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PHENANTHRENES OF *EULOPHIA NUDA*

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Key Word Index—*Eulophia nuda*; Orchidaceae; phenanthrene derivatives.

Abstract—From the tubers of *Eulophia nuda* six phenanthrene derivatives have been isolated: 9,10-dihydro-2,5-dimethoxyphenanthrene-1,7-diol, 9,10-dihydro-4-methoxyphenanthrene-2,7-diol, 1,5-dimethoxyphenanthrene-2,7-diol, 1,5,7,-trimethoxyphenanthrene-2,6-diol, 5,7-dimethoxyphenanthrene-2,6-diol and 4,4′,8,8′-tetramethoxy [1,1′-biphenanthrene]-2,2′,7,7′-tetrol. 4-Hydroxybenzaldehyde and 4-hydroxybenzyl alcohol were also isolated. The structures were assigned by spectroscopic methods and the structure of 9,10-dihydro-2,5-dimethoxyphenanthrene-1,7-diol was also determined by a single-crystal X-ray structure analysis of its acetate derivative.

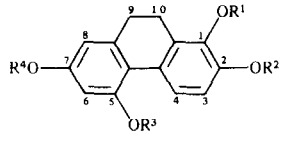
INTRODUCTION

Eulophia nuda Lindl. is a terrestial orchid found in the central and southeast Asian regions. It is reported to have some use in medicine [1]. In Thailand this orchid is used in traditional medicine for the treatment of skin rash. Indian workers have reported the isolation of eulophiol (9,10-dihydro-2,7-dimethoxyphenanthrene-1,5-diol) (**1**) [1] and nudol (3,4-dimethoxyphenanthrene-2,7-diol) (**2**) [2]; hexacosanol and lupeol have also been obtained [3]. In contrast to this result, we have obtained by chromatography of the extract of the tubers the following substances: 9,10-dihydro-2,5-dimethoxyphenanthrene-1,7-diol (**3**), 9,10-dihydro-4-methoxyphenanthrene-2,7-diol (**5**), 1,5-dimethoxyphenanthrene-2,7-diol (**7**), 1,5,7-trimethoxyphenanthrene-2,6-diol (**9**), 5,7-dimethoxyphenanthrene-2,6-diol (**12**) and 4,4′8,8′-tetramethoxy-[1,1′-biphenanthrene]-2,2′,7,7′-tetrol (**14**).

RESULTS AND DISCUSSION

The structures of the substances were determined largely by interpretation of 400 MHz ^{1}H NMR spectral data, making use especially of decoupling and NOE enhancement results. The hydroxyphenanthrenes were characterized as their acetate derivatives, which in general were more easily purified and gave better NMR spectra.

The diphenolic compound **3**, $C_{16}H_{16}O_4$, was clearly a dihydrophenanthrene from its UV spectrum. In the ^{1}H NMR spectrum (acetone-d_6) H-3 and H-4 resonated as a pair of doublets (J_o = 8.4 Hz) at δ6.78 and 7.72 respectively; H-6 and H-8 as doublets at δ6.45 and 6.38 (J_m = 2.4 Hz), and H_2-9 and H_2-10 as multiplets at δ 2.61 and 2.74 respectively; the C-2 and C-5 methoxyl groups resonated at δ3.86 and 3.82. At high resolution, the signal of H-8 was a doublet of triplets due to benzylic coupling



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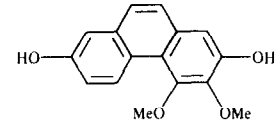

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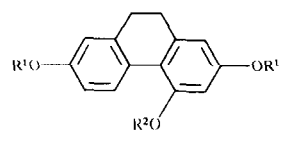

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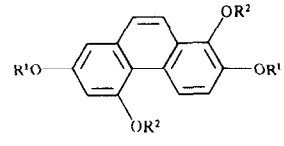

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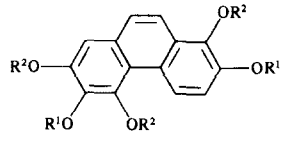

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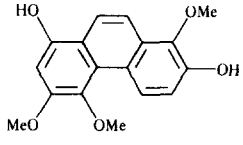

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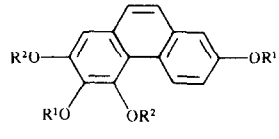
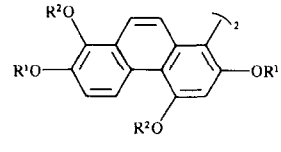


12 R¹ = H, R² = Me
13 R¹ = Ac, R² = Me



14 R¹ = H, R² = Me
15 R¹ = Ac, R² = Me
16 R¹ = R² = Me

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(J = 0.6 Hz) from H_2-9. The assignment of the methoxyl groups is based on the observation of the NOE enhancements: irradiation of the C-2 methoxyl group (δ3.86) gave an enhancement of the signal of H-3 (δ6.78) (10%), and irradiation of the C-5 methoxyl group (δ3.82) gave enhancements of the signals of H-6 (δ6.45) (16%) and H-4 (δ7.72) (2%). Additional data were obtained for **3** in $CDCl_3$ solution and for the diacetate derivative **4** in acetone-d_6 (see Experimental). This evidence clearly established the substitution pattern of the aromatic rings as shown in **3**. A single-crystal X-ray structure determination confirmed the structure **3** (see below).

Initially, it was believed that compound **3** was eulophiol **1** because it had the same melting point, 202–203°, as reported for eulophiol [1], although the melting points of the diacetate derivatives differed slightly. The NMR results confirmed that the substances are not identical.

