

Chemical Constituents of the Combretaceae. Part III.¹ Substituted Phenanthrenes, 9,10-Dihydrophenanthrenes, and Bibenzyls from the Heartwood of *Combretum psidioides*

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Ten new compounds isolated from the heartwood of *Combretum psidioides* have been shown to be 7-hydroxy-2,4,6-trimethoxy-, 7-hydroxy-2,3,4,6-tetramethoxy-, 2,7-dihydroxy-3,4,6-trimethoxy-, and 2,6,7-trihydroxy-3,4-dimethoxy-phenanthrene, the 9,10-dihydro-derivatives of these four compounds, and 4'-hydroxy-3,4,5-trimethoxy- and 4,4'-dihydroxy-3,5-dimethoxybibenzyl.

WE have described the isolation and structure elucidation of eight new phenanthrenes or 9,10-dihydrophenanthrenes from the heartwood of *Combretum apiculatum*² and *Combretum molle*,¹ together with a bibenzyl from the latter. We now report on the heartwood extractives of *Combretum psidioides*,³ which contain fourteen phenanthrenes or 9,10-dihydrophenanthrenes, eight of which are new, and three phenolic bibenzyls, of which two are new.

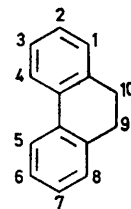
Light petroleum extraction removed an oily material from the heartwood. The subsequent ether extract, which consisted entirely of phenolic material, was chromatographed on t.l.c. plates yielding red gums from eight of the bands. These crude phenolic compounds exhibited no carbonyl absorption in the i.r. Acetylation followed by t.l.c. yielded crystalline acetates from bands B and E, amorphous acetates from bands C and G, and gums from bands A, D, F, and H. The designations (A—H) represent the order in which the phenols ran on the t.l.c. plates.

The acetate from band A separated into two bands on t.l.c. plates. The upper band gave an amorphous solid, which was shown by mass spectrometry and by n.m.r. to be a mixture of phenol (A₁) acetate (30%) and its dihydro-derivative, phenol (A₂) acetate (70%). Dehydrogenation of the amorphous acetate gave a single crystalline compound, phenol (A₁) acetate (C₁₉H₁₈O₅) which showed one acetoxy- and three methoxy-groups in the n.m.r. spectrum (Table 2) together with six aromatic protons, two of which appear as singlets, apparently *para* to one another, two as a two-proton singlet (H-9, H-10), with the remaining two as a pair of doublets (*J* 2 Hz) exhibiting *meta*-coupling. A comparison of the chemical shifts of the aromatic protons of phenol (A₁) acetate with those of 2,4,6,7-tetramethoxyphenanthrene² (Table 2) suggests phenol (A₁) to have the same substitution pattern as the latter and that the acetoxy-group is at C-7. Hydrolysis of phenol (A₁) acetate yielded the free phenol which on deuteration in deuterium oxide under basic conditions, followed by acetylation gave a monodeuteriated species (demonstrated by mass spectrometry) showing two *meta*-coupled protons (H-1, H-3), the two-proton singlet (H-9, H-10), and the low-field proton (H-5) in the n.m.r.

¹ Part II, R. M. Letcher, L. R. M. Nhamo, and I. T. Gumiro, *J.C.S. Perkin I*, 1972, 206.

² R. M. Letcher and L. R. M. Nhamo, *J. Chem. Soc. (C)*, 1971, 3070.

spectrum (Table 2). Consequently phenol (A₁) has structure (I). This structure was confirmed by a synthesis of the acetate of (I) which was identical with phenol (A₁) acetate, from 3'-acetoxy-3,4',5-trimethoxy-stilbene by an oxidative photochemical cyclisation¹ with iodine. Catalytic hydrogenation and hydrolysis of the amorphous acetate gave the crystalline phenol (A₂) with spectroscopic characteristics of a 9,10-dihydrophenanthrene (Tables 1 and 2) and which therefore has structure (II).



	Substituents				
	2-	3-	4-	6-	7-
9,10-Dihydrophenanthrenes:					
Phenol (A ₂) (II)	OMe	H	OMe	OMe	OH
Phenol (A ₄) (VI)	OMe	OMe	OMe	OMe	OH
(VII)	OMe	OMe	OH	OMe	OH
Phenol (C ₂) (VIII)	OH	OMe	OMe	OMe	OH
Phenol (H ₂) (XII)	OH	OMe	OMe	OH	OH
Phenanthrenes:					
Phenol (A ₁) (I)	OMe	H	OMe	OMe	OH
(III)	OMe	OMe	OH	OMe	OMe
(IV)	OH	OMe	OMe	OMe	OMe
Phenol (A ₃) (V)	OMe	OMe	OMe	OMe	OH
Phenol (C ₁) (IX)	OH	OMe	OMe	OMe	OH
(X)	OMe	OMe	OH	OH	OH
Phenol (H ₁) (XI)	OH	OMe	OMe	OH	OH

The lower band from the t.l.c. separation of the acetates of band A gave an amorphous solid which was shown by mass spectrometry and n.m.r. to be a mixture of phenol (A₃) acetate (20%) and its dihydro-derivative, phenol (A₄) acetate (80%). Dehydrogenation of the amorphous solid gave a crystalline product, phenol (A₃) acetate (C₂₀H₂₀O₆), showing spectral characteristics of a substituted phenanthrene (Tables 1 and 3). The n.m.r. spectrum showed signals for one acetoxy- and four methoxy-groups and five aromatic protons, all singlets (Table 3). A comparison of the chemical shifts of the aromatic protons of phenol (A₃) acetate with those of 2,3,4,6,7-pentamethoxyphenanthrene (Table 3) suggests

