Chemical Constituents of the *Combretaceae*. Part II.[1] Substituted Phenanthrenes and 9,10-Dihydrophenanthrenes and a Substituted Bibenzyl from the Heartwood of *Combretum molle*

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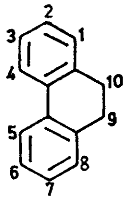
Four new compounds have been isolated from the heartwood of *Combretum molle* and have been shown both by chemical and spectroscopic methods and by synthesis to be 4,7-dihydroxy-2,3,6-trimethoxyphenanthrene, 4,6,7-trihydroxy-2,3-dimethoxy- and 2,6-dihydroxy-3,4,7-trimethoxy-9,10-dihydrophenanthrene, and 3,4′-dihydroxy-4,5-dimethoxybibenzyl. The relevance of the latter compound to the biogenesis of the phenanthrenes and 9,10-dihydrophenanthrenes is discussed. The phenol (C′) from *Combretum apiculatum* has now been unambiguously established by total synthesis to be 6,7-dihydroxy-2,3,4-trimethoxyphenanthrene.

We described recently[1] the isolation and structural elucidation of five new substituted phenanthrenes or 9,10-dihydrophenanthrenes from the heartwood of *Combretum apiculatum*. We now report on the heartwood extractives of *Combretum molle*,[2,3] which contain seven phenanthrenes or 9,10-dihydrophenanthrenes, three of which are new natural products, and a new phenolic bibenzyl.

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 five of the bands. These crude phenolic compounds exhibited no carbonyl absorption in the i.r. Acetylation followed by t.l.c. yielded a crystalline acetate from one of the bands [phenol (B)], amorphous acetates from three of the bands [each band being shown to be a mixture of two substances, *viz.* phenols (A), (A′); (D), (D′); and (E), (E′)], and an oil from the other band [phenol (C)]. The designations (A)—(E) represent the order in which the phenols ran on t.l.c. plates. With the exception of the acetate of phenol (C) all these acetates possessed u.v. spectra characteristic[1] of either a substituted phenanthrene or a substituted 9,10-dihydrophenanthrene.

The acetate from band A was isolated as an amorphous solid, and shown by mass spectrometry and, more quantitatively, by n.m.r. spectroscopy, to be a mixture of phenol (A) acetate (30%) and its dihydro-derivative, phenol (A′) acetate (70%). Dehydrogenation of the mixed acetate gave a single crystalline product, namely the acetate of phenol (A), identical (m.p., mixed m.p., i.r., and n.m.r.) with 4,7-diacetoxy-2,3,6-trimethoxyphenanthrene.[1] Alkaline hydrolysis of this acetate yielded the free phenol (A), which therefore has structure (I). Phenol (A′) (II) is thus the known[1] 9,10-dihydro-derivative of phenol (A).

The amorphous acetate from band D exhibited an n.m.r. spectrum very similar to that of the mixed acetate isolated from *Combretum apiculatum*.[1] Dehydrogenation gave a single crystalline substance [phenol (D) acetate], identical (m.p., mixed m.p., i.r. and n.m.r. spectra) with phenol (C′) acetate isolated from *Combretum apiculatum*.[1] We have previously shown that this phenol (C′) has either structure (III) or (IV), the latter being preferred on slender t.l.c. evidence. We have now carried out an unambiguous synthesis (see Scheme 1) of the acetate of (III), and have shown this to be identical with phenol (C′) acetate, thus making a revision of our previous assignment necessary. A Perkin condensation of 3,4,5-trimethoxyphenylacetic acid and 3,4-dihydroxybenzaldehyde gave the cinnamic acid (V), which on decarboxylation yielded the stilbene (VI), from which 6,7-diacetoxy-2,3,4-trimethoxyphenanthrene was obtained as the only isolable product from an oxidative photochemical reaction with iodine.[4] This photochemical cyclisation could conceivably give a second product, 5,6-diacetoxy-2,3,4-trimethoxyphenanthrene, but the steric effects make this most unlikely.[5] Such a product would not exhibit the characteristic low field 5-proton signal in the n.m.r. spectrum, shown by the isolated product. Consequently phenol (D) has structure (III) and phenol (D′) structure (VII); n.m.r. spectro-



	Substituents				
	2-	3-	4-	6-	7-
9,10-Dihydrophenanthrenes:					
Phenol (A′) (II)	OMe	OMe	OH	OMe	OH
Phenol (D′) (VII)	OMe	OMe	OMe	OH	OH
Phenol (E) (IX)	OMe	OMe	OH	OH	OH
Phenol (B) (X)	OH	OMe	OMe	OH	OMe
(XI)	OMe	OMe	OH	OH	OMe
Phenanthrenes:					
Phenol (A) (I)	OMe	OMe	OH	OMe	OH
Phenol (D) (III)	OMe	OMe	OMe	OH	OH
(IV)	OH	OMe	OMe	OH	OMe
Phenol (E′) (VIII)	OMe	OMe	OH	OH	OH

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[1] Part I, R. M. Letcher and L. R. M. Nhamo, *J. Chem. Soc.* (*C*), 1971, 3070.