Compound **5**, $C_{15}H_{14}O_3$, a dihydrophenanthrene (UV spectrum), was examined as its diacetate derivative **6**. In the NMR spectrum ($CDCl_3$–C_6D_6 1:1) of **6**, H-1 and H-3 resonated as broadened doublets at δ6.58 and 6.54 (J_m = 2.2 Hz) respectively, with H-1 showing benzylic coupling with H_2-9 and H-3 showing coupling with the C-4 methoxyl group (δ3.50); H-5, H-6 and H-8 gave an AMX pattern ($\delta_{H\text{-}5}$ 8.34, $J_{5,6}$ = 8.5 Hz, $\delta_{H\text{-}6}$ 7.00, $J_{6,5}$ = 8.5 Hz, $J_{6,8}$ = 2.5 Hz, $\delta_{H\text{-}8}$ 6.90, $J_{8,6}$ = 2.5 Hz); H_2-9 and H_2-10 were accidently equivalent at δ2.56. Double irradiation at δ2.56 caused sharpening of the signals from H-1 and H-8, and NOE enhancements were observed for H-3 (17%) and H-5 (3%) on irradiation of the C-4 methoxyl group, and H-1 (11%) and H-8 (11%) on irradiation of H_2-9/H_2-10, thus proving the substitution pattern present in the parent substance **5**.

Compound **7**, $C_{16}H_{14}O_4$, was a diphenolic phenanthrene (λ_{max} 262 nm, log ε 4.55). In the NMR spectrum of the diacetate derivative **8**, H-3 resonated as a doublet at δ7.34 (J_o = 9.1 Hz) and H-4 as a doublet of doublets at δ9.39 (J_o = 9.1 Hz, $J_{4,10}$ = 0.6 Hz); H-6 and H-8 resonated as doublets (J_m = 2.5 Hz) at δ6.91 and 7.28 respectively; H-9 resonated at δ7.69 as a doublet ($J_{9,10}$ = 8.8 Hz); the signal from H-10 (δ8.13) showed additional coupling of 0.6 Hz because of long range (extended W) coupling with H-4. Assignment f the two methoxyl group signals could be made from NOE results. Selective irradiation of the OMe group at δ3.98 gave rise to a NOE enhancement of the H-10 signal (6%); irradiation of the other methoxyl group (δ4.11) caused enhancement of the signals from both H-4 (5%) and H-6 (20%). These NMR data indicated unequivocally the structure **7**.

Compound **9** gave a diacetate derivative, the mass spectrum of which indicated that the molecular formula of the parent phenol was $C_{17}H_{16}O_5$. The NMR spectrum of the diacetate **10** was similar to that of the diacetate of **7** except for the presence of an extra methoxyl signal and a signal for one aromatic proton rather than the signals for a *meta*-coupled pair. For detailed analysis, the spectrum in C_6D_6 solution was more suitable than the spectrum in $CDCl_3$ as overlap of the methoxyl signals was removed. In this spectrum H-3 resonated as a doublet at δ7.33 (J_o = 9.2 Hz) and H-4 as a doublet of doublets at δ8.60 (J_o = 9.2 Hz, $J_{4,6}$ = 0.6 Hz); H-8 resonated as a singlet at δ6.82, and H-9 and H-10 as a doublet and doublet of doublets respectively at δ7.49 ($J_{9,10}$ = 8.8 Hz) and 8.19 ($J_{10,9}$ = 8.8 Hz, $J_{10,4}$ = 0.6 Hz). NOE enhancement results allowed the three methoxyl signals to be assigned and also confirmed the Ar-H assignments. Irradiation of the C-1 methoxyl group (δ3.77) selectively enhanced (5%) the signal for H-10 at δ8.19; irradiation of the C-5 methoxyl group (δ3.63) enhanced (6%) the signal for H-4 at δ8.60; and irradiation of the C-7 methoxyl group (δ3.44) enhanced (15%) only the signal from H-8 (δ6.82). The fact that a NOE enhancement was obtained between H-8 and H-9 (12%) ruled out the alternative structure **11** for the parent phenol and confirmed that the correct structure was **9**.

Compound **12** gave the diacetate derivative **13**. In the NMR spectrum ($CDCl_3$) of **13**, the signal from H-8 was a singlet at δ7.07 and signals from H-1, H-3 and H-4 gave an ABX pattern at δ7.58, 7.36 and 9.42, respectively. H-9 and H-10 accidently have the same chemical shift and resonated as a singlet at δ7.65. The substitution pattern was confirmed by NOE enhancement results. Irradiation of the C-5 methoxyl group (δ3.92) enhanced only the signal from H-4 (δ9.42) (8%), irradiation of the C-7 methoxyl group (δ3.99) enhanced only the signal from H-8 (δ7.07) (14%). H-8 gave NOE enhancements to the C-7 methoxyl and to H-9 (δ7.65) (14%); irradiation at δ7.65 (H-9, H-10) gave NOE enhancements of H-8 (15%) and of H-1 (13%). In C_6D_6 solution H-9, H-10 became nonequivalent and resonated as an AB quartet at δ7.38 and 7.43 respectively. Similar NOE results were obtained: in particular, irradiation of H-1 (δ7.60) enhanced only the signal from H-10 (δ7.43) (9%), and irradiation of H-8 (δ6.79) enhanced the signals from H-9 (δ7.38) (12%), and the C-7 methoxyl group (δ3.38) (4%).

