replaced by a lactone bridge in the former.

Contrary to expectations, coelogin (possessing a benzyl phenyl ether system) was resistant to hydrogenolysis with Pd–C in ethanol or acetic acid. However, attempted hydrogenolysis of coelogin with Pd–C in glacial acetic acid containing a trace of perchloric acid resulted in the formation of two products, compound A, $C_{17}H_{24}O_3$ ($M^{\cdot+}$ 276) and compound B, $C_{17}H_{18}O_4$ ($M^{\cdot+}$ 286).

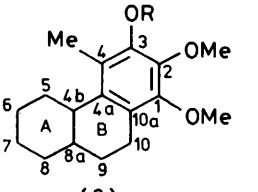
Compound A, obtained as a semisolid mass, showed an i.r. band for the hydroxy-group. The ^1H n.m.r. spectrum of the compound indicated the presence of one exchangeable proton (δ 5.67, OH), two aromatic methoxy-groups, three benzylic protons (one as a multiplet at δ 2.71 and the other two as a multiplet at δ 2.54), one aromatic methyl (δ 2.05) and eleven aliphatic protons (δ 1.39—1.82). It formed a monomethyl ether (2b), the ^1H n.m.r. spectrum of which is similar to that of compound A except that the hydroxy-signal of the latter has been replaced by a methoxy-singlet (δ 3.69) in the former. The ^{13}C n.m.r. spectrum of compound A showed six non-protonated aromatic carbons, two aromatic methoxy-carbons, two aliphatic methine and six methylene groups, and an aromatic methyl appearing unusually far upfield (δ 10.3) (Table). These spectral data coupled with the foregoing evidence suggest the benzodecalin structure (2a) for compound A, the A/B-*cis* stereochemistry being supported by the chemical shifts (δ 33.6 and 38.0) of the carbon atoms at the A/B ring juncture. An A/B-*trans* fusion would have resulted in greater downfield shifts of these carbon atoms. Furthermore, construction of Dreiding models shows that of the two conformations (3a) and (3b) the latter would be energetically highly unstable due to a severe nonbonding interaction between the aromatic methyl and the C-5 methylene groups. There would be a similar steric strain in an A/B-*trans* fused structure of compound A. A consideration of all these factors led us to believe that compound A exists exclusively as (3a), and the upfield shift of its aromatic methyl in the ^{13}C n.m.r. spectrum may be attributed to the cumulative effects of the adjacent substituents, increased electron density at C-4 by the *o*-hydroxy- and *p*-methoxy-groups, and some nonbonding steric interaction of the aromatic methyl group with the C-4b hydrogen atom.

TABLE [a]

^{13}C N.m.r. data of the shown compounds

	δc (p.p.m.)			
Assignments	Coelogin (1c)	Coeloginin diacetate (1f)	Compound A (2a)	Compound B (5)
C-1	149.1 (s)	150.3 (s)	147.6 (s)	142.2 (s)
C-2	136.6 (s)	145.6 (s)	137.0 (s)	130.9 (s)
C-3	142.9 (s)	144.4 (s)	145.2 (s)	137.9 (s)
C-4	117.3 (s)	108.3 (s)	120.6 (s)	121.3 (s)
C-4a	122.9 (s)	124.2 (s)	136.8 (s)	124.0 (s)
C-4b	112.2 (s)	128.7 (s)	38.0 (d)	129.3 (s)
C-5	156.2 (s)	156.1 (s)	28.5 (t)	74.6 (d)
C-6	101.3 (d)	107.5 (d)	26.7 (t)	28.6 (t)
C-7	154.4 (s)	151.3 (s)	23.5 (t)	20.8 (t)
C-8	108.9 (d)	116.5 (d)	32.2 (t)	29.3 (t)
C-8a	138.4 (s)	136.2 (s)	33.6 (d)	125.6 (s)
C-9	27.4 (m) [b]	26.1 (m) [b]	20.7 (t)	124.9 (d)
C-10	20.6 (m) [b]	20.2 (m) [b]	22.0 (t)	119.7 (d)
C-10a	109.8 (s)	112.3 (s)	116.8 (s)	110.5 (t)
OCH_2	63.2 (t)			64.2 (t)
$-C(O)O$		157.0 (s)		
$ArOCH_3$	60.1 (q), 61.3 (q)	60.5 (q), 61.1 (q)	59.4 (q), 60.3 (q)	61.0 (q)
$ArCH_3$			10.3 (q)	
$ArOCOCH_3$		20.7 (q), 20.5 (q)		
$ArOCOCH_3$		168.8 (s), 168.5 (s)		

