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PHENANTHRENES, DIHYDROPHENANTHRENES AND BIBENZYLS FROM THE ORCHID *BULBOPHYLLUM VAGINATUM*

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Key Word Index—*Bulbophyllum vaginatum*; Orchidaceae; phenanthrenes; 9,10-dihydrophenanthrenes; bibenzyls.

Abstract—Two new phenanthrenes (4,9-dimethoxyphenanthrene-2,5-diol and 4,6-dimethoxyphenanthrene-2,3,7-triol) and two new 9,10-dihydrophenanthrenes (4-methoxy-9,10-dihydrophenanthrene-2,3,7-triol and 4,6-dimethoxy-9,10-dihydrophenanthrene-2,3,7-triol), along with six known phenanthrenes, four known 9,10-dihydrophenanthrenes no known bibenzyls and the triterpenoid friedelin were isolated and characterized from the hexane extract of the orchid *Bulbophyllum vaginatum*. The structures of these compounds were determined by spectroscopic analyses. Copyright ©1996 Elsevier Science Ltd

INTRODUCTION

The genus *Bulbophyllum*, belonging to the subtribe Bulbophyllinae of the Orchidaceae consists of over 1000 species found in Africa and Asia [1]. Apart from screening studies which have indicated the presence of alkaloids [2, 3] in a few species, only six species, *B. leopardium* [4], *B. gymnopus* [5–7], *B. fuscopurpureum* [8], *B. guttulatum* [8], *B. odoratissimum* [9] and *B. triste* [10], have been investigated chemically. In most cases, phenanthrene derivatives were isolated, although *B. triste* contained bibenzyls.

RESULTS AND DISCUSSION

Bulbophyllum vaginatum (Lindl.) Reichb. f. is distributed in Peninsular Thailand and Malaysia, Sumatra, Bangka, Java, Borneo and Maluku [1]. The present study of the hexane extract of this plant, which was collected in Singapore, afforded bibenzyls as well as phenanthrene and 9,10-dihydrophenanthrene derivatives. The hexane extract of *B. vaginatum* was subjected to flash chromatography on silica gel. Further purification using gel permeation chromatography and HPLC afforded, in addition to four new compounds, 13 known compounds: the triterpenoid friedelin (**1**); the bibenzyls 3,4′-dihydroxy-5,5′-dimethoxybibenzyl (**2**) and 3,3′-dihydroxy-5-methoxybibenzyl (batatasin III) (**3**); the phenanthrenes 3,4,6-trimethenanthrene-2,7-diol (**4**), 3,4-dimethoxyphenanthrene-2,7-diol (nudol) (**5**), 2,4-dimethoxyphenanthrene-3,7-diol (**6**) 3,5-dimethoxyphenanthrene-2,7-diol (**7**), 4-methoxyphenanthrene-2,3,5-triol (fimbriol B) (**8**) and 4-methoxyphenanthrene-2,7-diol (flavanthrinin) (**9**); and the 9,10-dihydrophenanthrenes 3,4,6-trimethoxy-9,10-dihydrophenanthrene-2,7-diol (**10**), 4-methoxy-9,10-dihydrophenanthrene-2,7-diol (coelonin) (**11**), 3,5-dimethoxy-9,10-dihydrophenanthrene-2,7-diol (6-methoxycoelonin) (**12**) and 3,4-dimethoxy-9,10-dihydrophenanthrene-2,7-diol (erianthridin) (**13**). Wherever possible, structures were confirmed using difference NOE spectroscopy. The ^{13}C NMR assignments of **11** were determined by HMBC spectroscopy (see Experimental)

The first novel compound, 4,9-dimethoxyphenanthrene-2,5-diol (**14**), was obtained as a gum, $C_{16}H_{14}O_4$ (*m*/*z* 270.0892), which had UV absorptions at 260, 282, 306, 314, 344 and 362 nm indicative of an aromatic system. The IR spectrum showed hydroxyl absorption at 3271 cm^{-1} which, in addition to a positive reaction with ferric chloride, indicated the compound's phenolic nature. Its ^{1}H and ^{13}C NMR spectra (Table 1) showed resonances for a 1,2,3-trisubstituted benzene ring [δ_H 7.94 (1H, *dd*, $J = 1.5$ and 7.9 Hz, H-8), δ_C 114.1 (*d*, C-8); δ_H 7.50 (1H, *t*, $J = 7.9$ Hz, H-7), δ_C 126.9 (*d*, C-7); δ_H 7.25 (1H, *dd*, $J = 1.5$ and 7.9 Hz, H-6), δ_C 117.3 (*d*, C-6], a pair of *meta*-coupled aromatic protons [δ_H 6.88 (1H, *d*, $J = 2.6$ Hz, H-1), δ_C 106.3 (*d*, C-1); δ_H 6.69 (1H, *d*, $J = 2.6$ Hz, H-3), δ_C 99.4 (*d*, C-3)], an isolated aromatic proton [δ_H 6.73 (1H, *s*, H-10), δ_C 101.5 (*d*, C-10)], two hydroxyl protons [δ_H 9.50 (1H, *s*, 5-OH) and 5.29 (1H, *s*, 2-OH), both exchangeable with D_2O], two methoxyl groups [δ_H 4.06 (3H, *s*, 4-OMe),

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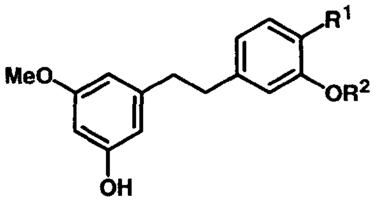

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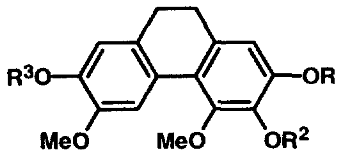

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(17) R^1 = R^2 = R^3 = H
(18) R^1 = R^2 = R^3 = Me
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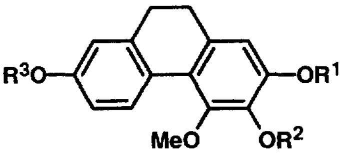

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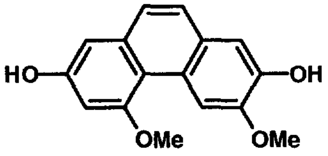

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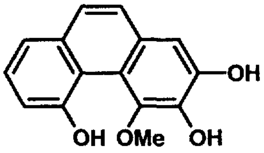

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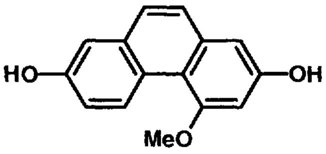

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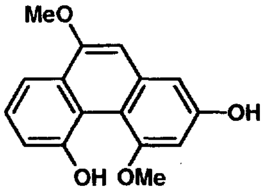

(14)

δ_C 58.3 (*q*, 4-OMe); 4.04 (3H, *s*, 9-OMe), δ_C 55.5 (*q*, 9-OMe)], and eight fully substituted aromatic carbons which constitute a tricyclic aromatic system. HMQC and HMBC spectroscopies (Table 1) were used to elucidate the structure and establish the ^{1}H and ^{13}C NMR assignments of **14**.