Compound **14** was purified through its acetate derivative **15**. The mass spectrum of **15** had a molecular ion peak at m/z 706 and showed four successive losses of 42 mass units (CH_2=C=O) (peaks at m/z 664, 622, 580 and 538); it also showed a significant peak at m/z 269 which can be assigned to the doubly charged ion arising from the ion m/z 538. This showed that the natural product was in fact a dimer, with the molecular formula $C_{32}H_{26}O_8$. The NMR spectrum of the acetate **15** showed the dimeric structure was based on a symmetrical coupling of two molecules of the phenolic phenanthrene **7** since there was no doubling up of signals from the two phenanthrene units present. The position of coupling was determined by decoupling and NOE enhancement studies. One methoxy group (δ4.20) gave NOE enhancement to H-3, H-3′ (singlet, δ7.12) (19%) and to H-5, H-5′ (δ9.52) (3%), and the other one (δ3.90) gave a 6% enhancement to the signal of H-9, H-9′ (δ7.91). The signal of H-5, H-5′ which showed J_o = 9.3 Hz from H-6, H-6′ also had a long range coupling (0.7 Hz) with H-9, H-9′. The fact that H-3, H-3′ appeared as a singlet indicated that the associated aromatic ring is otherwise fully substituted. An acetoxy group is located at positions C-2, C-2′ as in **8** and the biaryl linkage is located at C-1, C-1′. There is good chemical shift evidence for the latter proposal since, compared with the data for compound **8**, the signal of H-10, H-10′ (δ7.18) and the signal of one OAc group (δ1.90) are shifted markedly upfield because the groups on each aromatic ring lie in the shielding zone of the adjacent ring.

Further evidence for the location of the phenolic groups in **14** was obtained from the tetramethyl ether derivative **16**. The NMR spectrum of **16** showed four well-separated methoxyl signals which were assigned by NOE enhancement studies. Irradiation at δ3.79 (2,2′-OMe enhanced only the signal from H-3, H-3′ (δ7.04) (8%); irradiation at δ3.90 (8,8′-OMe) enhanced the signal from H-9, H-9′ (δ7.83) (4%); irradiation at δ4.02 (7,7′-

OMe) enhanced the signal from H-6, H-6′ (δ7.33) (12%) and irradiation at δ4.33 (4,4′-OMe) enhanced the signal from H-3, H-3′ (δ7.04) (13%) and from H-5, H-5′ (δ9.40) (3%).

Structures **5** and **7** have already been suggested on limited evidence for compounds isolated from *Coelogyne* species [4] and from *Oncidium Cebolleta* [5], respectively. The present work confirms the structures proposed for these compounds, and extends the array of phenanthrene derivatives isolated from orchids.

EXPERIMENTAL

Mps: uncorr.; UV: EtOH; ^{1}H NMR: 400 MHz, Me_2CO-d_6, unless otherwise stated. NOE were measured in the FT difference mode by the method of ref. [6]. Analyses were carried out by Australian Microanalytical Service, Melbourne. CC and prep. TLC were performed using Merck silica gel 60 PF_{254}. Chromatographic solvents were distilled at their boiling point ranges. Plant material was collected near Kanchanaburi and Uthaithani, Thailand.

Extraction. Oven dried (40-60°) finely powdered tubers of *Eulophia nuda* Lindl. (3.6 kg) were successively extracted with Me_2CO (11 l) in a Soxhlet for 20 hr and then with MeOH (7.5 l) for a further 15 hr. Evaporation of solvents from each extract yielded 372 and 337 g, respectively.

The Me_2CO extract was diluted with H_2O (500 ml) and the mixture extracted with Et_2O (5 × 300 ml). The aq. layer was further partitioned with *n*-BuOH (fraction A). The combined Et_2O extract was fractionated into neutral and acidic fractions by 10% aq. NaOH (2 1). The aq. alkaline extract was acidified in the cold with 6 M HCl (500 ml) and the liberated solid was taken into Et_2O and the extract washed consecutively with 10% $NaHCO_3$ and 10% Na_2CO_3. The Et_2O layer was evapd to dryness to leave 28.5 g of phenolic constituents (fraction **B**). The neutral fraction yielded 117 g of residue (fraction C). The $NaHCO_3$ and Na_2CO_3 fractions were acidified with 6 M HCl and then extracted with EtOAc. Removal of solvents yielded fractions D (5.1 g) and E (5.2 g), respectively.

Isolation of phenolic constituents. Fraction **B** (28.5 g) was first subjected to coarse separation by flash CC over silica gel, gradient eluting with 20% EtOAc–*n*-hexane–100% EtOAc, followed by 5 and 10% MeOH–EtOAc, respectively and finally with MeOH.

Elution with 35–40% EtOAc–*n*-hexane gave a semi-solid mixture (1.1 g) which was chromatographed (prep. TLC, 1% MeOH–CH_2Cl_2, triple developed). Three compounds in order of decreasing R_f value were isolated, namely 1,5,7-trimethoxyphenanthrene-2,6-diol (**9**) (13 mg), 9,10-dihydro-2,5-dimethoxyphenanthrene-1,7-diol (**3**) (876 mg) and 4-hydroxybenzaldehyde (63 mg).

Elution with 40–50% EtOAc–*n*-hexane gave a red gum which was chromatographed (prep. TLC), eluting with 5% MeOH–CH_2Cl_2 (double developed). In order of decreasing R_f value, four bands were isolated. The first band (590 mg) after prep. TLC (40% EtOAc–*n*-hexane, quadruple developed) gave **3** (212 mg) and **9** (161 mg). The second band (1.0 g) was rechromatographed on prep. TLC (50% EtOAc–*n*-hexane) to give 1,5-dimethoxyphenanthrene-2,7-diol (**7**) (452 mg) and 5,7-dimethoxyphenanthrene-2,6-diol (**12**) (109 mg). The third band (1.0 g) was further purified by prep. TLC (40% EtOAc–*n*-hexane, triple developed) to give 9,10-dihydro-4-methoxyphenanthrene-2,7-diol (**5**) (761 mg). The lowest band (168 mg) is now under investigation.