³ A. W. Exell, *Kirkia* (Journal of the Government Herbarium, Salisbury, Rhodesia), 1970, 7 (II), 196.

that the oxygenation pattern is the same and that the acetoxy-group is probably at C-2 or C-7. Hydrolysis of phenol (A_3) acetate gave the free phenol, which on deuteration, followed by acetylation, gave a mono-deuteriated species (shown by mass spectrometry) showing four aromatic protons (Table 3). The exchanged proton can be H-8 or H-1, and consequently phenol (A_3) can have structure (III), (IV), or (V). Phenol (A_3) acetate was identical with (V) acetate, which was synthesised from 3'-acetoxy-3,4,4',5-tetramethoxystilbene by the oxidative photochemical reaction. Therefore phenol (A_3) has structure (V). Catalytic

($C_{21}H_{22}O_7$), with spectroscopic characteristics of a 9,10-dihydrophenanthrene (Tables 1 and 3). The n.m.r. spectrum of phenol (C_2) acetate showed signals for three methoxy- and two acetoxy-groups, a singlet for four benzylic protons, and three aromatic protons, all singlets (Table 3). Hydrolysis of phenol (C_2) acetate yielded the free phenol, which on methylation, followed by dehydrogenation, gave a product identical with 2,3,4,6,7-pentamethoxyphenanthrene, thus establishing the oxygenation pattern of phenols (C_2) and (C_1). Deuteration of phenol (C_2) followed by acetylation gave a dideuteriated species (mass spectrometry) showing only one aromatic

TABLE 1
U.v. data [λ_{\max}/nm (log ϵ)]

9,10-Dihydrophenanthrene					
7-Hydroxy-2,4,6-trimethoxy- 7-Acetoxy-2,4,6-trimethoxy-	[Phenol (A_2)]	263 (4.18)	278 (4.19)	302 (4.16)	313sh (4.10)
7-Hydroxy-2,3,4,6-tetramethoxy- 7-Acetoxy-2,3,4,6-tetramethoxy-	[Phenol (A_4)]	265 (4.04)	275 (4.10)	301 (4.10)	311 (4.09)
2,7-Dihydroxy-3,4,6-trimethoxy- 2,7-Diacetoxy-3,4,6-trimethoxy-	[Phenol (C_2)]	270sh (4.28)	282 (4.27)	304 (4.17)	315 (4.16)
2,6,7-Triacetoxy-3,4-dimethoxy-	[Phenol (H_2) acetate]	267 (4.19)	279 (4.31)	301sh (4.16)	311 (4.19)
		265sh (4.39)	281.5 (4.24)	302sh (4.09)	315 (4.10)
			275 (4.21)	304sh (3.99)	310 (4.00)
			274 (4.40)	302sh (4.15)	
Phenanthrene					
7-Hydroxy-2,4,6-trimethoxy- 7-Acetoxy-2,4,6-trimethoxy-	[Phenol (A_1)]	261.5 (5.13)	283 (4.25)	295 (4.10)	306 (3.85)
7-Hydroxy-2,3,4,6-tetramethoxy- 7-Acetoxy-2,3,4,6-tetramethoxy-	[Phenol (A_3)]	261 (4.83)	281 (4.19)	294 (4.04)	306 (3.86)
2,7-Dihydroxy-2,4,6-trimethoxy- 2,7-Diacetoxy-3,4,6-trimethoxy-	[Phenol (C_1)]	260 (5.05)	281.5 (4.57)	291sh (4.32)	308 (4.12)
2,6,7-Triacetoxy-3,4-dimethoxy-	[Phenol (H_1) acetate]	259.5 (4.84)	280 (4.38)	290sh (4.09)	308 (3.98)
		259.5 (4.91)	282.5 (4.48)	298sh (4.21)	309sh (3.99)
		258.5 (4.99)	276 (4.51)	296 (4.28)	307 (4.30)
		257.5 (4.91)	280 (4.27)	290 (4.14)	302.5 (4.18)

TABLE 2
 ^1H N.m.r. spectra of phenols (A_1) and (A_2) and their derivatives (τ values; J in Hz)^a

	H-1 or H-3	H-3 or H-1	H-5	H-8	H-9 and H-10	OMe			OAc or OH
9,10-Dihydrophenanthrene									
7-Hydroxy-2,4,6-trimethoxy- Phenol (A_2)	3.65	3.65	2.23	3.33	7.33 (4H)	6.14 (3H), 6.16 (3H), 6.21 (3H)			4.53 (1H) *
7-Acetoxy-2,4,6-trimethoxy- [8- ^2H]-7-Acetoxy-2,4,6-tri- methoxy-	3.64	3.64	2.12	3.22	7.30 (4H)	6.16 (3H), 6.18 (3H), 6.21 (3H)			7.72 (3H)
	3.64	3.64	2.12		7.30 (4H)	6.16 (3H), 6.18 (3H), 6.21 (3H)			7.72 (3H)
Phenanthrene									
7-Hydroxy-2,4,6-trimethoxy- [Phenol (A_1)]	3.33 (d, J 2)	3.18 (d, J 2)	1.01	2.77	2.54 (2H)	5.97 (6H), 6.11 (3H)			4.2 (1H) *
7-Acetoxy-2,4,6-trimethoxy- [8- ^2H]-7-Acetoxy-2,4,6-tri- methoxy-	3.34 (d, J 2)	3.20 (d, J 2)	0.92	2.61	2.54 (2H)	5.95 (3H), 6.02 (3H), 6.10 (3H)			7.64 (3H)
2,4,6,7-Tetramethoxy- ²	3.34 (d, J 2)	3.19 (d, J 2)	0.98	2.87	2.51 (2H)	5.98 (6H), 6.04 (3H), 6.13 (3H)			

^a Unless indicated to the contrary all signals are one-proton singlets.