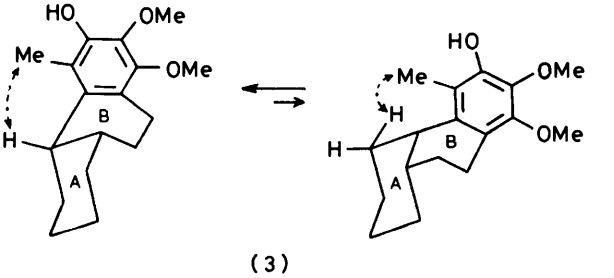
[a] Chemical shifts of the carbons are measured with δ (TMS) = δ ($CDCl_3$) + 76.9 p.p.m., letters in parentheses indicating the multiplicity of the signal in SFORD. [b] Possibly due to long-range coupling with the adjacent protons.



(2)

a ; R = H

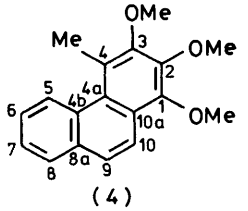
b ; R = Me



(3)

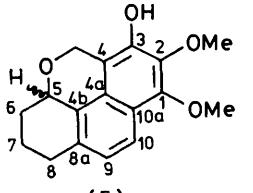
a b

High-temperature catalytic dehydrogenation of the methyl ether (2b) of compound A afforded the compound C, $C_{18}H_{18}O_3$ ($M^{\cdot+}$ 282). The ^{1}H n.m.r. spectrum of this last compound shows, besides the signal for three aromatic methoxy-groups and an aromatic methyl group (δ 2.84), six aromatic protons (δ 7.34—8.69), one of which (appearing as a multiplet at δ 8.63) is characteristic of a proton at C-4 or C-5 of a phenanthrene molecule. Based on these spectral data compound C was assigned the structure (4).



(4)

Compound B, m.p. 153 °C, exhibits considerable alkali-induced bathochromic shifts in its u.v. spectrum suggesting its phenolic character; this was confirmed by its i.r. spectrum. The ^{1}H n.m.r. spectrum of the compound shows two *ortho*-coupled aromatic protons at δ 7.05 and 7.75 (each d, J 9 Hz) instead of the two *meta*-coupled protons in coelogin. Besides a one-proton multiplet at δ 4.70, one exchangeable proton (δ 6.03, OH), two aromatic methoxy-signals, two benzylic protons (δ 2.84, m), and four aliphatic protons around δ 2.0, the spectrum also shows two methyleneoxy protons at δ 5.10 appearing as an AB quartet (J 15 Hz) instead of the singlet in the parent compound. The ^{13}C n.m.r. spectrum of compound B shows the presence of eight non-protonated and two unsubstituted aromatic carbons, an oxygenated sp^3 methine carbon (δ 74.6), and a methylene carbon (δ 64.2), in addition to three saturated methylene carbons. The chemical shifts of the various carbon atoms of compound B (Table) coupled with its other spectral data are in excellent accord with structure (5).



(5)

Compound B formed a monoacetate, $C_{19}H_{20}O_5$ ($M^{\cdot+}$ 328), the methyleneoxy protons of which are shifted upfield by 0.23 p.p.m. in its ^{1}H n.m.r. spectrum compared to those of compound B, thereby pin-pointing the position of the hydroxy-group in the latter as being at a position *ortho* to the oxymethylene group. The structure (5) for compound B was also supported by the fact that upon hydrogenolysis on Pd–C in glacial acetic acid in the presence of a trace of perchloric acid it was readily transformed into compound A. Alternatively, when coelogin was hydrogenated on Pd–C in glacial acetic acid in the presence of a larger amount of perchloric acid it was directly converted into compound A and no trace of compound B could be found. This suggests intermediacy of compound B in the formation of compound A from coelogin. Mechanistically the formation of compounds A and B appears to be initiated by the protonation of ring A of coelogin by perchloric acid followed by several steps [8] involving isomerisation, hydrogenolysis/dehydration, and hydrogenation.

The characterisation of compounds A, B, and C settled all structural points of the parent compounds. First, the isolation of compound C confirmed the gross skeleton of coelogin and coeloginin. Second, the appearance of the aromatic methyl in compounds A and C, and its assigned position, established the presence of the methyleneoxy bridge between C-4 and C-5 of the 9,10-dihydrophenanthrene skeleton of coelogin, and hence the lactone bridge at the same position in coeloginin. Finally, it also confirmed the substitution patterns of coelogin and coeloginin; the position of the hydroxy-group in ring A of each was justified by the two *meta*-coupled aromatic protons in the ^{1}H n.m.r. ($CDCl_3$) spectrum of coelogin [each of which appeared as a clear doublet at δ 6.18 and 6.28, J 2.5 Hz ($[CD_3]_2SO$)] and also by the fact that these two aromatic protons were shifted 0.15 p.p.m. downfield on acetylation showing their *ortho*-orientation with respect to the hydroxy-group in ring A. This was further corroborated by the following transformation of coelogin.