Elution with 50–55% EtOAc–*n*-hexane afforded a semi-solid mixture (4.9 g). Crystals (2.4 g) were collected after addition of CH_2Cl_2. This compound is still under examination. The residue (2.5 g) was rechromatographed (prep. TLC, 5% MeOH–CH_2Cl_2, double developed). One of the isolated bands (338 mg) was characterized as 4,4′,8,8′-tetramethoxy-[1,1′-biphenanthrene]-2,2′,7,7′-tetrol (**14**) but the others need to be further explored.

9,10-*Dihydro*-2,5-*dimethoxyphenanthrene*-1,7-*diol* (**3**). Colourless needles from $CHCl_3$–MeOH, mp 202–203°. (Found: C, 70.7; H, 5.8. $C_{16}H_{16}O_4$ requires: C, 70.6; H, 5.9%). IR ν_{max} cm^{-1}: 3400 (Ar-OH), 1595, 1450, 1375, 1275. UV λ_{max}^{EtOH} nm (log ε): 213 (4.56), 280 (4.32), 310 (4.05). ^{1}H NMR: δ2.16 (2H, *m*, H-9) 2.74 (2H, *m*, H-10), 3.82 (3H, *s*, C5-OMe), 3.86 (3H, *s*, C2-OMe), 6.38 (1H, *dt*, $J_{8.6}$ = 2.4 Hz, $J_{8,9}$ = 0.6 Hz, H-8), 6.45 (1H, *d*, $J_{6.8}$ = 2.4 Hz, H-6), 6.78 (1H, *d*, $J_{3,4}$ = 8.4 Hz, H-3), 7.72 (1H, *d*, $J_{4,3}$ = 8.4 Hz, H-4). ^{1}H NMR ($CDCl_3$): δ2.69 (2H, *m*, H-9), 2.81 (2H, *m*, H-10), 3.86 (3H, *s*, C5-OMe), 3.91 (3H, *s*, C-2-OMe), 6.35 (1H, *dt*, $J_{8.6}$ = 2.4 Hz, $J_{8,9}$ = 0.6 Hz, H-8), 6.41 (1H, *d*, $J_{6.8}$ = 2.4 Hz, H-6), 6.77 (1H, *d*, $J_{3,4}$ = 8.4 Hz, H-3), 7.78 (1H, *d*, $J_{4,3}$ = 8.4 Hz, H-4). MS *m/z* (rel. int.): 272 [M]$^+$ (100), 257 [M-15]$^+$ (65), 292 (13), 197 (9), 136 (7), 55 (9).

The diacetate **4** crystallized as colourless plates from *n*-hexane–CH_2Cl_2, mp 153–154°. (Found: C, 67.5; H, 5.4. $C_{20}H_{20}O_6$ requires: C, 67.4; H, 5.7%). IR ν_{max} cm^{-1}: 1760 (OCOMe), 1590, 1460, 1440, 1370, 1275. UV λ_{max}^{EtOH} nm (log ε): 212 (4.42), 279 (4.24), 293 (4.16), 306 (4.06). ^{1}H NMR: δ2.26 (3H, *s*, OCOMe), 2.30 (3H, *s*, OCOMe), 2.62 (2H, *m*, H-9), 2.69 (2H, *m*, H-10), 3.84 (3H, *s*, C-2-OMe), 3.89 (3H, *s*, C-5-OMe), 6.66 (1H, *dt*, $J_{8.6}$ = 2.3 Hz, $J_{8,9}$ = 0.7 Hz, H-8), 6.77 (1H, *d*, $J_{6.8}$ = 2.3 Hz, H-6), 6.95 (1H, *d*, $J_{3,4}$ = 8.9 Hz, H-3), 8.16 (1H, *d*, $J_{4,3}$ = 8.9 Hz, H-4). ^{1}H NMR ($CDCl_3$): δ2.31 (3H, *s*, OCOMe), 2.35 (3H, *s*, OCOMe), 2.64 (2H, *m*, H-9), 2.71 (2H, *m*, H-10), 3.85 (3H, *s*, C-2-OMe), 3.86 (3H, *s*, C-5-OMe), 6.62 (1H, *dt*, $J_{8.6}$ = 2.3 Hz, $J_{8,9}$ = 0.7 Hz, H-8), 6.63 (1H, *d*, $J_{6.8}$ = 2.3 Hz, H-6), 6.87 (1H, *d*, $J_{3,4}$ = 8.9 Hz, H-3), 8.14 (1H, *d*, $J_{4,3}$ = 8.9 Hz, H-4). MS *m/z* (rel. int.): 56 [M]$^+$ (15), 314 (16), 272 (36), 257 (13), 57 (10).

9,10-*Dihydro*-4-*methoxyphenanthrene*-2,7-*diol* (**5**). Colourless needles from *n*-hexane-$CHCl_3$, mp 95–96°. IR ν_{max} cm^{-1}: 3300 (Ar-OH), 1610, 1460, 1380. UV λ_{max}^{EtOH} nm (log ε): 216 (4.53), 269 (4.44), 279 (4.46), 292 (4.34). ^{1}H NMR: δ2.63 (4H, *s*, H-9, H-10), 3.83 (3H, *s*, OMe), 6.37 (1H, *d*, $J_{1,3}$ = 2.6 Hz, H-1), 6.45 (1H, *br d*, $J_{3,1}$ = 2.6 Hz, $J_{3,10}$ < 0.5 Hz, H-3), 6.68 (2H, *m*, H-6, H-8), 8.05 (1H, *m* (2nd order), H-5) MS *m/z* (rel. int.): 242.0941 M$^+$ (100) ($C_{15}H_{14}O_3$ requires 242.0943), 227 (15), 199 (34), 181 (14).