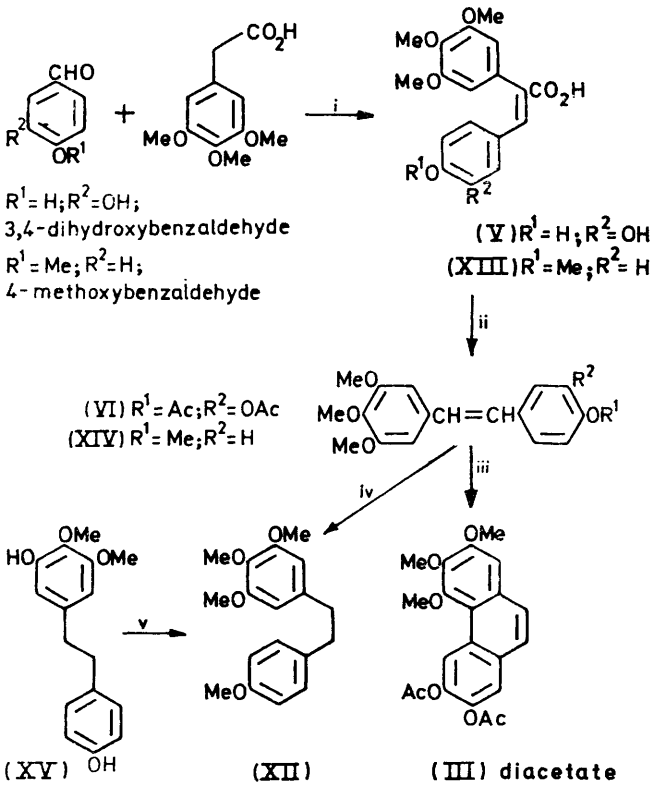
[2] A. W. Exell, *Kirkia* (Journal of the Government Herbarium, Salisbury, Rhodesia), 1970, **7** (II), 189.

[3] J. Coates-Palgrave, 'Trees of Central Africa,' National Publications Trust, 1957.

[4] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094.

[5] H. Erdtman and A. Ronlan, *Acta Chem. Scand.*, 1969, **23**, 249.

scopy indicated that these phenols were present in the ratio of 6 : 4, respectively.



SCHEME 1

Reagents: i, Ac_2O-Et_3N; ii, Cu–quinoline; iii, I_2–EtOH–$h\nu_{254}$; iv, H_2-PtO_2; v, MeI–K_2CO_3.

The acetate from band E, an amorphous solid, was shown by mass spectrometry and, more quantitatively, by n.m.r. spectroscopy to be a mixture of phenol (E′) acetate (55%) and its dihydro-derivative, phenol (E) acetate (45%). Dehydrogenation of this mixed acetate gave a single crystalline acetate, identical (m.p., mixed m.p., i.r. and n.m.r. spectra) with 4,6,7-triacetoxy-2,3-dimethoxyphenanthrene.[1] Consequently phenol (E′) has structure (VIII) and phenol (E), a new natural product, structure (IX). Catalytic hydrogenation of the mixed acetate gave a single product, which on acid hydrolysis yielded the free phenol (E).