* Signals are removed on shaking with D_2O .

hydrogenation of the mixed acetate from the lower band gave a single crystalline acetate of phenol (A_4), with spectral characteristics of a 9,10-dihydrophenanthrene (Tables 1 and 3). It follows that phenol (A_4) has structure (VI).

The acetate from band B was 4,7-diacetoxy-9,10-dihydro-2,3,6-trimethoxyphenanthrene.²

The amorphous acetate from band C was shown by mass spectrometry and n.m.r. to be a mixture of phenol (C_1) acetate (10%) and its dihydro-derivative, phenol (C_2) acetate (90%). Catalytic reduction of the amorphous solid gave the crystalline acetate of phenol (C_2)

proton (H-5) in its n.m.r. spectrum. Therefore, phenol (C_2) can have structure (VII) or (VIII). Since (VII) is already known² and is different from phenol (C_2), the structure of the latter is (VIII). Dehydrogenation of the amorphous acetate from band C gave a single crystalline acetate which on hydrolysis gave the free phenol (C_1) exhibiting spectral characteristics of a substituted phenanthrene (Tables 1 and 3). Thus phenol (C_1) has structure (IX).

The acetate from band D yielded crystalline phenol (D) ($C_{17}H_{20}O_4$) on hydrolysis, exhibiting an n.m.r. spectrum characteristic of a bibenzyl (Table 4), with

signals for one hydroxy- and three methoxy-groups, four equivalent benzylic protons, and six aromatic protons, four appearing as an AB quartet (J_{ortho} 8.5 Hz) and the remaining two as a singlet, indicating a symmetrical

and 3,4,5-trimethoxyphenylacetic acid followed by decarboxylation and catalytic reduction.

The acetate from band E was 4,7-diacetoxy-9,10-dihydro-2,6-dimethoxyphenanthrene.²

TABLE 3

Assignment ^a of chemical shifts (τ) in the ¹H n.m.r. spectra of phenols (A₃), (A₄), (C₁), and (C₂) and their derivatives, and derivatives of phenols (H₁) and (H₂)

	H-1 or H-8	H-8 or H-1	H-5	H-9 and H-10	OMe	OAc or OH
9,10-Dihydrophenanthrene						
7-Hydroxy-2,3,4,6-tetramethoxy- [Phenol (A ₄)]	3.52	3.32	2.14	7.34 (4H)	6.13 (6H), 6.18 (3H), 6.28 (3H)	4.46 (1H) *
7-Acetoxy-2,3,4,6-tetramethoxy- [8- ² H]-7-Acetoxy-2,3,4,6-tetramethoxy-	3.50	3.21	2.03	7.32 (4H)	6.13 (3H), 6.16 (3H), 6.19 (3H), 6.26 (3H)	7.70 (3H)
2,7-Dihydroxy-3,4,6-trimethoxy- [Phenol (C ₂)]	3.43	3.27	2.16	7.37 (4H)	6.13 (3H), 6.16 (3H), 6.19 (3H), 6.26 (3H)	7.70 (3H)
2,7-Diacetoxy-3,4,6-trimethoxy- [1,8- ² H ₂]-2,7-Diacetoxy-3,4,6-trimethoxy-	3.37	3.20	2.02	7.34 (4H)	6.07 (3H), 6.14 (3H), 6.29 (3H)	3.70 (2H) *
2,6,7-Triacetoxy-3,4-dimethoxy- [Phenol (H ₂) acetate]	3.38	3.05	1.94	7.30 (4H)	6.17 (3H), 6.20 (3H), 6.30 (3H)	7.71 (6H)
[1,5,8- ² H ₃]-2,6,7-Triacetoxy-3,4-dimethoxy- 2,3,4,6,7-Pentamethoxy- ²	3.48	3.34	2.08	7.30 (4H) 7.30 (4H)	6.18 (3H), 6.31 (3H) 6.15 (12H), 6.27 (3H)	7.71 (6H) 7.70 (3H), 7.73 (6H)
Phenanthrene						
7-Hydroxy-2,3,4,6-tetramethoxy- [Phenol (A ₃)]	3.04	2.70	1.06	2.60 (2H)	5.97 (3H), 6.03 (6H), 6.06 (3H)	4.16 (1H) *
7-Acetoxy-2,3,4,6-tetramethoxy- [8- ² H]-7-Acetoxy-2,3,4,6-tetramethoxy-	2.99	2.54	0.89	2.54 (2H)	6.01 (12H)	7.63 (3H)
2,7-Dihydroxy-3,4,6-trimethoxy- [Phenol (C ₁)]	2.99	2.78	0.89	2.54 (2H)	6.01 (12H)	7.63 (3H)
2,7-Diacetoxy-3,4,6-trimethoxy- [1,8- ² H ₂]-2,7-Diacetoxy-3,4,6-trimethoxy-	2.91	2.78	1.09	2.63 (2H)	5.96 (3H), 6.00 (3H), 6.07 (3H)	4.10 (2H) *
2,6,7-Triacetoxy-3,4-dimethoxy- [Phenol (H ₁) acetate]	2.74	2.59	0.89	2.59 (2H)	6.03 (9H)	7.63 (6H)
[1,5,8- ² H ₃]-2,6,7-Triacetoxy-3,4-dimethoxy- 2,3,4,6,7-Pentamethoxy- ²	2.73	2.43	0.70	2.59 (2H) 2.52 (2H)	6.03 (9H) 6.05 (6H)	7.63 (6H) 7.73 (3H), 7.75 (6H)
	3.03	2.90	1.03	2.52 (2H) 2.57 (2H)	6.05 (6H) 5.98 (3H), 6.04 (9H), 6.07 (3H)	7.73 (3H), 7.75 (6H)