The acetate **6** crystallized as colourless needles from *n*-hexane–CH_2Cl_2, mp 132–133°. (Found: C, 70.0; H, 5.4. Calc. for $C_{19}H_{18}O_5$: C, 69.9; H, 5.6%). IR ν_{max} cm^{-1}: 1750 (OCOMe), 1595, 1460, 1370 1200. UV λ_{max}^{EtOH} nm (log ε): 215 (4.43), 273 (4.22), 292 (4.10), 304 (3.99). ^{1}H NMR ($CDCl_3$: C_6D_6/1:1): δ1.98 (3H, *s*, OCOMe), 2.02 (3H, *s*, OCOMe), 2.56 (4H, *s*, H-9, H-10), 3.50 (H, *s*, C4-OMe), 6.54 (1H, *d*, $J_{3,1}$ = 2.2 Hz, H-3), 6.58 (1H, *br d*, $J_{1.3}$ = 2.2 Hz, $J_{1,10}$ < 0.5 Hz, H-1), 6.90 (1H, *br d*, $J_{8.6}$ = 2.5 Hz, $J_{8,9}$ < 0.5 Hz, H-8), 7.00 (1H, *dd*, $J_{6,5}$ = 8.5 Hz, $J_{6.8}$ = 2.5 Hz, H-6), 8.34 (1H, *d*, $J_{5.6}$ = 8.5 Hz, H-5). MS *m/z* (rel. int.): 326.1133 [M]$^+$ (30) ($C_{19}H_{18}O_5$ requires 326.1154), 284 (33), 242 (100), 227 (8), 199 (5), 57 (13).

1,5-*Dimethoxyphenanthrene*-2,7-*diol* (**7**). Magenta needles from $CHCl_3$–MeOH, mp 200–201°. (Found: C, 71.1; H, 5.1. Calc. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2%). IR ν_{max} cm^{-1}: 3340 (Ar-OH), 1620, 1570, 1450, 1375. UV λ_{max}^{EtOH} nm (log ε): 209 (4.15), 243 (4.28), 262 (4.55), 286 (4.07), 295 (3.82), 309 (3.76). ^{1}H NMR: δ3.91 (3H, *s*, C-1-OMe), 4.07 (3H, *s*, C-5-OMe), 6.80 (1H, *d*, $J_{6.8}$ = 2.4 Hz, H-6), 6.90 (1H, *d*, $J_{8.6}$ = 2.4 Hz, H-8), 7.11 (1H, *s*, OH), 7.20 (1H, *d*, $J_{3,4}$ = 9.4 Hz, H-3), 7.41 (1H, *s*, OH), 7.61 (1H, *d*, $J_{9,10}$ = 9.2 Hz, H-9), 7.96 (1H, *dd*, $J_{10,9}$ = 9.2 Hz, $J_{10.4}$ = 0.8 Hz, H-10), 9.19 (1H, *dd*, $J_{4,3}$ = 9.4 Hz, $J_{4,10}$ = 0.8 Hz, H-4). MS *m/z* (rel. int.): 270 [M]$^+$ (100), 255 [M-15]$^+$ (64), 242 (18), 227 (20), 223 (13).

The diacetate **8** crystallized as colourless fine needles from *n*-hexane–CH_2Cl_2, mp 147–148°. (Found: C, 67.8; H, 5.1. $C_{20}H_{18}O_6$ requires: C, 67.8; H, 5.1%). IR ν_{max} cm^{-1}: 1760 (OCOMe), 1615, 1580, 1470, 1370, 1300, 1190. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 213 (4.24), 253 (4.52), 276 (4.27), 306 (3.86). ^1H NMR ($CDCl_3$): δ2.38 (3H, *s*, OCOMe), 2.42 (3H, *s*, OCOMe), 3.98 (3H, *s*, C-1-OMe), 4.11 (3H, *s*, C-5-OMe), 6.91 (1H, *d*, $J_{6,8}$ = 2.5 Hz, H-6), 7.28 (1H, *d*, $J_{8,6}$ = 2.5 Hz, H-8), 7.34 (1H, *d*, $J_{3,4}$ = 9.1 Hz, H-3), 7.69 (1H, *d*, $J_{9,10}$ = 8.8 Hz, H-9), 8.13 (1H, *dd*, $J_{10,9}$ = 8.8 Hz, $J_{10,4}$ = 0.6 Hz, H-10), 9.39 (1H, *dd*, $J_{4,3}$ = 9.1 Hz, $J_{4,10}$ = 0.6 Hz, H-4). MS *m/z* (rel. int.): 354 $[M]^+$ (30), 312 $[M-42]^+$ (49), 270 (100), 255 (4).

1,5,7-*Trimethoxyphenanthrene*-2,6-*diol* (**9**). Colourless plates from CH_2Cl_2, mp 152–153°. IR ν_{max} cm^{-1}: 3360 (Ar-OH), 1600, 1430, 1285. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 232 (4.20), 2.64 (4.69), 285 (4.05), 300 (3.86), 313 (3.86). ^1H NMR: δ3.92 (3H, *s*, C-7-OMe), 3.93 (3H, *s*, C-5-OMe), 4.00 (3H, *s*, C-1-OMe), 7.24 (1H, *d*, $J_{3,4}$ = 9.3 Hz, H-3), 7.25 (1H, *s*, H-8), 7.67 (1H, *d*, $J_{9,10}$ = 9.2 Hz, H-9), 7.85 (1H, *dd*, $J_{10,9}$ = 9.2 Hz, $J_{10,4}$ = 0.8 Hz, H-10), 9.16 (1H, *dd*, $J_{4,3}$ = 9.3 Hz, $J_{4,10}$ = 0.8 Hz, H-4). MS *m/z* (rel. int.): 300.1000 $[M]^+$ (100) ($C_{17}H_{16}O_5$ requires 300.0098), 285 $[M-15]^+$ (50), 270 (15), 253 (19), 242 (5).