The acetate of phenol (B) showed spectroscopic characteristics (u.v. and n.m.r.) of a 9,10-dihydrophenanthrene, with signals in the n.m.r. for two acetoxy- and three methoxy-groups, and three aromatic protons, all as singlets. Dehydrogenation yielded a substance with spectroscopic characteristics of a substituted phenanthrene (see Tables 1 and 2). Alkaline hydrolysis of this compound followed by methylation gave a pentamethoxyphenanthrene, identical (m.p., mixed m.p., i.r., and n.m.r.) with 2,3,4,6,7-pentamethoxyphenanthrene,[1] thus establishing the oxygenation pattern of phenol (B). Alkaline hydrolysis of the acetate of phenol (B) yielded the free phenol, which on deuteriation in D_2O under basic conditions, followed by acetylation, gave a dideuteriated species (demonstrated by mass spectrometry) showing only one aromatic proton signal in the n.m.r. spectrum. This signal, which does not appear at a particularly low field, can be assigned to either 1- or 8-H.[1] Consequently structures (VII), (X), and (XI) are possible for phenol (B). Since the chemical shifts of the acetoxy-groups in the n.m.r. spectrum of the dehydrogenated derivative of phenol (B) are identical (indicating the absence of an acetoxy group at C-4),[1] structure (XI) is unlikely, especially since phenol (B) gives a negative response to a Gibbs test.[1] Phenol (D′) has already been assigned the structure (VII) on the basis of the unambiguous synthesis of phenol (III) and its dehydro-derivative (*vide supra*), and consequently phenol (B) must have structure (X).

The acetate of phenol (C), a gum, ran as a single spot on t.l.c. and behaved as a single substance. The mass spectrum (M^+, 358, $C_{20}H_{22}O_6$) indicated that the substance lost keten (2 molecules) and fragmented into two stable portions (see Scheme 2), one of which constituted the base peak. The n.m.r. spectrum (see Table 3) showed two methoxy- and two acetoxy-groups, together with four equivalent benzylic protons and six aromatic

TABLE 1

		λ_{max}/nm (log ε)			
9,10-Dihydrophenanthrenes					
2,6-Dihydroxy-3,4,7-trimethoxy-	[phenol (B)]	263 (4·08)	281 (4·27)	306sh (4·12)	315 (4·14)
2,6-Diacetoxy-3,4,7-trimethoxy-		262sh (4·27)	273 (4·36)	304sh (4·10)	
4,6,7-Trihydroxy-2,3-dimethoxy-	[phenol (E)]	264 (4·38)	278 (4·22)	302—310 (4·16)	
4,6,7-Triacetoxy-2,3-dimethoxy-		259 (4·36)	274 (4·32)	306 (4·13)	
Phenanthrenes					
4,7-Dihydroxy-2,3,6-trimethoxy-	[phenol (A)]	262 (4·98)	285 (4·17)	295sh (4·01)	309 (3·98)
2,6-Dihydroxy-3,4,7-trimethoxy-		259 (4·85)	284 (4·42)	300sh (4·14)	309 (4·02)
2,6-Diacetoxy-3,4,7-trimethoxy-		258 (4·90)	282sh (4·39)	291sh (4·26)	303 (4·12)
Bibenzyls					
3,4′-Dihydroxy-4,5-dimethoxy-	[phenol (C)]	210 (4·38)	224sh (4·19)	278 (3·34)	286sh (3·21)
3,4′-Diacetoxy-4,5-dimethoxy-		210 (4·60)	217sh (4·32)	274 (3·47)	300sh (2·94)
3,4,4′,5-Tetramethoxy-		207 (4·62)	225sh (4·26)	277 (3·30)	283 (3·14)
Stilbenes					
3,4′-Diacetoxy-4,5-dimethoxy-		258 (4·14)	303 (4·18)	318 (4·16)	
3,4,4′,5-Tetramethoxy-		235 (4·24)	293 (4·11)		

protons. Dehydrogenation of phenol (C) acetate, with simultaneous decrease of the benzylic proton signals in the n.m.r., took place much more slowly than the dehydrogenation of the 9,10-dihydrophenanthrenes.[1] Phenol (C) acetate, phenol (C) (obtained from the former by alkaline hydrolysis), and the fully methylated phenol all showed u.v. absorbance characteristics of a bibenzyl[6] (see Table 1). Phenol (C), a crystalline compound showing no carbonyl absorption in the i.r., is consequently a dihydroxydimethoxybibenzyl. In the n.m.r. spectrum (see Table 3), the six aromatic protons in the dimethyl ether of phenol (C) appear as an AB quartet (4H; J_{ortho} 8·5 Hz) and a singlet (2H), indicating the symmetrical structure (XII) for this ether. This oxygenation pattern was confirmed by a synthesis of (XII) (see Scheme 1). A Perkin condensation of 4-methoxybenzaldehyde and 3,4,5-trimethoxyphenylacetic acid gave the cinnamic acid (XIII), which on decarboxylation gave the stilbene (XIV), from which (XII) was obtained by catalytic hydrogenation; the product was identical with the dimethyl ether of phenol (C). Some dissymmetry was indicated in the structure of phenol (C), as its n.m.r. spectrum showed two AB quartets for six aromatic protons, one with J 8·5 Hz (4H) and the other with J_{meta} 2 Hz (2H). The exact position of the two hydroxy-groups was determined by deuteriation of phenol (C) with D_2O under basic conditions,[1] and subsequent acetylation, followed by spectroscopic examination of the acetate; the product was a tetradeuteriated species (demonstrated by mass spectrometry) showing only one singlet (2H) in the aromatic region of the n.m.r. spectrum. Consequently phenol (C) has structure (XV).