Starting from H-7, the central of the three neighbouring aromatic protons, ^3J correlations were observed to two substituted aromatic carbons (C-5 and C-8a), one of which (C-5) bears a hydroxyl group. The hydroxyl proton showed correlations to both C-5 and C-6. H-6 and H-8 both showed ^3J correlations to C-4b, establishing the substitution pattern and NMR assignments for one aromatic ring. H-8 and the more shielded methoxyl protons correlated with C-9, an oxygenated sp^2 carbon, by ^3J pathways; C-9 must therefore be attached to C-8a and must bear the methoxyl group. Correlations from H-10 to C-8a and C-9 allowed us to connect C-9 and C-10, also an *sp*^{2} carbon. H-10 showed further correlations to two aromatic carbons,

Table 1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data and HMBC correlations for 4,9-dimethoxyphenanthrene-2,5-diol (**14**) in CDCl$_3$ (J in Hz in parentheses)

		Correlations		
Position	δ_H	^2J	^3J	δ_C
1	6.88 *d* (2.6)		C-3, C-4a	106.3
2				154.3
3	6.69 *d* (2.6)	C-2, C-4	C-1, C-4a	99.4
4				155.4
4a				110.5
4b				119.9
5				153.8
6	7.25 *dd* (1.5, 7.9)		C-4b, C-8	117.3
7	7.50 *t* (7.9)		C-5, C-8a	126.9
8	7.94 *dd* (1.5, 7.9)		C-4b, C-9	114.1
8a				128.5
9				154.6
10	6.73 *s*	C-9	C-1, C-4a, C-8a	101.5
10a				136.8
2-OH	5.29 *s*			
5-OH	9.50 *s*		C-5, C-6	
4-OMe	4.06 *s*		C-4	58.3
9-OMe	4.04 *s*		C-9	55.5

one unsubstituted (C-1) and one substituted (C-4a). The lack of coupling between H-1 and H-10 indicated that the correlation between H-10 and C-1 occurred by a ^3J pathway and that C-1 and C-10 were not in the same ring. C-4a must be in the same ring as C-1 since both H-1 and its *meta*-coupled partner H-3 showed ^3J correlations to C-4a. H-3 showed ^2J correlations to two oxygenated aromatic carbons which must be C-2 and C-4. At this point, C-1, C-2, C-3, C-4 and C-4a had been identified as members of one aromatic ring. The one as yet unassigned aromatic ^{13}C resonance (136.8) showed no correlations in the HMBC spectrum but, by default, must be C-10a, the final member of this ring. Since all of the atoms were now accounted for, C-4a and C-4b could be joined, giving a 2,4,5,9-tetraoxygenated phenanthrene system. The final problem of whether C-2 or C-4 bears the second methoxyl group could not be resolved using the available HMBC data. Presaturation of the less shielded methoxyl protons enhanced both H-3 (10.5%) and the most deshielded hydroxyl proton (5-OH, 4.2%) in the difference NOE spectrum, clearly establishing that the methoxyl group is attached to C-4. The compound is therefore 4,9-dimethoxyphenanthrene-2,5-diol (**14**). This is the third example of a ring-B oxygenated phenanthrene derivative, the others being gymnopusin (3,4,9-trimethoxyphenanthrene-2,7-diol) from *B. gymnopus* [5–7] and fimbriol-A (3,4,9-trimethoxyphenanthrene-2,5-diol) from *Ephemerantha fimbriata* [11].

The second compound, 4-methoxy-9,10-dihydrophenanthrene-2,3,7-triol (**15**), $C_{15}H_{16}O_4$ (*m/z* 258.0892), had UV absorptions at 234, 282, 296 and 310 nm characteristic of a 9,10-dihydrophenanthrene [12]. A positive reaction with $FeCl_3$ along with hydroxyl absorption at 3515 and 3390 cm^{-1} in the IR spectrum indicated the compound's phenolic nature. Its ^{1}H and ^{13}C NMR spectra (Table 2) showed resonances for a 1,2,4-trisubstituted benzene ring [δ_H 8.08 (1H, *d*, $J = 8.8$ Hz, H-5), δ_C 128.6 (*d*, C-5); δ_H 6.73 (1H, *d*, $J = 2.7$ Hz, H-8), δ_C 115.4 (*d*, C-8); δ_H 6.72 (1H, *dd*, $J = 2.7$ and 8.8 Hz, H-6), δ_C 114.2 (*d*, C-6)], an isolated aromatic proton [δ_H 6.53 (1H, *s*, H-1), δ_C 111.6 (*d*, C-1)], three hydroxyl protons [δ_H 8.26 (1H, *s*, 7-OH), 7.68 (1H, *br s*, 2-OH) and 7.49 (1H, *br s*, 3-OH), all exchangeable with D_2O], one *ortho*-disubstituted methoxyl group [δ_H 3.61 (3H, *s*, 4-OMe); δ_C 60.0 (*q*, 4-OMe)] and eight fully substituted aromatic carbons. HMQC and HMBC spectroscopy (Table 2) were again used to determine the structure and ^{1}H and ^{13}C NMR assignments.

Beginning from the trisubstituted aromatic ring, the group between the two *meta*-coupled protons (H-6 and H-8) was seen to be a hydroxyl since the OH proton showed ^3J correlations to both C-6 and C-8. A ^2J correlation established the assignment of C-7. The correlations of H-5, H-6 and H-8 identified the other two carbons of this aromatic ring (C-4b and C-8a). A ^3J correlation from H-8 to the C-9 methylene carbon established a connection between C-8a and C-9 and correlations from the C-10 methylene protons to C-8a and C-9 showed that the two methylene carbons are connected. The remainder of the molecule consists of a pentasubstituted aromatic ring which carries one methoxyl and two hydroxyl groups. C-4b and C-10 must therefore be directly attached to this second aromatic ring and **15** is therefore a 9,10-dihydrophenanthrene. A correlation between the singlet aromatic proton and C-10 identified the proton as H-1. H-1 also showed correlations to two oxygenated aromatic carbons; these must be C-2 and C-3 and must bear the two remaining hydroxyl groups since the methoxyl protons did not show a correlation to either of these carbons. By default, the methoxyl group must be attached to C-4. C-4a and C-10a can be differentiated