* Signals are removed on shaking with D₂O.

^a All signals are singlets and have the appropriate integrated intensities.

TABLE 4

Assignment of chemical shifts (τ) in the ¹H n.m.r. spectra of bibenzyls ^a

	2-H,6-H	3',5'- or 2',6'-H	2',6'- or 3',5'-H	α,α' -H	OMe	OAc or OH
4'-Hydroxy-3,4,5-trimethoxy- [Phenol (D)]	3.75	3.09 (d, J 8.5)	3.35 (d, J 8.5)	7.22 (4H)	6.25 (9H)	4.86 (1H) *
4'-Acetoxy-3,4,5-trimethoxy-	3.72	2.92 (d, J 8)	3.08 (d, J 8)	7.16 (4H)	6.23 (9H)	7.75 (3H)
4,4'-Dihydroxy-3,5-dimethoxy- [Phenol (F)]	3.79	3.13 (d, J 8.5)	3.38 (d, J 8.5)	7.25 (4H)	6.26 (6H)	5.06 (2H) *
4,4'-Diacetoxy-3,5-dimethoxy-	3.72	2.93 (d, J 8)	3.12 (d, J 8)	7.18 (4H)	6.28 (6H)	7.73 (3H) 7.78 (3H)
2,6-[² H ₂]-4,4'-Diacetoxy-3,5-dimethoxy-	3.74	2.95		7.18 (4H)	6.28 (6H)	7.73 (3H) 7.79 (3H)
3,4,4',5'-Tetramethoxy- ¹	3.70	2.98 (d, J 8.5)	3.28 (d, J 8.5)	7.20 (4H)	6.22 (9H) 6.27 (3H)	

* Signals removed on shaking with D₂O.

^a Unless indicated to the contrary all signals are singlets and have the appropriate integrated intensities; J in Hz.

structure for phenol (D). A comparison of the n.m.r. spectra of phenol (D) and phenol (D) acetate with that of 3,4,4',5'-tetramethoxybibenzyl (Table 4) suggests phenol (D) to be 4'-hydroxy-3,4,5-trimethoxybibenzyl. This was confirmed from the synthesis of 4'-acetoxy-3,4,5-trimethoxybibenzyl, which proved to be identical with phenol (D) acetate. The bibenzyl was prepared from a Perkin condensation of 4-hydroxybenzaldehyde

The acetate from band F exhibited n.m.r. and mass spectra which suggested that it was a mixture of two isomeric bibenzyls in nearly equal amounts. Careful separation on t.l.c. afforded two bands, the lower of which was 3,4'-diacetoxy-4,5-dimethoxybibenzyl.¹

The upper band gave an oily acetate of phenol (F), hydrolysis of which yielded crystalline phenol (F) (C₁₆H₁₈O₄) exhibiting an n.m.r. spectrum characteristic

of a bibenzyl (Table 4) with signals for two hydroxy- and two methoxy-groups, four equivalent benzylic protons, and six aromatic protons, four appearing as an AB quartet (J_{ortho} 8.5 Hz) and the remaining two as a singlet indicating a symmetric structure for phenol (F). Methylation of phenol (F) gave 3,4,4',5-tetramethoxy-bibenzyl,¹ which establishes its oxygenation pattern. Deuteration of phenol (F) followed by acetylation gave a dideuteriated species (mass spectrometry) in which the exchangeable aromatic protons were shown to be part of the AB quartet. Consequently phenol (F) is 4,4'-dihydroxy-3,5-dimethoxybibenzyl. This structure was confirmed by a synthesis of 4,4'-diacetoxy-3,5-dimethoxybibenzyl *via* a Perkin condensation of 4-hydroxybenzaldehyde and 4-hydroxy-3,5-dimethoxyphenylacetic acid followed by decarboxylation and catalytic reduction.