TABLE 2

Assignments of chemical shifts (τ) in the ^1H n.m.r. spectra of the phenanthrenes and 9,10-dihydrophenanthrenes[a]

		1- or 8-H	8- or 1-H	5-H	9- and 10-H	OMe	OAc or OH
9,10-Dihydrophenanthrenes							
2,6-Dihydroxy-3,4,7-trimethoxy-	[phenol (B)]	3·34	3·44	2·14	7·34 (4H)	6·07 (3H), 6·14 (3H), 6·25 (3H)	4·22 (1H),* 4·54 (1H) *
2,6-Diacetoxy-3,4,7-trimethoxy-		3·27	3·38	2·04	7·30 (4H)	6·17 (3H), 6·21 (3H), 6·32 (3H)	7·70 (6H)
[1,5-$^2H_2$]-2,6-Diacetoxy-3,4,7-trimethoxy-		3·27			7·30 (4H)	6·17 (3H), 6·21 (3H), 6·32 (3H)	7·70 (6H)
4,6,7-Trihydroxy-2,3-dimethoxy-	[phenol (E)]	3·33	3·68	2·11	7·35 (4H)	6·15 (6H)	6·05 (1H),* 6·80 (2H) *
4,6,7-Triacetoxy-2,3-dimethoxy-		3·36	3·03	2·34	7·28 (4H)	6·18 (3H), 6·21 (3H)	7·68 (3H), 7·74 (6H)
Phenanthrenes							
4,7-Dihydroxy-2,3,6-trimethoxy-	[phenol (A)]	3·17	2·75	0·94	2·57 (2H)	5·97 (3H), 6·02 (3H), 6·05 (3H)	3·01 (1H),* 4·19 (1H) *
2,6-Dihydroxy-3,4,7-trimethoxy-		2·86	2·89	1·03	2·56 (2H)	5·94 (3H), 6·00 (3H), 6·06 (3H)	4·05 (1H),* 4·18 (1H) *
2,6-Diacetoxy-3,4,7-trimethoxy-		2·76	2·82	0·88	2·54 (2H)	6·05 (3H), 6·07 (6H)	7·63 (6H)

* Signals removed on shaking with D_2O.

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

TABLE 3

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

Bibenzyls		2- or 6-H	6- or 2-H	3′,5′- or 2′,6′-H	2′,6′- or 3′,5′-H	α,α′	OMe	OAc or OH
3,4′-Dihydroxy-4,5-dimethoxy-	[phenol (C)]	3·64 (d, J 2)	3·84 (d, J 2)	3·08 (d, J 8·5)	3·33 (d, J 8·5)	7·26 (4H)	6·21 (3H), 6·27 (3H)	4·3 (2H) *
3,4′-Diacetoxy-4,5-dimethoxy-		3·58	3·58	2·94 (d, J 8)	3·12 (d, J 8)	7·20 (4H)	6·26 (3H), 6·29 (3H)	7·73 (3H), 7·79 (3H)
[$^2H_2$]-3,4′-Diacetoxy-4,5-dimethoxy-				2·94		7·18 (4H)	6·25 (6H)	7·72 (3H), 7·76 (3H)
3,4,4′,5-Tetramethoxy-		3·70	3·70	2·98 (d, J 8·5)	3·28 (d, J 8·5)	7·20 (4H)	6·22 (9H), 6·27 (3H)	

* Signal removed on shaking with D_2O.