Table 2. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data and HMBC correlations for 4-methoxy-9,10-dihydrophenanthrene-2,3,7-triol (**15**) in Me_2CO-d_6 (J in Hz in parentheses)

		Correlations		
Position	δ_H	^2J	^3J	δ_C
1	6.53 *s*	C-2	C-3, C-4a, C-10	111.6
2				137.8^a
3				145.0^a
4				146.6
4a				119.9
4b				125.5
5	8.08 *d* (8.8)		C-4a, C-7, C-8a	128.6
6	6.72 *dd* (2.7, 8.8)	C-7	C-4b, C-8	114.2
7				156.6
8	6.73 *d* (2.7)	C-7	C-4b, C-6, C-9	115.4
8a				140.2
9	2.65 *m*	C-10	C-4b, C-8, C-10a	31.0
10	2.59 *m*	C-9	C-1, C-4a, C-8a	30.3
10a				130.2
2-OH	7.68 *br s*	C-2	C-1, C-3	
3-OH	7.49 *br s*	C-3	C-2, C-4	
7-OH	8.26 *s*	C-7	C-6, C-8	
4-OMe	3.61 *s*	—	C-4	60.0

^{a}Interchangeable signals.

since the latter showed a correlation with the C-9 methylene protons. However, although the 2-OH and 3-OH protons could be distinguished, C-2 and C-3 could not be assigned on the basis of the observed correlations. C-3 was assigned the more shielded resonance since it is *ortho* to two oxygen substituents. The compound is thus 4-methoxy-9,10-dihydrophenanthrene-2,3,7-triol. Methylation of the triol afforded the tetramethyl ether **16**. The spectroscopic properties of **16** in particular the difference NOE results, were in agreement with the proposed structure.

The third compound, 4,6-dimethoxy-9,10-dihydrophenanthrene-2,3,7-triol (**17**), $C_{16}H_{16}O_5$ (*m/z* 288.0998), had UV absorptions at 214, 234, 282, 310 and 318 nm characteristic of a 9,10-dihydrophenanthrene derivative [12]. This compound was also shown to be phenolic from its IR spectrum (3525 and 3280 cm^{-1}) and its reaction with ferric chloride. The ^1H NMR and ^{13}C NMR spectra (Table 3) had resonances for three isolated aromatic protons [δ_H 7.83 (1H, *s*, H-5), δ_C 109.6 (*d*, C-5); δ_H 6.79 (1H, *s*, H-8), δ_C 114.0 (*d*, C-8); δ_H 6.62 (1H, *s*, H-1), δ_C 111.2 (*d*, C-1)], three hydroxyl protons [δ_H 6.12 (1H, *br s*), and 5.91 (2H, *br s*), all exchangeable with D_2O], two methoxyl groups, one of which is *ortho*-disubstituted [δ_H 3.91 (3H, *s*, 6-OMe), δ_C 56.2 (*q*, 6-OMe); δ_H 3.66 (3H, *s*, 4-OMe) δ_C 60.4 (*q*, 4-OMe)], two benzylic methylene groups [δ_H 2.66 (4H, *m*, H_2-9 and H_2-10), δ_C 29.1 (*t*, C-9) and 29.7 (*t*, C-10)], and nine substituted aromatic carbons. HMBC correlations were again useful in determining the structure.

H-5 and H-8 must be placed *para* to each other in the same ring since each proton showed correlations to the same two oxygenated aromatic carbons (C-6 and C-7). C-7 must bear a hydroxyl since an OH proton (δ 5.91, 7-OH) showed correlations to C-6, C-7 and C-8 whereas C-6 must bear a methoxyl group since correlations were seen between the aromatic carbon and the more deshielded methoxyl protons. Additional evidence for the position of this methoxy came from the difference NOE spectrum where an enhancement of H-5 (12.0%) was observed when the methoxyl protons were saturated. The second aromatic ring therefore carries the remaining aromatic proton as well as two hydroxyls and a methoxyl. The four benzylic methylene protons showed correlations to C-1 and C-8 suggesting that C-8a and C-10a are connected by a CH_2CH_2 bridge. H-1 showed correlations to both C-2 and C-3, both of which are oxygenated but neither of which carries the second methoxyl group. The most deshielded hydroxyl proton also showed correlations to C-2 and C-3 indicating that the carbon atoms are indeed bonded and that one is bonded to C-1. The ^3J correlations to C-4a from both H-1 and H-5 established that a bond exists between C-4a and C-4b and that the second methoxyl group is *para* to H-1. Compound **17** is therefore 4,6-dimethoxy-9,10-dihydrophenanthrene-2,3,7-triol. Methylation of **17** gave the expected pentamethyl ether (**18**), the physical properties of which are identical with those of the same compound made by methylation of 2,3,6-trimethoxy-9,10-dihydrophenanthrene-4,7-diol from *Combretum apiculatum* [12].

The final compound 4,6-dimethoxyphenanthrene-2,3,7-triol (**19**), $C_{16}H_{14}O_5$ (*m/z* 386.0841), showed UV absorptions at 238, 258, 282 and 310 nm characteristic of a phenanthrene derivative [12]. The phenolic nature of the compound was indicated by its reaction with ferric chloride and its IR spectrum which showed hydroxyl absorptions at 3520 and 3315 cm^{-1}. The ^1H NMR and ^{13}C NMR spectra had resonances for five aromatic CH groups [δ_H 8.99 (1H, *s*, H-5), δ_C 107.9 (*d*, C-5); δ_H 7.42 (2H, *s*, H-9 and H-10), δ_C 124.9 (*d*, C-9)

Table 3. ^1H (500 MHz) and ^{13}C (125 MHz) NMR data and HMBC correlations for 4,6-dimethoxy-9,10-dihydrophenanthrene-2,3,7-triol (**17**) in $CDCl_3$

		Correlations		
Position	δ_H	^2J	^3J	δ_C
1	6.62 *s*	C-2	C-3, C-4a, C-10	111.2
2				135.3^a
3				142.6^a
4				144.4
4a				119.3
4b				124.3^b
5	7.83 *s*	C-6	C-4a, C-7	109.6
6				145.2
7				144.1
8	6.79 *s*	C-7	C-6	114.0
8a				131.5^b
9	2.66 *m*		C-8	29.1
10	2.66 *m*		C-1, C-4a	29.7
10a				130.9
2-OH	6.12 *br s*	C-2	C-3	
5-OH	5.91 *br s*			
7-OH	5.91 *br s*	C-7	C-6, C-8	
4-OMe	3.66 *s*		C-4	60.4
6-OMe	3.91 *s*		C-6	56.2

^{a,b} Interchangeable signals.

and 125.5 (*d*, C-10); δ_H 7.27 (1H, *s*, H-8), δ_C 112.4 (*d*, C-8); and δ_H 7.16 (1H, *s*, H-1), δ_C 109.3 (*d*, C-1)], three hydroxyl protons [δ_H 8.36 (2H, *br s*, 2-OH and 7-OH) and 8.06 (1H, *br s*, 3-OH), all exchangeable with D_2O], two methoxyl groups, one being *ortho*-substituted [δ_H 4.02 (3H, *s*, 6-OMe), δ_C 56.0 (*q*, 6-OMe); 3.95 (3H, *s*, 4-OMe), 60.1 (*q*, 4-OMe)], and nine tetrasubstituted aromatic carbons which constitute a tricyclic system. In this case, the observed HMBC correlations were again very valuable in the structure elucidation.