While coelogin is comparatively insensitive to alkali, coeloginin is slowly destroyed in an alkaline medium. In an attempt to purify coelogin easily from traces of accompanying coeloginin, a difficult task chromatographically, a chloroform solution of the mixture was vigorously shaken with 2N-aqueous sodium hydroxide and the mass was left overnight to enable the resultant emulsion to break up. Chromatography of the ether extract of the acidified aqueous phase yielded, along with some unchanged coelogin, two golden-yellow isomeric compounds D and E, analysed as $C_{18}H_{16}O_6$ ($M^{\cdot+}$ 328).

Compound D, m.p. 190 °C, shows considerable bathochromic shifts in its u.v. spectrum on addition of alkali indicating its phenolic character. Its i.r. spectrum shows bands at 3 430 (OH) and 1 648 cm^{-1} (chelated >CO) with weak bands at 2 820 and 2 860 cm^{-1} (CHO). The ^{1}H n.m.r. spectrum of the compound shows close resemblance to that of compound (1a) except that the signals for the two *meta*-coupled aromatic protons in coelogin (1a) have been replaced by two one-proton singlets at δ 6.27 (ArH) and 10.14 (CHO) with a concomitant large downfield shift of one of the two phenolic proton signals to δ 11.69 (chelated phenolic OH). Its mass spectrum shows significant peaks at *m/e* 328 ($M^{\cdot+}$), 327 (M — 1), 313 (M — 15), and 299 (M — 29). These spectral data establish that compound D is simply a Reimer–Tiemann reaction product of coelogin in which one of the two *meta*-coupled aromatic protons in the latter has been replaced by an aldehyde group in the former.

Compound E, m.p. 187—188 °C, shows u.v., i.r., and

mass spectra similar to those of compound D, differing essentially from the latter in the ^{1}H n.m.r. spectral pattern of its 9- and 10-methylene protons. Thus, although the ^{1}H n.m.r. spectrum of compound E indicates the presence of identical functionalities as occur in compound D, its 9- and 10-methylene protons no longer appear as a four-proton singlet, as in the case of compound D, but as two two-proton multiplets at δ 2.83 and 3.05. Such multiplicities of the 9- and 10-methylene protons of compound E is clearly the result of the magnetic non-equivalence of the two methylene groups caused by the diamagnetic anisotropic effect of the aldehyde function in ring A on the 9-methylene protons, which are appreciably deshielded (δ 3.05) compared with those at C-10 (δ 2.83). This is possible only if the CHO group is at C-8 in compound E (1g). Hence, compound D should have the structure (1h) in which the CHO group is too far away to have any significant preferential deshielding effect on the 9-methylene protons. That the aldehyde functions in both compounds are chelated is corroborated by their i.r. and ^{1}H n.m.r. spectra. This conclusively establishes the assigned position of the hydroxy-group in ring A, since otherwise both compounds D and E would not be able to have chelated aldehyde functions.

The foregoing spectral and chemical evidence thus firmly establishes the structures of coelogin and coeloginin as being (1a) and (1b), respectively; the possibility of the latter being an artefact is ruled out by the isolation of the two compounds separately from two different *Coelogyne* species, other than *C. cristata*, currently under investigation in our laboratory.

It is pertinent to mention here that both compounds (1a) and (1b) would be expected to display optical activity since each molecule is asymmetric as a whole. However, they are in fact inactive under ordinary conditions. This is explained by the fact that for each of these two compounds the optical antipodes happen to be the flip conformers of each other (Dreiding models). It is evident that the energy barrier between the two forms in each case is so low that at room temperature they continuously interchange so that each sample is optically inactive. It is interesting to note, incidentally, that this also accounts for the fact that even in such tetracyclic compounds not only the 9,10-methylene protons but also the protons in the oxymethylene bridge [in compound (1a)] appear as singlets in the ^{1}H n.m.r. spectra.

Coelogin and coeloginin thus represent novel structural variations of the naturally occurring 9,10-dihydrophenanthrenes reported so far since they have an additional ring (involving C-4 and C-5) presumably formed by the aromatic *C*-methylation of a phenolic 9,10-dihydrophenanthrene followed by oxidation of the methyl group to an aldehyde group, cyclisation, and appropriate biochemical modification.