The diacetate **10** crystallized as colourless needles from *n*-hexane–CH_2Cl_2, mp 167–168°. IR ν_{max} cm^{-1}: 1760 (OCOMe), 1610, 1470, 1300, 1190. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 217 (4.28), 260 (4.75), 283 (4.13), 292 (3.98), 305 (3.97). ^1H NMR ($CDCl_3$): δ2.42 (3H, *s*, OCOMe), 2.45 (3H, *s*, OCOMe), 3.91 (3H, *s*, C-5-OMe), 3.98 (3H, *s*, C-1-OMe), 3.99 (3H, *s*, C-7-OMe), 7.16 (1H, *s*, H-8), 7.34 (1H, *d*, $J_{3,4}$ = 9.2 Hz, H-3), 7.68 (1H, *d*, $J_{9,10}$ = 8.8 Hz, H-9), 8.09 (1H, *dd*, $J_{10,9}$ = 8.8 Hz, $J_{10,4}$ = 0.6 Hz, H-10), 9.20 (1H, *dd*, $J_{4,3}$ = 9.2 Hz, $J_{4,10}$ = 0.6 Hz, H-4). ^1H NMR ($CDCl_3$–C_6D_6/1:1): δ1.93 (3H, *s*, OCOMe), 2.08 (3H, *s*, OCOMe), 3.44 (3H, *s*, C-7-OMe), 3.63 (3H, *s*, C-5-OMe), 3.77 (3H, *s*, C-1-OMe), 6.82 (1H, *s*, H-8), 7.33 (1H, *d*, $J_{3,4}$ = 9.2 Hz, H-3), 7.49 (1H, *d*, $J_{9,10}$ = 8.8 Hz, H-9), 8.19 (1H, *dd*, $J_{10,9}$ = 8.8 Hz, $J_{10,4}$ = 0.6 Hz, H-10), 8.60 (1H, *dd*, $J_{4,3}$ = 9.2 Hz, $J_{4,10}$ = 0.6 Hz, H-4). MS *m/z* (rel. int.): 384.1210 $[M]^+$ (27) ($C_{21}H_{20}O_7$ requires 384.1209), 342 (55), 300 (100), 285 (41), 57 (14).

5,7-*Dimethoxyphenanthrene*-2,6-*diol* (**12**). Colourless prisms, mp 185°. IR ν_{max} cm^{-1}: 3425 (Ar-OH), 1625, 1460, 1375, 1285, 1220, 1150, 1130. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 310 (3.94), 283 (4.35), 257 (4.87), 235 (4.41), 215 (4.29). ^1H NMR: δ3.93 (3H, *s*, C-5-OMe), 3.99 (3H, *s*, C-7-OMe), 7.19 (1H, *dd*, $J_{3,4}$ = 9.3 Hz, $J_{1,3}$ = 2.8 Hz, H-3), 7.22 (1H, *s*, H-8), 7.24 (1H, *br d*, $J_{1,3}$ = 2.8 Hz, H-1), 7.45 (1H, *ddd*, $J_{10,9}$ = 9.0 Hz, $J_{10,4}$ = 0.6 Hz, $J_{10,1}$ = 0.3 Hz, H-10), 7.59 (1H, *d*, $J_{9,8}$ = 9.0 Hz, H-9), 9.34 (1H, *dt*, $J_{4,3}$ = 9.3 Hz, $J_{4,10}$ = 0.6 Hz, $J_{4,1}$ = 0.4 Hz, H-4). MS *m/z* (rel. int.): 270 $[M]^+$ (100), 255 (54), 241 (12), 233 (15), 184 (17).

The diacetate **13** crystallized as colourless needles from *n*-hexane–$CHCl_3$, mp 144–145°. (Found: C, 67.5; H, 5.2. $C_{20}H_{18}O_6$ requires: C, 67.8; H, 5.1%). IR ν_{max} cm^{-1}: 1760 (OCOMe), 1612, 1470, 1440, 1370, 1350, 1300, 1275. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 300 (3.70), 288 (3.89), 279 (4.00), 257 (4.64), 215 (4.11). ^1H NMR: δ2.38 (3H, *s*, OCOMe), 3.92 (3H, *s*, C-5-OMe), 3.99 (3H, *s*, C-7-OMe), 7.07 (1H, *s*, H-8), 7.36 (1H, *dd*, $J_{3,4}$ = 9.4 Hz, $J_{3,1}$ = 2.7 Hz, H-3), 7.58 (1H, *dd*, $J_{1,3}$ = 2.7 Hz, $J_{1,4}$ = 0.5 Hz, H-1), 7.65 (2H, *s*, H-9, H-10) 9.42 (1H, *br d*, $J_{4,3}$ = 9.4 Hz, H-4). ^1H NMR (C_6D_6): δ1.88 (3H, *s*, OCOMe), 2.05 (3H, *s*, OCOMe), 3.38 (3H, *s*, C-7-OMe), 3.61 (3H, *s*, C-5-OMe), 6.79 (1H, *s*, H-8), 7.38 (1H, *d*, $J_{9,10}$ = 9.0 Hz, H-9), 7.39 (1H, *dd*, $J_{3,4}$ = 9.4 Hz, $J_{1,3}$ = 2.6 Hz, H-3), 7.43 (1H, *dt*, $J_{10,9}$ = 9.0 Hz, $J_{10,1}$ = 0.5 Hz, $J_{10,4}$ = 0.5 Hz, H-10), 7.60 (1H, *dt*, $J_{1,3}$ = 2.6 Hz, $J_{1,4}$ = 0.5 Hz, $J_{1,10}$ = 0.5 Hz, H-1), 9.57 (1H, *dt*, $J_{4,3}$ = 9.4 Hz, $J_{4,1}$ = 0.5 Hz, $J_{4,10}$ = 0.5 Hz, H-4). MS *m/z* (rel. int.): 354.1113 $[M]^+$ (20), ($C_{20}H_{18}O_6$ requires 354.1103) 312 (55), 270 (100), 255 (30), 241 (8).