As in the case of compound **17**, H-5 and H-8 could be placed *para* to each other in one aromatic ring since they both correlated to the same two oxygenated aromatic carbons (C-6 and C-7). C-6 is methoxylated since the more deshielded methoxyl protons correlated to C-6 and a NOE (16.5%) was observed at H-5 when the methoxyl protons were saturated. ^3J correlations from H-5 and H-8 identified but did not distinguish the two remaining carbons of this aromatic ring (C-4b and C-8a). A ^3J correlation from H-8 to C-9 allowed us to position C-9 *ortho* to H-8, confirmation coming from NOE at H-9 (11.2%) when H-8 was irradiated. The lack of a correlation from H-9 to C-6 suggested that the 6-methoxyl group and C-9 are *para* to each other. The lack of coupling between H-1 and H-10 and the presence of a ^3J correlation between H-1 and C-10 indicated that these two CH groups are not in the same ring and that C-10 is *ortho* to H-1. This agrees with the 12.2% NOE at H-10 which was observed when H-1 was saturated. Correlations to C-4a from both H-1 and H-5 suggested the presence of a bond betwen C-4a and C-4b and therefore that the compound is a phenanthrene. C-2 and C-3 must be hydroxylated to account for the correlations observed from H-1 to two oxygenated aromatic carbons. The more shielded methoxyl protons did not correlate to either C-2 or C-3 and so this group must be placed at C-4, H-5 showed the expected enhancement (6.4%) in the difference NOE spectrum when the C-4 methoxyl was irradiated. These results are consistent with structure **19**, 4,6-dimethoxyphenanthrene-2,3,7-triol. Methylation of **19** gave the known pentamethyl ether **20** [12]. In addition, hydrogenation of **19** afforded its 9,10-dihydro derivative (**17**).

EXPERIMENTAL

General. Mps uncorr. Unless stated otherwise, the following conditions were used for spectroscopic and chromatographic analyses. CC: silica gel (40 μm particle size); Isocratic HPLC: RI detection; UV: EtOH; IR: CCl_4; EI-MS: 70 eV; NMR: $CDCl_3$ at 500 MHz (^1H) or 125 MHz (^{13}C) relative to TMS at $\delta = 0.00$. ^{13}C multiplicities were determined using the DEPT pulse sequence and difference NOE experiments were carried out using the NOEMULT pulse program. Difference NOE results are reported in the following manner: H irradiated [H enhanced (% enhancement)]. Proton detected HMQC experiments were optimized for $^1J_{CH} = 140$ Hz. The relaxation delay was 2.5 s. In t_1, 512 increments were used with zero-filling to 1K before 2D Fourier transformation. In t_2, 2K points were used with no zero-filling. Gaussian multiplication was used in both dimensions to improve the signal to noise ratio and to suppress truncation errors. Proton detected HMBC experiments were performed under the same conditions with the addition of modulation tuning which was optimized for $^nJ_{CH} = 10$ Hz.

Extraction and isolation. Air dried whole plant of *B.*

vaginatum (2.3 kg) was subjected to exhaustive extraction using hot hexane. The hexane extract (20 g) was then chromatographed on silica gel eluting with an EtOAc–hexane gradient to give 26 frs. Fr. 2 was crystallized from hexane to give **1** which was identified by comparison with an authentic sample. Frs. 15–19 were subjected to gel permeation [Fractogel TSK gel HW-40 (F) (MeOH–$CHCl_3$ 1:1)] and flash chromatography (silica gel, 30% EtOAc–hexane) followed by HPLC (Lichrosorb Diol, 10 μm, 10 × 250 mm, 30% EtOAc–hexane) to afford, in order of elution, **10** (98 mg), **4** (57 mg), **2** (86 mg), a mixture of **5** and **12**, **3** (21 mg) and **11** (36 mg). Further HPLC (silica gel, 35% EtOAc–hexane) gave **5** (16 mg) and **12** (26 mg).

Fr. 20 was subjected to the same gel column as above followed by HPLC (Lichrosorb Diol, 10 μm, 10 × 250 mm, 40% EtOAc–hexane) to give seven frs, A–G. Fr. A afforded **13** (0.3 mg) and **4** (10 mg) after HPLC purification (silica gel, 30% EtOAc–hexane). Fr. B was identified as **2** (3 mg). Fr. C was fractionated by HPLC (silica gel, 30% EtOAc–hexane) to afford **14** (2 mg), **5** (5 mg), **3** (5 mg), **12** (18 mg) and **4** (6 mg). Fr. D upon repeated HPLC (silica gel, 22% EtOAc–hexane) afforded **11** (63 mg), **6** (3 mg), **7** (2 mg) and **8** (24 mg). Fr. E afforded **9** (7 mg) and **17** (154 mg) upon HPLC (silca gel, 30% EtOAc–hexane). The last two frs. were identified as **15** (58 mg) and **19** (5 mg), respectively.

3,4′-*Dihydroxy*-5,5′-*dimethoxybibenzyl* (**2**). Oil. IR, EI-MS identical to literature values [13]. HR-MS *m/z* 274.1205 ($C_{16}H_{18}O_4$ requires 274.1205). UV λ_{max}^{EtOH} nm: 208, 224 sh, 280. ^{1}H NMR: δ 6.82 (1H, *d*, J=8.0 Hz, H-3′), 6.66 (1H, *dd*, J=1.9 and 8.0 Hz, H-2′), 6.61 (1H, *d*, J=1.9 Hz, H-6′), 6.31 (1H, *t*, J=2.2, H-6), 6.25 (1H, *t*, J=2.2, H-4), 6.24 (1H, *t*, J=2.2, H-2), 5.62 (1H, *s*, 3-OH or 4′-OH), 5.56 (1H, *s*, 4′-OH or 3-OH), 3.82 (3H, *s*, 5′-OMe), 3.73 (3H, *s*, 5-OMe), 2.78 (4H, *m*, CH_2CH_2). Difference NOE: CH_2CH_2 [H-2′ (3.7), H-6′ (3.8), H-2 (4.3), H-6 (4.5)]; 5′-OMe [H-6′ (11.7)]; 5-OMe [H-6 (7.3), H-4 (7.4)].