In view of the report of the 9,10-hydrophenanthrenes such as orchinol [9] among phytoalexins,[9] it would be worthwhile to study the physiological activity of coelogin and coeloginin.

EXPERIMENTAL

Light petroleum (b.p. 60—80 °C) was used as a solvent. Column chromatography was carried out over silica gel (60—100 mesh) using as eluants light petroleum and mixtures of light petroleum and ethyl acetate in order of increasing polarity. T.l.c. was carried out over silica gel G. M.p.s were determined in a Köfler block and are uncorrected. U.v. spectra were run in 95% ethanol (aldehyde free) and i.r. spectra on KBr discs. Optical rotations were measured for ethanol solutions. N.m.r. spectra were recorded for [^{2}H]chloroform ($CDCl_3$) solutions in a VARIAN CFT-20 instrument, except for the ^{1}H n.m.r. spectrum of coelogin in [$^2H_6$]dimethyl sulphoxide (DMSO), which was run on a JEOL-JNM-PS-100, and that in [^{2}H]chloroform, which was run on a 270 MHz BRUCKER HFX-10 instrument. The ^{1}H chemical shifts were measured in p.p.m. downfield from tetramethylsilane (TMS), with values italicised to indicate the signals which disappeared on deuterium exchange. Identity of a known compound was established from its mixed m.p., co-t.l.c., and superimposability of i.r. spectra. *m** Denotes metastable peaks in the mass spectra.

Isolation of 2,6-*Dihydroxy*-7,8-*dimethoxy*-9,10-*dihydro*-5H-*phenanthro*[4,5-bcd]*pyran* (*Coelogin*) (1a) *and* 2,6-*Dihydroxy*-7,8-*dimethoxy*-9,10-*dihydro*-5H-*phenanthro*[4,5-bcd]*pyran*-5-*one* (*Coeloginin*) (1b).—Air-dried, finely ground whole plant *Coelogyne cristata* (1 kg) was extracted with light petroleum in a Soxhlet apparatus for 48 h. The extract (*ca.* 5 l), after filtration and subsequent concentration to 150 ml, was kept and finally yielded a scanty deposit collected by filtration. T.l.c. of the solid developing with light petroleum–ethyl acetate (3 : 1) showed two spots very close in R_F values (0.25 to 0.3). The filtrate also showed these two spots, along with others, on t.l.c. The solid as well as the filtrate, on separate column chromatography, furnished only mixtures of compounds (1a) and (1b) of varying enrichments. These fractions, on repeated column chromatography, finally afforded a pure solid corresponding to the less polar compound (1b) in the early fractions [with light petroleum–ethyl acetate (7 : 1) as eluant]. It crystallised from light petroleum–ethyl acetate as yellowish, heavy needles (300 mg), m.p. 198 °C, $[\alpha]_D$ ±0° (*c* 0.9) (Found: C, 64.85; H, 4.50. $C_{17}H_{14}O_6$ requires C, 64.97; H, 4.46%); $\lambda_{max.}$ 252, 287—288, and 366 nm (log ε 4.42, 4.03, and 3.94); $\lambda_{max.}$ (0.01M-NaOH–EtOH) 223, 262, 296, 310sh, and 404—405 nm (log ε 4.47, 4.49, 4.08, 3.98, and 4.13); $\nu_{max.}$ 3 450, 2 980, 1 650, 1 605, 1 466, and 1 428 cm^{-1}; $\nu_{max.}$ ($CDCl_3$) 3 450 and 1 650 (unchanged on dilution) cm^{-1}; *m/e* 314 ($M^{\cdot+}$), 299 (M − 15; 100%), 271 (M − 15 − 28), 239, 228, 200, 171, 157 (M^{2+}), 144, 128, and 115; *m** 284.7. The later fractions of the light petroleum–ethyl acetate (7 : 1) eluate containing mainly the more polar compound (1a) were combined and evaporated. A diethyl ether solution of the residue was extracted with 2M-aqueous sodium hydroxide solution which destroyed the last traces of compound (1b). The alkaline extract was acidified (dil. HCl) in the cold (*ca.* 0 °C), extracted with diethyl ether and the extract chromatographed. The last fractions of the light petroleum–ethyl acetate (7 : 1) eluate gave pure compound (1a) on evaporation which crystallised from light petroleum–benzene–ethyl acetate as fine, colourless needles (250 mg), m.p. 151 °C, $[\alpha]_D$ ±0° (*c* 0.8) (Found: C, 67.85; H, 5.3. $C_{17}H_{16}O_5$ requires C, 68.00; H, 5.33%); $\lambda_{max.}$ 224, 284, 307, and 318 nm (log ε 4.61, 4.15, 4.21, and 4.16); $\lambda_{max.}$ (0.01M-NaOH–EtOH) 224, 286sh, 320, and 332sh nm (log ε 4.60, 4.10, 4.20, and 4.05);