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

Only one bibenzyl appears to have been isolated previously as a natural product, *viz.* 3-hydroxy-5-methoxybibenzyl from the heartwood of *Pinus albicaulis*.[7] Lindstedt's studies on the genus *Pinus* show that this bibenzyl co-occurs only with flavonoids and stilbenes, and that the bibenzyl probably arises from the more ubiquitous stilbenes.[8]

The unique association of a bibenzyl with phenanthrenes and 9,10-dihydrophenanthrenes in *Combretum molle* gives rise to considerable biogenetic speculation. It is conceivable that the bibenzyls are the immediate precursors of the phenanthrenes and 9,10-dihydrophenanthrenes, the latter being formed *via* phenolic oxidation of the bibenzyls. The presence of the particular bibenzyl (XV) may be associated with the fact that *para–para* and *ortho–para* coupling to produce the 9,10-dihydrophenanthrene directly is not possible,

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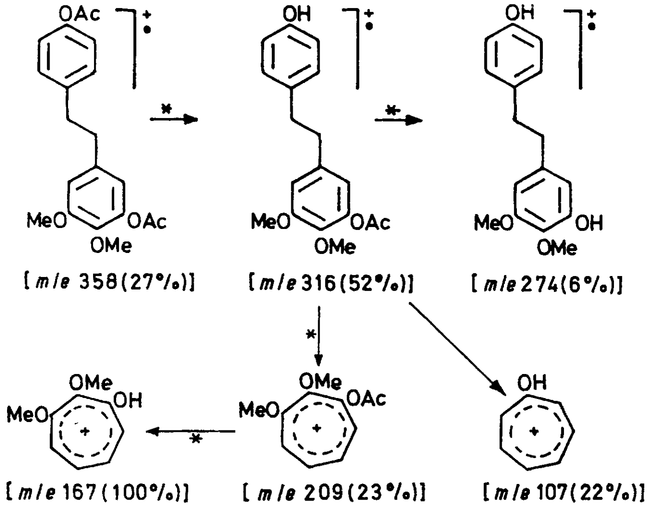
[6] E. S. Stern and C. J. Timmons, 'Electronic Absorption Spectroscopy in Organic Chemistry,' Arnold, London, 3rd edn., **1970**, ch. 6.

[7] G. Lindstedt, *Acta Chem. Scand.*, 1950, **4**, 1246.

[8] G. Lindstedt, *Acta Chem. Scand.*, 1951, **5**, 129.

unless of course a dienone–phenol rearrangement[9] is involved. All the eight phenanthrenes and 9,10-dihydrophenanthrenes so far reported[1] from the *Combretaceae* have oxygen functions in the appropriate positions for the compounds to have arisen *via ortho–para* or *para–para* coupling of the hypothetical bibenzyl, or in some cases the unmethylated hypothetical bibenzyl.



SCHEME 2

One other, though less likely explanation for the presence of the bibenzyl, is that it may arise from the 9,10-dihydrophenanthrene by a reductive ring opening (*i.e.*, a reversal of the phenol oxidation process).

It has been shown[10] that the 10-nitro-phenanthrene-1-carboxylic acids in the genus *Aristolochia* arise *via* the aporphine alkaloids, which are themselves tyrosine- or dihydroxyphenylalanine-based, but no biogenetic studies appear to have been carried out on the very few nitrogen-free phenanthrenes and 9,10-dihydrophenanthrenes known in nature.[1] Since the phenanthrenes, 9,10-dihydrophenanthrenes and bibenzyl in *Combretum molle* are present in the heartwood, direct proof of biogenetic theories by isotope labelling would not be easy.

EXPERIMENTAL

Combustion analyses were carried out in the Microanalytical Laboratory of the University of Natal, Pietermaritzburg. M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were recorded with a Unicam SP 800 spectrometer for solutions in 95% ethanol. I.r. spectra were recorded with a Unicam SP 200 spectrometer for potassium bromide discs unless otherwise stated; only bands over 1500 cm^{-1} are quoted. N.m.r. spectra are for solutions in [^{2}H]chloroform and were obtained with a Perkin-Elmer R 12 spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded with an A.E.I. MS-9 spectrometer. Preparative t.l.c. was performed on plates prepared with Kieselgel GF$_{254}$ (Merck). The general techniques and reactions are described in reference 1.

Extraction of the Heartwood.—By the procedure we have described,[1] the dark coloured heartwood (760 g) yielded a brown oily light petroleum extract (5 g) and a brown solid (16 g) from the ether extraction.

Isolation of the Phenolic Constituents.—The ether extract (9·6 g) was chromatographed as previously described,[1] and yielded a red-coloured gum from each band: (A) (0·6 g), B (0·8 g), C (1·0 g), D (0·6 g), and E (1·0 g) (R_F 0·78, 0·70, 0·57, 0·50, and 0·35 respectively). These phenolic products (which exhibited no carbonyl absorption in the i.r.) were acetylated, purified by t.l.c., and isolated as previously described,[1] yielding an amorphous acetate from band A (200 mg) [phenol (A) acetate and phenol (A′) acetate], a crystalline acetate from band B (350 mg) [phenol (B) acetate], an oil from band C (500 mg) [phenol (C) acetate], and amorphous acetates from band D (200 mg) [phenol (D) acetate and phenol (D′) acetate] and band E (250 mg) [phenol (E) acetate and phenol (E′) acetate].