3,3′-*Dihydroxy*-5-*methoxybibenzyl* (*batatasin III*) (**3**). Solid, mp 89.5–90.5° (lit. 93.5–94.5° [15]). UV, IR, EI-MS identical to literature values [15]. HR-MS *m/z* 244.1099 ($C_{15}H_{16}O_3$ requires 244.1099). ^{1}H NMR: δ 7.12 (1H, *t*, J=7.9 Hz, H-5′), 6.73 (1H, *br d*, J=7.9 Hz, H-6′), 6.65 (1H, *dd*, J=2.5 and 7.9 Hz, H-4′), 6.62 (1H, *t*, J=1.8 Hz, H-2′), 6.30 (1H, *t*, J=1.8 Hz, H-6), 6.25 (1H, *t*, J=2.0 Hz, H-2 or H-4), 6.24 (1H, *t*, J=2.0, H-4 or H-2), 5.60 (1H, *br s*, 3-OH or 3′-OH), 5.52 (1H, *br s*, 3′-OH or 3-OH), 3.72 (3H, *s*, 5-OMe), 2.79 (4H, *m*, CH_2CH_2). ^{13}C NMR: δ: 160.8 (*s*), 156.6 (*s*), 155.5 (*s*), 144.5 (*s*), 143.6 (*s*), 129.6 (*d*), 121.0 (*d*), 115.5 (*d*), 112.9 (*d*), 108.1 (*d*), 106.8 (*d*), 99.2 (*d*), 55.3 (*q*), 37.7 *t*, 37.3 (*t*). Difference NOE: CH_2CH_2 [H-2 (3.0), H-6 (3.2), H-2′ (2.8), H-6′ (2.4)]; 5-OMe [H-4 (4.9), H-6 (5.5)].

3,4,6-*Trimethoxyphenanthrene*-2,7-*diol* (**4**). Solid, mp, UV, IR identical to literature values [16]. EI-MS *m/z* (rel. int.): 300 $[M]^+$ (100), 285 (34), 240 (4), 185 (5), 126 (4), 121 (5), 115 (5). HR-MS *m/z* 300.0998 ($C_{17}H_{16}O_5$ requires 300.0998). ^{1}H NMR: δ 9.02 (1H, *s*, H-5), 7.51 and 7.45 (2H, ABq J_{AB}=8.8 Hz, H-9 and H-10), 7.30 (1H, *s*, H-1 or H-8), 7.17 (1H, *s*, H-8 or H-1), 5.95 (1H, *br s*, 2-OH or 7-OH), 5.87 (1H, *br s*, 7-OH or 2-OH), 4.12 (3H, *s*, 3-OMe), 4.10 (3H, *s*, 6-OMe), 3.99 (3H, *s*, 4-OMe).

3,4-*Dimethoxyphenanthrene*-2,7-*diol* (*nudol*) (**5**). Solid, mp 154–155° (lit. mp 138° [17]). UV, IR, EI-MS are identical to reported values [17]. HR-MS *m/z* 270.0892 ($C_{16}H_{14}O_4$ requires 270.0892). ^{1}H NMR: δ 9.27 (1H, *d*, J=9.1 Hz, H-5), 7.43 and 7.39 (2H, ABq, J_{AB}=8.8 Hz, H-9 and H.10), 7.10 (1H, *d*, J=2.9 Hz, H-8), 7.08 (1H, *dd*, J=2.9 and 9.1 Hz, H-6), 7.08 (1H, *s*, H-1), 5.94 (1H, *br s*, 2-OH or 7-OH), 5.26 (1H, *br s*, 7-OH or 2-OH), 4.01 (3H, *s*, 3-OMe), 3.88 (3H, *s*, 4-OMe). Difference NOE: 4-OMe [3-OMe (1.0), H-5 (4.6)], 3-OMe [4-OMe (1.0)]

2,4-*Dimethoxyphenanthrene*-3,7-*diol* (**6**). Solid, mp, UV, IR, EI-MS are identical to reported values [18]. HR-MS *m/z* 270.0892 ($C_{16}H_{14}O_4$ requires 270.0892). ^{1}H NMR: δ 9.33 (1H, *d*, J=9.1 Hz, H-5′), 7.56 and 7.47 (2H, ABq, J_{AB}=8.8 Hz, H-9 and H.10), 7.21 (1H, *d*, J=2.8 Hz, H-8), 7.18 (1H, *dd*, J=2.8 and 9.1 Hz, H-6), 7.07 (1H, *s*, H-1), 5.98 (1H, *s*, 3-OH), 5.08 (1H, *s*, 7-OH), 4.04 (3H, *s*, 2-OMe), 3.95 (3H, *s*, 4-OMe). ^{13}C NMR: δ 153.2 (*s*), 146.7 (*s*), 143.9 (*s*), 139.2 (*s*), 133.8 (*s*), 128.5 (*d*), 127.4 (*d*), 126.0 (*s*), 124.9 (*d*), 123.7 (*s*), 119.0 (*s*), 116.3 (*d*), 111.6 (*d*), 104.9 (*d*), 59.8 (*q*, 4-OMe), 56.1 (*q*, 2-OMe). Difference NOE: 4-OMe [3-OH (2.2), H-5 (7.4)] 2-OMe [H-1 (14.4)].

3,5-*Dimethoxyphenanthrene*-2,7-*diol* (**7**). Solid, mp 173–174° (subl.) (lit. 193–194° [14]. UV, IR, EI-MS are identical to literature values [14]. HR-MS *m/z* 270.0892 ($C_{16}H_{14}O_4$ requires 270.0892). ^{1}H NMR: δ 9.07 (1H, *s*, H-4), 7.56 and 7.43 (2H, ABq, J_{AB}=8.7 Hz, H-9 and H-10), 7.30 (1H, *s*, H-1), 6.84 (1H, *d*, J=2.5 Hz, H-8), 6.71 (1H, *d*, J=2.5 Hz, H-6), 5.83 (1H, *s*, 2-OH or 7-OH), 5.03 (1H, *br s* 7-OH or 2-OH), 4.10 (3H, *s*, 5-OMe), 4.08 (3H, s, 3-OMe). ^{13}C NMR: δ 159.5 (*s*), 153.2 (*s*), 146.5 (*s*), 144.1 (*s*), 134.7 (*s*), 127.7 (*d*), 127.6 (*s*), 124.8 (*s*), 124.7 (*d*), 115.6 (*s*), 111.2 (*d*), 108.3 (*d*), 104.9 (*d*), 98.8 (*d*), 55.9 (*q*) 55.8 (*q*). Difference NOE: 3-OMe [H-4 (8.6), 5-OMe [H-6 (10.0), H-4 (1.9)].