$\nu_{max.}$ 3 400, 2 960, 2 870, 1 605, 1 450, and 1 425 cm^{-1}; δ 2.80 (4 H, s, 9- and 10-H), 3.84 and 3.93 (each 3 H, s, $ArOCH_3$), *4.95* (1 H, br s, ArOH), 5.19 (2 H, s, $ArOCH_2Ar'$), *5.72* (1 H, s, ArOH), 6.30 (1 H, d, *J* 2.5 Hz, ArH), and 6.32 (1 H, d, *J* 2.5 Hz, ArH); δ [$(CD_3)_2SO$] 2.70 (4 H, s, 9- and 10-H), 3.75 (6 H, s, $ArOCH_3$), 5.02 (2 H, s, $ArOCH_2Ar'$), 6.18 (1 H, d, *J* 2.5 Hz, ArH) and 6.28 (1 H, d, *J* 2.5 Hz, ArH), *9.20* and *9.48* (each 1 H, br s, ArOH); *m/e* 300 ($M^{\cdot+}$; 100%), 285 (*M* − 15), 241, 225, 213, 197, 185, 184, 150 (M^{2+}), 139, 127, 125, and 116; *m** 270.8.

Methylation of Coelogin (1a) *and Coeloginin* (1b).—Coelogin (50 mg), on methylation with dimethyl sulphate (0.5 ml) and anhydrous potassium carbonate (2 g) in dry acetone (100 ml) under reflux for 24 h, afforded 2,6,7,8-tetramethoxy-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran (dimethyl coelogin) (1c) (45 mg) which refused to crystallise (Found: C, 69.35; H, 6.05. $C_{19}H_{20}O_5$ requires C, 69.51; H, 6.10%); $\lambda_{max.}$ 224, 285, 305, and 318 nm (log ε 4.58, 4.17, 4.18, and 4.12); $\nu_{max.}$ 2 940, 2 870, 1 600, 1 495, 1 460, and 1 415 cm^{-1}; δ 2.72 (4 H, s, 9- and 10-H), 3.66, 3.73, 3.76, and 3.78 (each 3 H, s, $ArOCH_3$), 5.03 (2 H, s, $ArOCH_2Ar'$) and 6.24 (2 H, br s, ArH); *m/e* 328 ($M^{\cdot+}$; 100%), 314, 313, 296, 284, 269, 268, 226, and 164 (M^{2+}); *m** 298.7 Coeloginin (50 mg) on similar treatment with dimethyl sulphate (0.5 ml) and anhydrous potassium carbonate (2 g) in dry acetone (100 ml) under reflux for 40 h furnished 2,6,7,8-tetramethoxy-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran-5-one (1d) (dimethyl coeloginin) which crystallised from light petroleum–ethyl acetate as colourless needles (45 mg), m.p. 136 °C (Found: C, 66.75; H, 5.3. $C_{19}H_{18}O_6$ requires C, 66.67; H, 5.26%); $\lambda_{max.}$ 224, 228—230sh, 252, 286—287, and 350 nm (log ε 4.41, 4.41, 4.47, 4.14, and 3.96); $\nu_{max.}$ 2 990, 2 950, 1 725, 1 630, 1 600, 1 465, and 1 415 cm^{-1}; δ 2.92 (4 H, s, 9- and 10-H), 3.75 and 3.86 (each 3 H, s, $ArOCH_3$), 3.92 (6 H, s, $ArOCH_3$), and 6.54 (2 H, br s, ArH); *m/e* 342 ($M^{\cdot+}$; 100%), 328, 327, 313, 312, 300, 299, 284, 270, 269, 241, 171 (M^{2+}), 163, 158, 142, 127, 126, and 114; *m** 312.7 and 273.4.