4,4′,8,8′-*Tetramethoxy*[1,1′-*biphenanthrene*]-2,2′,7,7′-*tetrol* (**14**). Pink needles from Et_2O–$CHCl_3$–Me_2CO, mp 310° (dec.). IR ν_{max} cm^{-1}: 3430 (Ar-OH), 3300 (Ar-OH), 1610, 1595, 1460, 1375. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 214 (4.44), 264 (4.72), 302 (4.15), 318 (4.15). ^1H NMR: δ3.89 (6H, *s*, C-8,8′-OMe), 4.26 (6H, *s*, C-4,4′-OMe), 7.09 (2H, *s*, H-3,3′), 7.16 (2H, *d*, $J_{10,9}$ and $J_{10',9'}$ = 9.6 Hz, H-10, 10′), 7.31 (2H, *d*, $J_{6,5}$ and $J_{6',5'}$ = 9.6 Hz, H-6, 6′), 7.84 (2H, *dd*, $J_{9,10}$ and $J_{9',10'}$ = 9.6 Hz, $J_{9,5}$ and $J_{9',5'}$ = 0.7 Hz, H-9,9′), 9.39 (2H, *dd*, $J_{5,6}$ and $J_{5',6'}$ = 9.6 Hz, $J_{5,9}$ and $J_{5',9'}$ = 0.7 Hz, H-5,5′). MS *m/z* (rel. int.): 538 $[M]^+$ (1), 406 (23), 284 (100), 270 (45), 255 (28), 242 (23), 167 (72), 137 (23).

The tetraacetate **15** crystallized as colourless needles from EtOH, mp 172–173°. (Found: C, 68.0; H, 5.1. $C_{40}H_{34}O_{12}$ requires: C, 68.0; H, 4.9%). IR ν_{max} cm^{-1}: 1760 (OCOMe), 1600, 1580, 1460, 1370, 1340, 1250. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 216 (4.60), 254 (4.74), 279 (4.55), 300 (4.20), 312 (4.16). ^1H NMR ($CDCl_3$): δ1.90 (6H, *s*, OCOMe), 2.42 (6H, *s*, OCOMe), 3.90 (6H, *s*, C-8,8′-OMe), 4.20 (6H, *s*, C-4,4′-OMe), 7.12 (2H, *s*, H-3,3′), 7.18 (2H, *d*, $J_{10,9}$ and $J_{10',9'}$ = 9.6 Hz, H-10, 10′), 7.38 (2H, *d*, $J_{6,5}$ and $J_{6',5'}$ = 9.6 Hz, H-6,6′), 7.91 (2H, *dd*, $J_{9,10}$ and $J_{9',10'}$ = 9.6 Hz, $J_{9,5}$ and $J_{9',5'}$ = 0.7 Hz, H-9,9′), 9.52 (2H, *dd*, $J_{5,6}$ and $J_{5',6'}$ = 9.6 Hz, $J_{5,9}$ and $J_{5',9'}$ = 0.7 Hz, H-5, 5′). MS *m/z* (rel. int.): 706 $[M]^+$ (50), 664 (100), 662 (80), 580 (60), 538 (93), 500 (25), 311 (20), 269 (55), 43 (75).

The tetramethyl ether derivative **16** crystallized as colourless needles, from *n*-hexane–CH_2Cl_2, mp 258–259°. IR ν_{max} cm^{-1}: 1603, 1456, 1335,1284, 1192, 1087. UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 320 (3.83), 306 (3.85), 293 (4.10), 280 (4.31), 266 (4.45), 261 (4.40), 245 (4.21), 213 (4.15). ^1H NMR: δ3.79 (6H, *s*, C-2,2′-OMe), 3.90 (6H, *s*, C-8,8′-OMe), 4.02 (6H, *s*, C-7, 7′*p*-OMe), 4.23 (6H, *s*, C-4,4′-OMe), 7.04 (2H, *s*, H-3,3′), 7.10 (2H, *d*, $J_{10,9}$ and $J_{10',9'}$ = 9.6 Hz, H-10,10′), 7.33 (2H, *d*, $J_{6,5}$ and $J_{6',5'}$ = 9.6 Hz, H-6,6′), 7.83 (2H, *dd*, $J_{9,10}$ and $J_{9',10'}$ = 9.6 Hz, $J_{9,5}$ and $J_{9',5'}$ = 0.8 Hz, H-9,9′), 9.40 (2H, *dd*, $J_{5,6}$ and $J_{5',6'}$ = 9.6 Hz, $J_{5,9}$ and $J_{5',9'}$ = 0.8 Hz, H-5,5′). MS *m/z* (rel. int.): 594.2249 $[M]^+$ (100) ($C_{36}H_{34}O_8$ requires 594.2253), 297 $[M/2]^+$ (13), 43 (32).