4-*Methoxyphenanthrene*-2,3,5-*triol* (*fimbriol-B*) (**8**). Needles, mp 208–209°. UV, IR, EI-MS, ^{1}H and ^{13}C NMR ($CDCl_3$) are in agreement with reported values [11]. HR-MS *m/z* 256.0735 ($C_{15}H_{12}O_4$ requires 256.0736). ^{1}H NMR (Me_2CO-d_6): δ 10.30 (1H, *s*, 5-OH), 8.71 (2H, *br s*, 2-OH and 3-OH), 7.54 and 7.51 (2H, ABq, J_{AB}=8.8 Hz, H-9 and H-10), 7.44 (1H, *t*, J=7.6 Hz, H-7), 7.39 (1H, *dd*, J=1.6 and 7.7 Hz, H-6 or H-8), 7.28 (1H, *s*, H-1) 7.11 (1H, *dd*, J=1.6 and 7.7 Hz, H-8 or H-6), 3.77 (3H, *s*, 4-OMe). ^{13}C NMR (Me_2CO-d_6): δ 156.0 (*s*), 147.7 (*s*), 143.3 (*s*), 140.9 (*s*), 136.1 (*s*), 128.9 (*s*), 128.4 (*d*), 127.7 (*d*), 127.6 (*d*), 121.5 (*d*), 119.4 (*s*), 117.4 (*s*), 116.7 (*d*), 111.7 (*d*), 63.2 (*q*). Difference NOE: 4-OMe [5-OH (3.6)].

4-*Methoxyphenanthrene*-2,7-*diol* (*flavanthrinin*) (**9**) Solid, mp 174–175.5°. UV values agree with published data [18]. EI-MS *m/z* (rel. int.): 240 $[M]^+$ (100), 225 (26), 197 (15). 149 (13), 57 (10). HR-MS *m/z* 240.0786 ($C_{15}H_{12}O_3$ requires 240.0786). ^{1}H NMR (Me_2CO-d_6): δ 9.37 (1H, *d*, *J*=9.3 Hz, H-5), 8.50 (2H, *br s*, 2-OH and 7-OH), 7.55 and 7.51 (2H, ABq, J_{AB}=8.8 Hz, H-9 and H-10), 7.23 (1H, *d*, *J*=2.7 Hz, H-8), 7.14 (1H, *dd*, *J*=2.7 and 9.3 Hz, H-6), 6.90 (1H, *d*, *J*=2.4 Hz, H-1), 6.82 (1H, *d*, *J*=2.4 Hz, H-3), 4.09 (3H, *s*, 4-OMe). ^{13}C NMR (Me_2CO-d_6): δ 160.2 (*s*), 156.1 (*s*), 155.2 (*s*), 135.4 (*s*), 134.3 (*s*), 130.0 (*d*), 128.3 (*d*), 127.8 (*d*), 125.1 (*s*), 117.3 (*d*), 115.6 (*s*), 112.2 (*d*), 105.6 (*d*), 100.3 (*d*), 55.9 (*q*). Difference NOE: 4-OMe [H-3 (18.0), H-5 (4.0)]

3,4,6-*Trimethoxy-9,10-dihydrophenanthrene-2,7-diol* (**10**). Crystals (EtOAc–hexane). Mp, UV, IR, ^{1}H and ^{13}C NMR are identical to lit. values [12, 19]. EI-MS *m/z* (rel. int.): 302 $[M]^+$ (100), 255 (17), 121 (13), 104 (15), 92 (18), 85 (17), 71 (25), 69 (16), 57 (50). HR-MS *m/z* 302.1154 ($C_{17}H_{18}O_5$ requires 302.1154). Difference NOE: H_2-9 and H_2-10 [H-1 and H-8 (7.7 and 7.2)], 4-OMe [3-OMe (1.1), (4.4)], 6-OMe [H-5 (13.5)], 3-OMe [4-OMe (1.2)].

4-*Methoxy-9,10-dihydrophenanthrene-2,7-diol* (*coelonin*) (**11**). Plates (EtOAc–hexane), mp 87–88° (lit. mp 84° [18]). UV, IR, EI-MS, NOE results are identical to reported data [20]. HR-MS *m/z* 242.0939 ($C_{15}H_{14}O_3$ requires 242.0943). ^{1}H NMR: δ 8.11 (1H, *d*, *J*=8.0 Hz, H-5), 6.72 (1H, *dd*, *J*=2.7 and 8.0 Hz, H-6), 6.70 (1H, *d*, *J*=2.7, H-8), 6.41 (1H, *d*, *J*=2.5 Hz, H-3), 6.34 (1H, *J*=2.5 Hz, H-1), 4.72 (1H, *s*, 2-OH or 7-OH), 4.64 (1H, *s*, 7-OH or 2-OH), 3.86 (3H, *s*, 4-OMe), 2.71 (4H, *s*, H_2-9 and H_2-10). ^{1}H NMR (Me_2CO-d_6): δ 8.30 (1H, *s*, 2-OH), 8.16 (1H, *s*, 7-OH), 8.05 (1H, *d*, *J*=8.0 Hz, H-5), 6.69 (1H, *br s*, H-8), 6.68 (1H, *J*=2.7 Hz, H-6), 6.46 (1H, *d*, *J*=2.5 Hz, H-3), 6.37 (1H, *d*, *J*=2.5 Hz, H-1), 3.82 (3H, *s*, 4-OMe), 2.63 (4H, *s*, H_2-9 and H_2-10). ^{13}C NMR (Me_2CO-d_6: δ 158.7 (*s*, C-4), 157.3 (*s*, C-2), 156.0 (*s*, C-7), 141.2 (*s*, C-10a), 140.0 (*s*, C-8a), 129.8 (*d*, C-5), 125.7 (*s*, C-4b), 116.3 (*s*, C-4a), 115.0 (*d*, C-8), 113.5 (*d*, C-6), 108.2 (*d*, C-1), 99.2 (*d*, C-3), 55.7 (*q*, 4-OMe), 31.3 (*t*, C-10), 30.7 (*t*, C-9). HMBC: H-1 (^2J, C-2; ^3J, C-3, C-4a, C-10); H-3 (^2J, C-2, C-4; ^3J, C-1, C-4a); H-5 (^3J, C-4a, C-7, C-8a); H-6 (^2J, C-7; ^3J, C-4b, C-8); H-8 (^2J, C-7; ^3J, C-4b, C-6, C-9); H_2-9 (^2J, C-8a; ^3J, C-4b, C-8, C-10a); H_2-10 (^2J, C-10a; ^3J, C-1, C-4a, C-8a); 2-OH (^2J, C-2; ^3J, C-1, C-3); 7-OH (^2J, C-7; ^3J, C-6, C-8); 4-OMe (^3J, C-4).