Acetylation of Coelogin (1a) *and Coeloginin* (1b).—Acetylation of coelogin (25 mg) with acetic anhydride (1 ml) and pyridine (1 ml) gave pure 7,8-dimethoxy-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran-2,6-diyl diacetate (1e) (coelogin diacetate) which crystallised from light petroleum–ethyl acetate mixture as colourless granules (25 mg), m.p. 128 °C (Found: C, 65.55; H, 5.2. $C_{21}H_{20}O_7$ requires C, 65.63; H, 5.21%); $\lambda_{max.}$ 221, 270, 282—283, 301, and 315sh nm (log ε 4.56, 3.98, 4.14, 4.07, and 4.00); $\nu_{max.}$ 2 940, 2 840, 1 755, 1 607, 1 452, 1 415, 1 275, and 1 198 cm^{-1}; δ 2.20 and 2.27 (each 3 H, s, OAc), 2.80 (4 H, s, 9- and 10-H), 3.77 (6 H, s, $ArOCH_3$), 4.92 (2 H, s, $ArOCH_2Ar'$), and 6.46 (2 H, br s, ArH); *m/e* 384 ($M^{\cdot+}$), 342 (*M* − 42), 300 (*M* − 84; 100%), 285, 225, 213, 192 (M^{2+}), 127, 116, 43, and 42. Coeloginin (25 mg) was similarly acetylated to give pure 7,8-dimethoxy-5-oxo-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran-2,6-diyl diacetate (1f) (coeloginin diacetate) which crystallised from light petroleum–ethyl acetate as colourless needles (25 mg), m.p. 163 °C (Found: C, 63.45; H, 4.5. $C_{21}H_{18}O_8$ requires C, 63.32; H, 4.52%); $\lambda_{max.}$ 228, 250, 279—280, and 334—335 (log ε 4.33, 4.38, 4.03, and 3.84); $\nu_{max.}$ 2 960, 1 762, 1 720, 1 625, 1 600, 1 455, 1 415, 1 285, and 1 197 cm^{-1}; δ 2.24 and 2.39 (each 3 H, s, OAc), 2.98 (4 H, s, 9- and 10-H), 3.82 and 3.93 (each 3 H, s, $ArOCH_3$), and 6.77 (2 H, br s, ArH); *m/e* 398 ($M^{\cdot+}$), 356 (*M* − 42), 314 (*M* − 84; 100%), 299, 285, 271, 270, 228, 199 (M^{2+}), 149, 115, 43, and 42; *m** 284.7 and 277.0.

Conversion of Dimethylcoeloginin (1d) *into Dimethylcoelogin* (1c).—Dimethylcoeloginin (50 mg) in tetrahydrofuran (THF) solution (25 ml) was refluxed with lithium aluminium hydride (5 mg) for 4 h. After the usual work-up the resultant mixture was chromatographed to give an amorphous solid (40 mg) which was identified as dimethylcoelogin.

Conversion of Coelogin (1a) *into Coeloginin* (1b).—Air was bubbled for 50 h through an ethanolic solution (25 ml) of pure coelogin (25 mg). Evaporation of the solvent left a residue which on t.l.c. showed mainly one spot corresponding to coelogin with a weak stain for coeloginin above it. Although a complete separation of the two compounds failed, careful repeated chromatography ultimately yielded pure coeloginin (1 mg) as well as the mixture with coelogin.

Conversion of Dimethylcoelogin (1c) *into Dimethylcoeloginin* (1d).—An ethanolic solution (10 ml) of dimethylcoelogin (10 mg) was treated exactly as above with air. Careful chromatography afforded pure dimethylcoeloginin (*ca.* 1 mg) and unconverted dimethylcoelogin (8 mg).

Transformation of Coelogin (1a) *to* 6-*Hydroxy*-7,8-*dimethoxy*-5-*methyl*-1,2,3,4,4a,9,10,10a-*octahydrophenanthrene* (2a) (*Compound A*) *and* 6-*Hydroxy*-7,8-*dimethoxy*-1,2,3,3a-*tetrahydro*-5H-*phenanthro*[4,5-bcd]*pyran* (5) (*Compound* B).—To a solution of coelogin (100 mg) in glacial acetic acid (50 ml) were added 10% Pd–C (10 mg) and a trace of perchloric acid, and the mixture was constantly stirred for 8 h in a hydrogen atmosphere. The product obtained on usual work-up of the resultant mixture on t.l.c. showed mainly two spots of higher R_F than that for some unconverted coelogin also present. This product, on column chromatography, gave pure compound A as a semisolid mass (20 mg) from the light petroleum–ethyl acetate (30 : 1) eluate (Found: C, 74.05; H, 8.75. $C_{17}H_{24}O_3$ requires C, 73.92; H, 8.70%); $\nu_{max.}$ 3 460, 2 940, 1 588, 1 475, and 1 425 cm^{-1}; δ 1.39—1.82 (11 H, aliphatic-H), 2.05 (3 H, s, $ArCH_3$), 2.54—2.77 (3 H, benzylic-H), 3.67 and 3.76 (each 3 H, s, $ArOCH_3$), and *5.67* (1 H, br s, ArOH); *m/e* 276 ($M^{\cdot+}$; 100%), 262, 261 (*M* − 15), 233, 219, 205, 194, 191, 187, and 167; *m** 246.8. 6,7,8-Trimethoxy-5-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (2b) was obtained as an amorphous solid, δ 1.34—1.86 (11 H, aliphatic-H), 2.07 (3 H, s, $ArCH_3$), 2.53—2.79 (3 H, benzylic-H), 3.69, 3.71, and 3.77 (each 3 H, s, $ArOCH_3$).