The crude acetate from band G was shown by mass spectrometry and by n.m.r. to be a mixture of a phenanthrene and its dihydro-derivative. Dehydrogenation of the crude acetate gave only 6,7-diacetoxy-2,3,4-trimethoxyphenanthrene;¹ the latter was hydrolysed and converted into 6,7-methylenedioxy-2,3,4-trimethoxyphenanthrene, which was synthesised from 4,5-methylenedioxy-2-nitrobenzaldehyde and 3,4,5-trimethoxyphenylacetic acid by standard methods. Catalytic reduction of the crude acetate from band G gave only 6,7-diacetoxy-9,10-dihydro-2,3,4-trimethoxyphenanthrene.^{1,2}

The acetate from band H separated into two bands on t.l.c. plates. The upper band gave a gum which was shown to be a mixture of phenol (H_1) acetate (45%) and its dihydro-derivative, phenol (H_2) acetate (55%). Dehydrogenation of the gum gave a crystalline acetate of phenol (H_1) ($C_{22}H_{20}O_3$) which showed spectroscopic characteristics of a substituted phenanthrene (Tables 1 and 3), with signals in the n.m.r. for three acetoxy- and two methoxy-groups, and five aromatic protons, all singlets. Acidic hydrolysis of phenol (H_1) acetate yielded a phenolic gum which could not be crystallised, but which on methylation gave 2,3,4,6,7-pentamethoxyphenanthrene,² thus establishing the oxygenation pattern of both phenols (H_1) and (H_2). Deuteration of the phenolic gum (H_1) followed by acetylation gave a trideuteriated species (mass spectrometry) showing only two aromatic protons (H-9, H-10) in its n.m.r. spectrum. Thus phenol (H_1) can have structure (X) or (XI). As (X) is already known² and is different from phenol (H_1), the latter must have structure (XI). Hydrogenation of the mixture of phenol (H_1) and (H_2) acetates gave a single product (n.m.r. and mass spectra, t.l.c.), phenol (H_2) acetate, which on being hydrolysed and methylated gave 9,10-dihydro-2,3,4,6,7-pentamethoxyphenanthrene.² Consequently the structure of phenol (H_2) is (XII).

The lower band from the t.l.c. separation of the acetates from band H gave an amorphous solid, which was shown by mass spectrometry and n.m.r. to be a mixture of a substituted phenanthrene (45%) and its

dihydro-derivative (55%). Dehydrogenation of the amorphous solid gave 4,6,7-triacetoxy-2,3-dimethoxyphenanthrene.² Thus, besides phenols (H_1) and (H_2), band H also contains 4,6,7-trihydroxy-2,3-dimethoxyphenanthrene and its 9,10-dihydro-derivative.¹

EXPERIMENTAL

General experimental details are described in Parts I² and II.¹

Extraction of the Heartwood.—By the procedure we have described,² the brown heartwood (700 g) yielded a brown oily light petroleum extract (4 g) and a brown solid (90 g) from the ether extraction.

Isolation of the Phenolic Constituents.—The ether extract (1 g) was chromatographed as previously described² in 5% methanol-chloroform and yielded a red-coloured gum from each band: A (100 mg), B (110 mg), C (85 mg), D (50 mg), E (80 mg), F (70 mg), G (80 mg), and H (60 mg) with R_F 0.86, 0.76, 0.67, 0.51, 0.42, 0.35, 0.26, and 0.18, respectively. These crude phenolic products (which exhibited no carbonyl absorption in the i.r.) were acetylated and purified by t.l.c. as previously described,² yielding two amorphous acetates from band A (upper band 9 mg; lower band 45 mg), a crystalline acetate from band B (44 mg), an amorphous acetate from band C (36 mg), a gum from band D (24 mg), a crystalline acetate from band E (40 mg), a gum from band F (48 mg), an amorphous acetate from band G (26 mg), and from band H, a gum (upper band; 24 mg) and an amorphous acetate (lower band; 20 mg).

7-Hydroxy-2,4,6-trimethoxyphenanthrene [*Phenol* (A_1)].—The upper band from the t.l.c. separation of the acetates from band A gave an amorphous acetate, m.p. 140—155°, m/e 328, 326, 286 (base peak), and 284, which on dehydrogenation² gave plates of 7-acetoxy-2,4,6-trimethoxyphenanthrene, m.p. 159—161° (from methanol) identical (mixed m.p., i.r., and n.m.r.) with the synthetic product (see later). Acidic hydrolysis¹ gave 7-hydroxy-2,4,6-trimethoxyphenanthrene as plates, m.p. 177—179° (from chloroform-light petroleum), ν_{max} 3400, 2920, 1610, 1580, and 1530 cm^{-1} , m/e 284 (base peak) and 269 (M^+ , 284.1029). $C_{17}H_{16}O_4$ requires M , 284.1049.

7-Hydroxy-9,10-dihydro-2,4,6-trimethoxyphenanthrene [*Phenol* (A_2)].—The amorphous acetate was hydrogenated² in ethanol to give 7-acetoxy-9,10-dihydro-2,4,6-trimethoxyphenanthrene as prisms, m.p. 152—154° (from methanol), ν_{max} 2930, 1760, 1605, and 1510 cm^{-1} , m/e 328 and 286 (base peak) (M^+ , 328.1331). $C_{19}H_{20}O_5$ requires M , 328.1311). Acidic hydrolysis gave 7-hydroxy-9,10-dihydro-2,4,6-trimethoxyphenanthrene as plates, m.p. 107—110° (from light petroleum-chloroform), ν_{max} 3400, 2920, 1605, 1580, and 1520 cm^{-1} , m/e 286 (base peak) and 271 (M^+ , 286.1205). $C_{17}H_{18}O_4$ requires M , 286.1205).