3,5-*Dimethoxy-9,10-dihydrophenanthrene-2,7-diol* (*6-methoxycoelonin*)(**12**). Gum (lit. mp 118–120° [21]). UV, IR, NOE results agree with lit. values [21]. EI-MS *m/z* (rel. int.): 272 $[M]^+$ (100), 271 (12), 270 (24), 225 (24), 149 (19), 136 (9). HR-MS *m/z* 272.1049 ($C_{16}H_{16}O_4$ requires 272.1049). ^{1}H NMR: δ 7.86 (1H, *s*, H-4), 6.78 (1H, *s*, H-1), 6.42 (1H, *d*, *J*=2.4 Hz, H-6), 6.35 (1H, *d*, *J*=2.4 Hz, H-8), 5.58 (1H, *s*, 2-OH or 7-OH), 5.60 (1H, *s*, 7-OH or 2-OH), 3.91 (3H, *s*, 3-OMe), 3.87 (3H, *s*, 5-OMe), 2.68 (4H, *m*, H_2-9 and H_2-10). ^{13}C NMR: δ 157.6 (*s*), 154.7 (*s*), 144.4 (*s*), 143.5 (*s*), 141.2 (*s*), 131.4 (*s*), 124.8 (*s*), 116.6 (*s*), 113.6 (*d*), 111.4 (*d*), 107.6 (*d*), 98.4 (*d*), 56.2 (*q*), 55.7 (*q*), 30.8 (*t*), 29.0 (*t*).

3,4-*Dimethoxy-9,10-dihydrophenanthrene-2,7-diol* (*erianthridin*) (**13**). Solid, mp 147–148°. UV, EI-MS, ^{1}H NMR values identical to lit. values [22]. HR-MS *m/z* 272.1049 ($C_{16}H_{16}O_4$ requires 272.1049). ^{13}C NMR: δ 153.9 (*s*), 150.5 (*s*), 147.5 (*s*), 139.8 (*s*), 139.1 (*s*), 134.9 (*s*), 128.6 (*d*), 125.5 (*s*), 120.3 (*s*), 114.5 (*d*), 113.3 (*d*), 110.0 (*d*), 61.2 (*q*), 60.1 (*q*), 30.0 (2×t). Difference NOE: H_2-9 and H_2-10 [H-8 (5.6), H-1 (6.7)], 4-OMe [3-OMe (1.0), H-5 (3.0)], 3-OMe [4-OMe (3.1), 2-OH (2.3)].

4,9-*Dimethoxyphenanthrene-2,5-diol* (**14**). Brownish gum. UV λ_{max}^{EtOH} nm: 260, 282, 306, 314, 344, 362. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3271 (OH), 1607, 1537, 1460 (benzene ring). EI-MS *m/z* (rel. int.): 270 $[M]^+$ (100), 227 (39), 212 (9), 149 (7), 139 (19). HR-MS *m/z* 270.0892 ($C_{16}H_{14}O_4$ requires 270.0892). ^{1}H and ^{13}C NMR: Table 1. Difference NOE: 9-OMe [H-10 (12.6)], 4-OMe [H-3 (10.5), 5-OH (4.2)], H-3 [4-OMe (6.5)], H-10 [9-OMe (6.5), H-1 (3.0)], H-1 [H-10 (6.5)].

4-*Methoxy-9,10-dihydrophenanthrene-2,3,7-triol* (**15**). Gum. UV EtOH λ_{max}^{EtOH} nm: 210, 234 sh, 282, 296, 310. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3515, 3390 (OH), 1599, 1491, 1447 (benzene ring). EI-MS *m/z* (rel. int.): 258 $[M]^+$ (100), 225 (13), 197 (16), 157 (12), 149 (37), 139 (11), 71 (15), 69 (13), 63 (10), 57 (19), 55 (14), 45 (30). HR-MS: *m/z* 258.0892 ($C_{15}H_{14}O_4$ requires 258.0892). ^{1}H and ^{13}C NMR: Table 2. Difference NOE (Me_2CO-d_6): H_2-9 and H_2-10 [H-1 (6.7), H-8 (6.6)], 4-OMe [H-5 (4.0)].

Methylation of **15**. Compound **15** (22 mg) was methylated with MeI–K_2CO_3 in Me_2CO. HPLC of the crude product (silica gel, 6% EtOAc–hexane) gave 2,3,4,7-tetramethoxy-9,10-dihydrophenanthrene (**16**) (10.3 mg) as a solid, mp 141–143°. UV $\lambda_{max}^{CHCl_3}$ nm: 286,296 sh. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3405 (OH), 1599, 1574, 1472, 1451 (benzene ring). EI-MS *m/z* (rel. int.): 300 $[M]^+$ (100), 285 (20), 226 (9), 150 (11), 121 (9). HR-MS *m/z* 300.1361 ($C_{18}H_{20}O_4$ requires 300.1362). ^{1}H NMR (300 MHz): δ 8.23 (1H, *d*, *J*=8.7 Hz, H-5), 6.82 (1H, *dd*, *J*=2.8 and 8.7 Hz, H-6), 6.77 (1H, *d*, *J*=2.8 Hz, H-8), 6.58 (1H, *s*, H-1), 3.92 (3H, *s*, 3-OMe), 3.88 (3H, *s*, 2-OMe), 3.84 (3H, *s*, 7-OMe), 3.78 (3H, *s*, 4-OMe), 2.75 (4H, *m*, H_2-9 and H_2-10). ^{13}C NMR (75 MHz): δ 158.06 (*s*), 151.70 (*s*), 151.63 (*s*), 141.59 (*s*), 139.37 (*s*), 134.11 (*s*), 128.57 (*d*), 125.51 (*s*), 120.95 (*s*), 113.25 (*d*), 111.67 (*d*), 107.51 (*d*), 61.10 (*q*), 60.45 (*q*), 56.03 (*q*), 55.21 (*q*), 30.4 (*t*), 30.3 (*t*). Difference NOE: H_2-9 and H_2-10 [H-1 (7.5), H-8 (7.9)], 4-OMe [3-OMe (1.0), H-5 (6.6)], 7-OMe [H-8 (8.5), H-6 (10.2)], 2-OMe [H-1 (16.4)], 3-OMe [4-OMe (1.3)].

4,6-*Dimethoxy-9,10-dihydrophenanthrene-2,3,7-triol* (**17**). Gum. UV λ_{max}^{EtOH} nm: 214, 234 sh, 282, 310, 318. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3525, 3280 (OH), 1598, 1482, 1456 (benzene ring). EI-MS *m/z* (rel. int.): 288 $[M]^-$ (100), 286 (39), 271 (12), 241 (17), 119 (14), 51 (12).