Further elution furnished compound B with light petroleum–ethyl acetate (12 : 1) as eluant. It crystallised from light petroleum–benzene–ethyl acetate mixture as colourless needles (25 mg), m.p. 153 °C (Found: C, 71.4; H, 6.25. $C_{17}H_{18}O_4$ requires C, 71.33; H, 6.29%); $\lambda_{max.}$ 241, 293—295 and 331—333 nm (log ε 4.80, 3.76, and 3.05); $\lambda_{max.}$ (0.01M-NaOH–EtOH) 221, 256, 302, 313, and 351—355 nm (log ε 4.22, 4.71, 3.76, 3.73, and 3.63); $\nu_{max.}$ 3 350, 3 000, 2 950, 1 590, 1 508, 1 475, 1 460, and 1 422 cm^{-1}; δ 1.73—2.40 (4 H, m, aliphatic-H), 2.84 (2 H, m, benzylic-H), 3.97 and 4.03 (each 3 H, s, $ArOCH_3$), 4.70 (1 H, m, $W_{\frac{1}{2}}$ 7.5 Hz; 5-H), 5.10 (2 H, q, *J* 15 Hz, $ArOCH_2Ar'$), *6.03* (1 H, s, ArOH), 7.05 and 7.75 (each 1 H, d, *J* 9 Hz, ArH); *m/e* 286 ($M^{\cdot+}$; 100%), 285, 258, 257, 255, 243, 231, 230, 227, 215, 211, 187, 183, 172, 165, 153, 152, 143 (M^{2+}), 141, 139, 129, 128, 127, 121, and 115; *m** 229.8. The monoacetate was obtained as fine colourless needles from light petroleum–ethyl acetate, m.p. 165 °C (Found: C, 69.4; H, 6.15. $C_{19}H_{20}O_5$ requires C, 69.51; H, 6.10%); $\lambda_{max.}$ 238, 290, and 328 nm (log ε 4.71, 3.73, and 3.05); $\nu_{max.}$ 2 980, 2 955, 1 755, 1 595, 1 515, 1 458, 1 418, 1 280, and 1 203 cm^{-1}; δ 1.58—

2.45 (4 H, m, aliphatic-H), 2.31 (3 H, s, OAc), 2.81 (2 H, m, benzylic-H), 3.85 and 3.91 (each 3 H, s, $ArOCH_3$), 4.75 (1 H, m, 5-H), 4.87 (2 H, q, *J* 15 Hz, $ArOCH_2Ar'$), 7.10 and 7.78 (each 1 H, d, *J* 9 Hz, ArH); *m/e* 328 ($M^{\bullet+}$), 286 (*M* − 42; 100%), 285 (*M* − 43), 271, 270, 269, 258, 255, 243, 230, 227, 226, 215, 211, 199, 183, 153, 152, 143, 141, 139, 128, 127, and 115; *m** 249.4, 232.7, and 229.8.

Catalytic Dehydrogenation of 6,7,8-*Trimethoxy*-5-*methyl*-1,-2,3,4,4a,9,10,10a-*octahydrophenanthrene* (2b).—The methylated derivative (2b) of compound A (100 mg) was subjected to dehydrogenation in the presence of 10% Pd–C (10 mg) at *ca.* 320 °C over a metal bath for 1 h. The resultant mixture was stirred with diethyl ether and filtered. T.l.c. of the concentrated ether extract with a double run developing in light petroleum–ethyl acetate (15 : 1) showed one main spot in u.v. light along with several other very faint spots. Repeated column chromatography failed to furnish the major product in a pure state, so preparative t.l.c. on a 0.1-mm layer of silica gel G was used. After three successive runs developing in light petroleum–ethyl acetate (20 : 1) the zone corresponding to the main spot under u.v. light was scooped out and eluted. Removal of the solvent gave 6,7,8-trimethoxy-5-methylphenanthrene (4) (compound C) in a pure but amorphous form (10 mg) (Found: C, 76.5; H, 6.4. $C_{18}H_{18}O_3$ requires C, 76.60; H, 6.38%); $\lambda_{max.}$ 221, 228—229, 258, 295, and 306—307 nm (log ε 4.31, 4.32, 4.67, 3.98, and 3.99); $\nu_{max.}$ 2 940, 2 880, 1 588, 1 460, 1 400, and 1 380 cm^{-1}; δ 2.84 (3 H, s, $ArCH_3$), 3.85, 3.93, and 3.94 (each 3 H, s, $ArOCH_3$), 7.34—7.99 (5 H, m, ArH), and 8.63 (1 H, m, ArH); *m/e* 282 ($M^{\bullet+}$), 267, 239, 224, 181, 175, 165, 153, 152, 149 (100%), and 141 (M^{2+}); *m** 252.8.