7-Hydroxy-2,3,4,6-tetramethoxyphenanthrene [*Phenol* (A_3)].—The lower band from the t.l.c. separation of the acetates from band A gave an amorphous solid, m.p. 110—130°, m/e 358, 356, 316 (base peak), and 314. Dehydrogenation gave 7-acetoxy-2,3,4,6-tetramethoxyphenanthrene as prisms, m.p. 138—140° (from methanol) identical (mixed m.p., i.r., and n.m.r.) with the synthetic product (see later). Acidic hydrolysis gave 7-hydroxy-2,3,4,6-tetramethoxyphenanthrene as plates, m.p. 176—178° (from chloroform-light petroleum), ν_{max} 3420, 2920, 1635, 1610, 1575, 1530, and 1510 cm^{-1} , m/e 314 (base peak) and 299 (M^+ , 314.1155). $C_{18}H_{18}O_5$ requires M , 314.1154).

7-Hydroxy-9,10-dihydro-2,3,4,6-tetramethoxyphenanthrene

[*Phenol* (A₄)].—Hydrogenation of the amorphous acetate in ethanol gave 7-acetoxy-9,10-dihydro-2,3,4,6-tetramethoxyphenanthrene as prisms, m.p. 115—116° (from ether—light petroleum), ν_{\max} 2930, 1770, 1600, and 1515 cm^{-1} , m/e 358 and 316 (base peak) (M^+ , 358.1430. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires M , 358.1416). Acidic hydrolysis gave 7-hydroxy-9,10-dihydro-2,3,4,6-tetramethoxyphenanthrene as plates, m.p. 156—158° (from light petroleum—chloroform), ν_{\max} 3450, 2930, 1620, 1595, and 1520 cm^{-1} , M (mass spectrum), 316 (M^+ , 316.1328. $\text{C}_{18}\text{H}_{20}\text{O}_5$ requires M , 316.1311).

The acetate from band B gave prisms, m.p. 152—154°, identical (mixed m.p., i.r., and n.m.r.) with 4,7-diacetoxy-9,10-dihydro-2,3,6-trimethoxyphenanthrene.²

2,7-Dihydroxy-3,4,6-trimethoxyphenanthrene [*Phenol* (C₁)].—The amorphous acetate from band C, m.p. 110—130°, m/e 386, 384, 344, 342, 302 (base peak), and 300, was dehydrogenated to give 2,7-diacetoxy-3,4,6-trimethoxyphenanthrene as prisms, m.p. 179—181° (from ethanol), ν_{\max} 2920, 1770, 1750, 1610, 1570, 1530, and 1510 cm^{-1} , m/e 384, 342, and 300 (base peak) (Found: C, 65.5; H, 5.3. $\text{C}_{21}\text{H}_{20}\text{O}_7$ requires C, 65.6; H, 5.2%). Acidic hydrolysis gave 2,7-dihydroxy-3,4,6-trimethoxyphenanthrene as plates, m.p. 143—144° (from chloroform—light petroleum), ν_{\max} 3400, 2920, 1625, 1580, and 1520 cm^{-1} , m/e 300 (base peak) and 285 (Found: C, 67.6; H, 5.4. $\text{C}_{17}\text{H}_{16}\text{O}_5$ requires C, 68.0; H, 5.4%). Methylation gave 2,3,4,6,7-pentamethoxyphenanthrene.²

2,7-Dihydroxy-9,10-dihydro-3,4,6-trimethoxyphenanthrene [*Phenol* (C₂)].—Hydrogenation of the amorphous acetate in ethanol gave 2,7-diacetoxy-9,10-dihydro-3,4,6-trimethoxyphenanthrene as prisms, m.p. 110—112° (from light petroleum—ether), ν_{\max} 2920, 1760, 1590, and 1515 cm^{-1} , m/e 386, 344, and 302 (base peak) (Found: C, 65.4; H, 5.6. $\text{C}_{21}\text{H}_{22}\text{O}_7$ requires C, 65.3; H, 5.7%). Acidic hydrolysis gave plates of 9,10-dihydro-2,7-dihydroxy-3,4,6-trimethoxyphenanthrene, m.p. 111—113° (from chloroform—light petroleum), ν_{\max} 3410, 3160, 2930, 1610, 1595, and 1510 cm^{-1} , m/e 302 (base peak) and 287 (Found: C, 67.7; H, 6.3. $\text{C}_{17}\text{H}_{18}\text{O}_5$ requires C, 67.5; H, 6.0%). Methylation gave 9,10-dihydro-2,3,4,6,7-pentamethoxyphenanthrene.²

4'-Hydroxy-3,4,5-trimethoxybibenzyl [*Phenol* (D)].—The acetate from band D was obtained as a gum, identical (i.r. and n.m.r.) with 4'-acetoxy-3,4,5-trimethoxybibenzyl (see later). Acidic hydrolysis gave 4'-hydroxy-3,4,5-trimethoxybibenzyl as prisms, m.p. 115—116° (from chloroform—light petroleum), ν_{\max} 3320, 2920, 1595, and 1525 cm^{-1} , λ_{\max} 207 (log ϵ 4.64), 225sh (4.31), 278 (3.46), and 286sh nm (3.36), m/e 288, 181 (base peak), and 107 (Found: C, 70.5; H, 6.95. $\text{C}_{17}\text{H}_{20}\text{O}_4$ requires C, 70.8; H, 7.0%).