Structure determination of the acetate derivative of **3**. [The only material at all appropriate for crystallographic work was a couple of plate-like specimens, micaceously twinned; these were broken down to a useful size and the most congenially diffracting specimen, still somewhat oversize, used for the structure determination. Although the results give a useful degree of precision, this may be illusory and subject to systematic error in view of the above difficulty; a useful guide as to the degree of its trustworthiness may be the extent of the agreement between similar bonding parameters in the two independent molecules of the asymmetric unit].

A unique data set was measured within the limited $2\theta_{max} = 50°$ using a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode. 6235 independent reflections were measured, 3941 with $I > 3\sigma(I)$ being considered 'observed' and used in the 9 × 9 block diagonal least squares refinement without absorption correction after solution of the structure by direct methods. Anisotropic thermal parameters were refined for C, O; (*x*, *y*, *z*, U_{iso})$_H$ were constrained at estimated values. Residuals *R*, *R* on |*F*| at convergence were 0.072, 0.089, statistical reflection weights derived from $\sigma^2(I) = \sigma^2(I)_{diff} + 0.0005\,\sigma^4(I)_{diff}$ being used. Neutral complex scattering factors were used [7]; computation used the XTAL program system [8] implemented on a Perkin–Elmer 3240 computer. The data are deposited at the Cambridge Crystallographic Data Centre. Atom numbering is shown in the figure.

Crystal data. $C_{20}H_{20}O_6$, *M* 356.4, Triclinic, space group *P*1 (C_i^1, No. 2), *a* 27.019 (7), *b* 8.490 (3), *c* 7.941 (3) Å, α 94.96 (3), β 97.33 (3), γ 98.79(2)°, *U* 1775(1)Å^3. D_c (*z* = 4) 1.33 g·cm^{-3}. *F* (000) 752. Monochromatic MoKα radiation, λ 0.71069 Å, μ 1.1 cm^{-1}. *T* ~ 295 K.

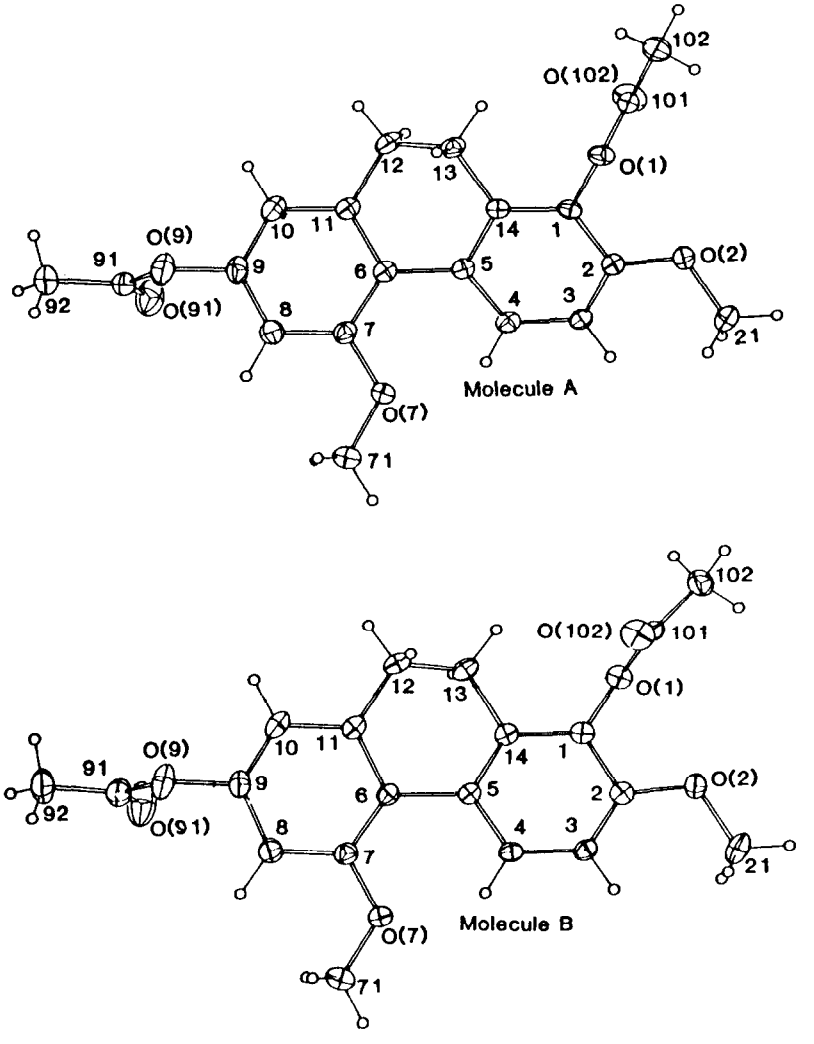

Fig 1. Projections of molecules A and B showing atom labelling, 20% thermal ellipsoids for the non-hydrogen atoms, and hydrogen atoms with arbitrary radius 0.1 Å. Note the differences in conformation of the two molecules.

Structural commentary. The results of the structure determination are consistent with the above stoichiometry and connectivity; the asymmetric unit of the structure comprises two independent molecules with different conformations (Fig. 1). Dihedral angles between the two phenyl rings are 28.1 and 20.8°; dihedral angles between C.CO.O planes to the associated phenyl ring at C (1,9) are 85.5, 76.7° (molecule A), 84.9, 78.4° (molecule B). Torsions angles in the C (11, 12, 13, 14) strings are 55.5 and −52.3°. The unit cell is controsymmetric and the compound a racemate in the crystal.

Bond lengths and angles are substantially as expected. Methoxyl groups at C (2, 7) are substantially coplanar with the rings with the usual angular asymmetry at the point of attachment.

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