Transformation of Compound B (5) *into Compound* A (2a).—Coelogin and pure compound B (10 mg) were separately subjected to catalytic hydrogenolysis similar to that in which the latter compound and compound A were produced from coelogin, the only difference being an increase in the amount of perchloric acid added. Work-up of the resultant mixture gave a solution which on t.l.c. revealed the presence of compound A as the major product; no trace of compound B could be detected.

Formation of 2,6-*Dihydroxy*-7,8-*dimethoxy*-9,10-*dihydro*-5H-*phenanthro*[4,5-bcd]*pyran*-1-*carbaldehyde* (1h) (*Compound D*) *and* 2,6-*Dihydroxy*-7,8-*dimethoxy*-9,10-*dihydro*-5H-*phenanthro*[4,5-bcd]*pyran*-3-*carbaldehyde* (1g) (*Compound E*) *from Coelogin* (1a).—A solution of crude coelogin (100 mg), contaminated only with traces of coeloginin (1b), in chloroform (50 ml) was shaken vigorously with 2M-aqueous sodium hydroxide solution in a separating funnel and left overnight. The aqueous layer was then acidified (dil. HCl) in the cold and extracted with diethyl ether. The concentrated ether extract on t.l.c. with a double run developing with light petroleum–ethyl acetate (5 : 1) showed two yellow spots (R_F 0.3 and 0.4) as well as that of unconverted coelogin. This mixture on column chromatography furnished pure compound D (1h) in the earlier fractions (with light petroleum–ethyl acetate (15 : 1) as eluant) which crystallised from light petroleum–ethyl acetate as heavy, golden-yellow needles (20 mg), m.p. 190 °C (Found: C, 65.7; H, 4.85. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.89%); $\lambda_{max.}$ 232sh, 280, 286, and 387 nm (log ε 4.41, 4.44, 4.43, and 3.44); $\lambda_{max.}$ (0.01M-NaOH–EtOH) 238, 286—287, 329—330, and 420—421 nm (log ε 4.34, 4.42, 4.21, and 3.57); $\nu_{max.}$ 3 430, 2 930, 2 860, 2 820, 1 648, 1 585, 1 542, 1 500, 1 462, and 1 420 cm^{-1}; δ 2.75 (4 H, s, 9- and 10-H), 3.75 and 3.84 (each 3 H, s, $ArOCH_3$), 5.19 (2 H, s, $ArOCH_2Ar'$), *5.69* (1 H, s, ArOH), 6.27 (1 H, s, ArH), 10.14 (1 H, s, CHO), and *11.69* (1 H, s, ArOH); *m/e* 328 ($M^{\bullet+}$), 327 (*M* − 1), 314, 313 (100%), 299, 285, 253, 242, 239, and 164 (M^{2+}); *m** 298.7. Later fractions of the light petroleum–ethyl acetate (15 : 1) eluate on evaporation afforded compound E (1g) which crystallised from light petroleum–ethyl acetate as golden-yellow granules (15 mg), m.p. 187—188 °C (Found: C, 65.95; H, 4.85. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.89%); $\lambda_{max.}$ 226, 276, and 373—374 nm (log ε 4.47, 4.59, and 3.58); $\lambda_{max.}$ (0.01M-NaOH–EtOH) 242sh, 268, 282—283, and 414 nm (log ε 4.34, 4.40, 4.43, and 3.74); $\nu_{max.}$ 3 430, 2 930, 2 860, 2 810, 1 622, 1 587, 1 488, 1 450, and 1 430 cm^{-1}; δ 2.83 (2 H, m, 10-H), 3.05 (2 H, m, 9-H), 3.76 and 3.85 (each 3 H, s, $ArOCH_3$), 5.15 (2 H, s, $ArOCH_2Ar'$), *5.65* (1 H, s, ArOH), 6.26 (1 H, s, ArH), 10.11 (1 H, s, CHO), and *12.21* (1 H, s, ArOH); *m/e* 328 ($M^{\bullet+}$; 100%), 327 (*M* − 1), 314, 313, 299, 298, 297, 253, 241, 225, and 164 (M^{2+}); *m** 298.7.

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