The acetate from band E gave prisms, m.p. 140—142°, identical (mixed m.p., i.r., and n.m.r.) with 4,7-diacetoxy-9,10-dihydro-2,6-dimethoxyphenanthrene.²

Careful t.l.c. separation (repeated elution with chloroform) of the acetates from band F, m/e 358, 316, 274, 209, 167 (base peak), and 107 afforded two bands, the lower of which yielded a gum identical (i.r. and n.m.r.) with 3,4'-diacetoxy-4,5-dimethoxybibenzyl,¹ and which on acidic hydrolysis gave prisms, m.p. 128—130°, identical (mixed m.p. and i.r.) with 3,4'-dihydroxy-4,5-dimethoxybibenzyl.¹

4,4'-Dihydroxy-3,5-dimethoxybibenzyl [*Phenol* (F)].—The acetate from the upper band in the t.l.c. separation of the acetates from band F was identical with 4,4'-diacetoxy-3,5-dimethoxybibenzyl (see later). Acidic hydrolysis gave 4,4'-dihydroxy-3,5-dimethoxybibenzyl as prisms, m.p. 139—141° (from chloroform—light petroleum), ν_{\max} 3410, 2930,

1613, and 1520 cm^{-1} , λ_{\max} 214 (log ϵ 4.25), 225sh (4.16), and 278 nm (3.45), m/e 274, 167 (base peak), and 107 (Found: C, 69.6; H, 6.5. $\text{C}_{16}\text{H}_{18}\text{O}_4$ requires C, 70.05; H, 6.6%). Methylation gave 3,4,4',5-tetramethoxybibenzyl.¹

The amorphous acetate from band G, m.p. 110—120°, m/e 386, 384, 344, 342, 302 (base peak), and 300, on dehydrogenation gave prisms, m.p. 121—123°, identical (mixed m.p., i.r., and n.m.r.) with 6,7-diacetoxy-2,3,4-trimethoxyphenanthrene.¹ Acidic hydrolysis followed by treatment with diiodomethane, gave prisms of 2,3,4-trimethoxy-6,7-methylenedioxyphenanthrene, identical (mixed m.p., i.r., and n.m.r.) with the synthetic product (see later). Catalytic reduction of the amorphous acetate gave prisms, m.p. 130—133°, identical (mixed m.p., i.r. and n.m.r.) with 6,7-diacetoxy-9,10-dihydro-2,3,4-trimethoxyphenanthrene.^{1,2}

2,6,7-Triacetoxy-3,4-dimethoxyphenanthrene [*Phenol* (H₁) Acetate].—T.l.c. of the acetates from band H gave two bands; the upper band yielded a gum, m/e 414, 412, 372, 370, 330, 328, 288 (base peak), and 286, which on dehydrogenation gave 2,6,7-triacetoxy-3,4-dimethoxyphenanthrene as prisms, m.p. 138—140° (from ethanol), ν_{\max} 2920, 1760, 1610, 1570, and 1510 cm^{-1} , m/e 412, 370, 328, and 286 (base peak) (Found: C, 64.1; H, 5.0. $\text{C}_{22}\text{H}_{20}\text{O}_8$ requires C, 64.05; H, 4.9%). Acidic hydrolysis gave a phenolic gum which on methylation gave 2,3,4,6,7-pentamethoxyphenanthrene.

2,6,7-Triacetoxy-9,10-dihydro-3,4-dimethoxyphenanthrene [*Phenol* (H₂) acetate].—Hydrogenation of the gum gave 2,6,7-triacetoxy-9,10-dihydro-3,4-dimethoxyphenanthrene as a gum, ν_{\max} (film), 3000, 2900, 1760, 1590, and 1505 cm^{-1} , m/e 414, 372, 330, and 288 (base peak) (M^+ , 414.1313. $\text{C}_{22}\text{H}_{22}\text{O}_8$ requires M , 414.1315). Acidic hydrolysis gave a phenolic gum which on methylation gave 9,10-dihydro-2,3,4,6,7-pentamethoxyphenanthrene.

The lower band from the t.l.c. separation of the acetates from band H gave an amorphous solid, m.p. 150—170°, which on dehydrogenation gave 4,6,7-triacetoxy-2,3-dimethoxyphenanthrene,² m.p. 170—173° (identified from mixed m.p., i.r., and n.m.r.).

Synthesis of 7-Acetoxy-2,4,6-trimethoxyphenanthrene.—A Perkin condensation¹ of isovanillin and 3,5-dimethoxyphenylacetic acid² gave α -(3,5-dimethoxyphenyl)-3-hydroxy-4-methoxycinnamic acid as needles, m.p. 295—299° (from methanol), ν_{\max} 3360, 2940, 1680, 1600, and 1520 cm^{-1} (Found: C, 65.4; H, 5.45. $\text{C}_{18}\text{H}_{18}\text{O}_6$ requires C, 65.4; H, 5.5%), which after acetylation and decarboxylation² was irradiated¹ in ethanol (containing 0.005% iodine) with a Hanovia medium-pressure mercury arc submerged in the solution in quartz apparatus, yielding 7-acetoxy-2,4,6-trimethoxyphenanthrene* as plates, m.p. 159—161° (from methanol), ν_{\max} 2920, 1755, 1615, 1575, 1535, and 1510 cm^{-1} , m/e 326 and 284 (base peak) (M^+ , 326.1144. $\text{C}_{19}\text{H}_{18}\text{O}_6$ requires M , 326.1154).