HR-MS *m/z* 288.0997 ($C_{16}H_{16}O_5$ requires 288.0998). ^{1}H and ^{13}C NMR ($CDCl_3$): Table 3. ^{1}H NMR (Me_2CO-d_6): δ 7.92 (1H, *s*, H-5), 7.70 (1H, *br s*, OH), 7.42 (2H, *br s*, 2×OH), 6.72 (1H, *s*, H-1 or H-8), 6.56 (1H, *s*, H-8 or H-1), 3.85 (3H, *s*, 6-OMe), 3.66 (3H, *s*, 4-OMe), 2.60 (4H, *m*, H_2-9 and H_2-10). ^{13}C NMR (Me_2CO-d_6: δ 146.7 (*s*), 146.3 (*s*), 145.7 (*s*), 145.0 (*s*), 137.7 (*s*), 131.8 (*s*), 130.2 (*s*), 125.2 (*s*), 119.9 (*s*), 115.3 (*d*), 111.7 (*d*), 111.4 (*d*), 60.1 (*q*, 4-OMe), 56.4 (*q*, 6-OMe), 30.5 (*t*), 29.9 (*t*). Difference NOE: H_2-9 and H_2-10 [H-1 (5.0), H-8 (6.2)], 4-OMe [H-5 (4.5)], 6-OMe [H-5 (12.0)].

Methylation of **17**. A soln of **17** (22 mg) was methylated with MeI–K_2CO_3 in Me_2CO. The crude product was subjected to HPLC (silica gel, 16% EtOAc–hexane) to give 2,3,4,6,7-pentamethoxy-9,10-dihydrophenanthrene (**18**) (5 mg, 20%) as a solid, mp 104–105° (lit. 100–103° [12]). UV, EI-MS are identical with lit. values [12]. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1588, 1502, 1449 (benzene ring). HR-MS *m/z* 330.1468 ($C_{19}H_{22}O_5$ requires 330.1467). ^{1}H NMR: δ 8.00 (1H, s, H-5), 6.74 and 6.59 (each 1H, *s*, H-1 and H-8), 3.93, 3.92, 3.91, 3.89, 3.78 (each 3H, s, OMe), 2.73 (4H, m, H_2-9 and $H_2$10). ^{13}C NMR: δ 151.7 (*s*), 151.5 (*s*), 147.4 (*s*), 147.3 (*s*), 141.6 (*s*), 134.2 (*s*), 130.4 (*s*), 125.2 (*s*), 120.9 (*s*), 111.2 (*d*), 110.9 (*d*), 107.7 (*d*), 61.2 (*q*), 60.6 (*q*), 56.1 (*q*), 56.0 (*q*), 55.9 (*q*), 30.6 (*t*), 29.4 (*t*).

4,6-*Dimethoxyphenanthrene*-2,3,7-*triol* (**19**). Solid, mp 201–202°. UV λ_{max}^{EtOH} nm: 238, 258, 282, 310. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 3315 (OH), 1578, 1505, 1468 (benzene ring). EI-MS *m/z* (rel. int.): 286 $[M]^+$ (100), 285 (6), 271 (55), 171 (6), 115 (7), 112 (5). HR-MS *m/z* 286.0841 ($C_{16}H_{14}O_5$ requires 286.0841). ^{1}H and ^{13}C NMR: Table 4. Difference NOE (Me_2CO-d_6): 4-OMe [H-5 (2.7)], 6-OMe [H-5 (16.5)], H-1 [H-10 (12.2), 2-OH (2.5)], H-8 [H-9 (11.2), 7-OH (1.9)].

Methylation of **19**. Phenol **19** (21 mg) was methylated with MeI–K_2CO_3 in Me_2CO. HPLC of the crude product (silica gel, 19% EtOAc–hexane) gave 2,3,4,6,7-pentamethoxyphenanthrene (**20**) (10 mg, 41%) as a solid, mp 131–132° (lit. 134–136° [12]). UV, IR, EI-MS are identical to lit. values [12]. HR-MS *m/z* 328.1310 ($C_{19}H_{20}O_5$ requires 328.1311). ^{1}H NMR; δ 9.08 (1H, s, H-5), 7.57 and 7.52 (2H, ABq, $J_{AB}=8.7$ Hz, H-9 and H-10), 7.21 (1H, *s*, H-1 or H-8), 7.08 (1H, *s*, H-8 or H-1), 4.10 (3H, *s*, 6-OMe), 4.04 (6H, *s*, 2-OMe), 4.03 (3H, *s*, OMe), 4.01 (3H, *s*, 2-OMe or 7-OMe). ^{13}C NMR: δ 151.8 (*s*), 151.6 (*s*), 148.8 (*s*), 148.1 (*s*), 142.6 (*s*), 129.5 (*s*), 127.1 (*s*), 126.1 (*d*), 124.8 (*d*), 124.4 (*s*), 118.6 (*s*), 108.1 (*d*), 107.7 (*d*), 105.2 (*d*), 61.4 (*q*), 60.5 (*q*), 55.9 (*q*), 55.8 (*q*), 55.7 (*q*). Difference NOE: 2-OMe or 7-OMe [H-1 or H-8 (16.7)], 6-OMe [H-5 (19.2)].

Hydrogenation of **19**. The phenanthrene **19** (10 mg) and 10% Pd-C catalyst in EtOAc were stirred under a H_2 atmosphere at atmospheric pressure and room temp. HPLC (silica gel, 30% EtOAc–hexane) of the crude product gave **17** (2 mg), identical with the natural product.

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Table 4. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data and HMBC correlations for 4,6-dimethoxyphenanthrene-2,3,7-triol (**19**) in Me_2CO-d_6

Position	δ_H	Correlations ^2J	Correlations ^3J	δ_C
1	7.16 *s*	C-2	C-3, C-4a, C-10	109.3
2				139.8[a]
3				146.1[a]
4				145.1
4a				118.6
4b				124.1[b]
5	8.99 *s*	C-6	C-4a, C-7	107.9
6				148.4
7				146.3
8	7.27 *s*	C-7	C-6, C-9	112.4
8a				128.5[b]
9	7.42 *s*	C-8a	C-4b, C-8, C-10a	124.9
10	7.42 *s*	C-10a	C-1	125.5
10a				127.2
2-OH	8.36 *br s*			
3-OH	8.06 *br s*			
7-OH	8.36 *br s*			
4-OMe	3.95 *s*		C-4	60.1
6-OMe	4.02 *s*		C-6	56.0

[a,b] Interchangeable signals.

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