Synthesis of 7-Acetoxy-2,3,4,6-tetramethoxyphenanthrene.—After a Perkin condensation (see later) of isovanillin and 3,4,5-trimethoxyphenylacetic² acid, followed by the sequence of reactions just described, the following compounds were isolated: 3-acetoxy-4-methoxy- α -(3,4,5-trimethoxyphenyl)cinnamic acid as needles, m.p. 173—178° (from benzene—methanol), ν_{\max} 2950, 2600, 1770, 1670, 1610, 1585, and 1515 cm^{-1} , m/e 402, 360 (base peak), 358, and 345 (Found: C, 62.6; H, 5.6. $\text{C}_{21}\text{H}_{22}\text{O}_8$ requires C, 62.7; H, 5.5%); 7-acetoxy-2,3,4,6-tetramethoxyphenanthrene* as

* Yields in the photochemical cyclisations, 35—40%.

prisms, m.p. 138—140° (from methanol), ν_{\max} 2920, 1755, 1625, 1605, 1570, 1525, and 1510 cm^{-1} , m/e 356, 314 (base peak), and 299 (Found: C, 67.3; H, 5.7. $\text{C}_{20}\text{H}_{20}\text{O}_6$ requires C, 67.4; H, 5.7%).

Synthesis of 4'-Acetoxy-3,4,5-trimethoxybibenzyl.—A mixture of 4-hydroxybenzaldehyde (0.6 g), 3,4,5-trimethoxyphenylacetic acid (1.0 g), acetic anhydride (1 ml), and triethylamine (0.5 ml) was heated at 90° for 12 h, then evaporated under reduced pressure, leaving a gum which solidified on the addition of conc. hydrochloric acid (2 ml). The solid was filtered off and washed with water, leaving 4'-acetoxy- α -(3,4,5-trimethoxyphenyl)cinnamic acid (1.5 g), m.p. 220—224° (from ethanol), ν_{\max} 2930, 2600, 1765, 1670, 1600, 1590, and 1510 cm^{-1} , m/e 372, 330 (base peak), 328, and 315 (Found: C, 64.3; H, 5.3. $\text{C}_{20}\text{H}_{20}\text{O}_7$ requires C, 64.5; H, 5.4%), which on decarboxylation followed by hydrogenation in ethanol for 3 h, gave a gum, 4'-acetoxy-3,4,5-trimethoxybibenzyl (0.75 g), ν_{\max} (film) 2900, 1750, and 1510 cm^{-1} , m/e 330, 181 (base peak), and 107 (M^+ , 330.1446. $\text{C}_{19}\text{H}_{22}\text{O}_5$ requires M , 330.1467).

Synthesis of 4,4'-Diacetoxy-3,5-dimethoxybibenzyl.—A mixture of 4-hydroxybenzaldehyde (0.15 g), 4-hydroxy-3,5-dimethoxyphenylacetic acid⁴ (0.2 g) (prepared by a photochemical Arndt-Eistert reaction from 4-hydroxy-3,5-dimethoxybenzoic acid), acetic anhydride (0.4 ml), and triethylamine (0.2 ml) was heated at 100° for 12 h. The solution was evaporated under reduced pressure, leaving a gum, which was refluxed with quinoline (5 ml) and copper chromite powder (0.2 g) for 5 min. The cooled mixture was taken up in ether and filtered, and the filtrate was washed with dilute hydrochloric acid and then with dilute sodium hydrogen sulphite, dried (MgSO_4), and evaporated. The resulting gum was purified by t.l.c. and hydrogenated to give 4,4'-diacetoxy-3,5-dimethoxybibenzyl (45 mg) as a gum, ν_{\max} (film) 2930, 1760, 1600, and 1500 cm^{-1} , m/e 358,

316, 274, 209, 167 (base peak), and 107 (M^+ , 358.1419. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires M , 358.1415).

Synthesis of 2,3,4-Trimethoxy-6,7-methylenedioxyphenanthrene.—Under conditions similar to those described² previously, a Pschorr synthesis from 3,4,5-trimethoxyphenylacetic acid and 4,5-methylenedioxy-2-nitrobenzaldehyde gave the following compounds: 4,5-methylenedioxy-2-nitro- α -(3,4,5-trimethoxyphenyl)cinnamic acid as needles, m.p. 207—210° (from acetic acid-water), τ 0.42br (1H), 1.95 (1H, s), 2.53 (1H, s), 3.71 (2H, s), 3.75 (1H, s), 4.02 (2H, s), 6.20 (3H, s), and 6.32 (6H, s) (Found: C, 56.4; H, 4.2. $\text{C}_{19}\text{H}_{17}\text{NO}_9$ requires C, 56.6; H, 4.25%); 2,3,4-trimethoxy-6,7-methylenedioxyphenanthrene-10-carboxylic acid as needles, m.p. 272—274° (from acetone), M (mass spectrum) 356 (Found: C, 64.0; H, 4.5. $\text{C}_{19}\text{H}_{16}\text{O}_7$ requires C, 64.0; H, 4.5%), λ_{\max} 262 (log ϵ 4.75), 284 (4.15), and 314 nm (4.07); 2,3,4-trimethoxy-6,7-methylenedioxyphenanthrene as needles, m.p. 129—130° (from methanol), ν_{\max} 2920, 1605, and 1510 cm^{-1} , λ_{\max} 258 (log ϵ 4.88), 284 (4.31), 300sh (4.01), and 310 nm (3.74), τ 1.13 (1H, s), 2.62 (2H, s), 2.95 (1H, s), 3.07 (1H, s), 4.05 (2H, s), and 6.07 (9H, s), M (mass spectrum) 312 (Found: C, 68.8; H, 5.1. $\text{C}_{18}\text{H}_{16}\text{O}_5$ requires C, 69.2; H, 5.2%).

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⁴ F. Mauther, *J. prakt. Chem.*, 1935, **142**, 32.