4,7-*Dihydroxy*-2,3,6-*trimethoxyphenanthrene* [*Phenol* (*A*)].—The amorphous acetate from band A had m.p. 125—145°, τ 1·42, 2·46, 2·54, 2·85, 3·16, 3·34, 6·04, 6·10, 6·15, 6·19, 7·32, 7·54, 7·66, and 7·70, *m*/*e* 386, 384, 344, 342, 302 (base peak), and 300. Dehydrogenation gave quantitatively a crystalline substance, m.p. 157—159°, identical (mixed m.p., i.r., and n.m.r.) with 4,7-diacetoxy-2,3,6-trimethoxyphenanthrene.[1] Alkaline hydrolysis of this acetate gave 4,7-*dihydroxy*-2,3,6-*trimethoxyphenanthrene* as prisms, m.p. 195—196° (from ethanol), $\nu_{max.}$ 3400, 1635, 1620, 1585, and 1525 cm^{-1}, *m*/*e* 300 (base peak) and 285 (Found: C, 68·0; H, 5·5. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·4%). The phenol gives a positive response to Gibbs test.[1] For u.v. and n.m.r. spectral data see Tables 1 and 2 respectively.

The amorphous acetate from band D had m.p. 114—124°, τ 0·60, 1·95, 2·30, 2·40, 2·87, 3·05, 3·50, 5·95, 5·97, 6·08, 6·18, 7·28, 7·62, 7·63, and 7·73. Dehydrogenation gave prisms, m.p. 121—123°, identical (mixed m.p., i.r., and n.m.r.) with phenol (C′) acetate isolated from *Combretum apiculatum*.[1]

4,6,7-*Trihydroxy*-2,3-*dimethoxy*-9,10-*dihydrophenanthrene* [*Phenol* (*E*)].—The amorphous acetate from band E had m.p. 148—167°, τ 1·16, 2·34, 2·42, 2·49, 2·86, 3·03, 3·36, 6·04, 6·10, 6·16, 6·21, 7·28, 7·51, 7·67, and 7·74, *m*/*e* 414, 412, 372, 370, 330, 328, 288 (base peak), and 286. Dehydrogenation gave (quantitatively) prisms, m.p. 168—171°, identical (mixed m.p., i.r., and n.m.r.) with 4,6,7-triacetoxy-2,3-dimethoxyphenanthrene.[1] Hydrogenation of the amorphous acetate (100 mg) with Adams catalyst (50 mg) in glacial acetic acid (20 ml) under hydrogen (20 lb in^{-2}) with shaking for 24 h at room temperature gave (quantitatively) 4,6,7-*triacetoxy*-2,3-*dimethoxy*-9,10-*dihydrophenanthrene* as prisms, m.p. 143—146° (from ethanol), $\nu_{max.}$ 1763, 1610, and 1500 cm^{-1}, *m*/*e* 414, 372, 330, and 288 (base peak) (Found: C, 63·7; H, 5·4. $C_{22}H_{22}O_8$ requires C, 63·8; H, 5·35%).

4,6,7-Triacetoxy-2,3-dimethoxy-9,10-dihydrophenanthrene (44 mg) dissolved in ethanol (2 ml) was heated under reflux for 5 min in concentrated hydrochloric acid (3 ml) under nitrogen. The ethanol was evaporated off under reduced pressure, whereupon the clear solution became turbid. This acidic solution was saturated with sodium chloride and extracted with chloroform (4 × 20 ml). Evaporation of the washed (saturated sodium chloride solution) and dried ($MgSO_4$) chloroform extracts gave (almost quantitatively) 4,6,7-*trihydroxy*-2,3-*dimethoxy*-9,10-*dihydrophenanthrene* as slightly pink laths, m.p. 189—190° (from benzene), $\nu_{max.}$ 3500—3150br, 2930, 1625sh, 1615,

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[9] D. H. R. Barton and T. Cohen, 'Festschrift A. Stoll,' Birkhauser, Basel, 1957, p. 125.

[10] I. D. Spenser and H. P. Tiwari, *Chem. Comm.*, 1966, 55.

1595sh, and 1520 cm^{-1}, *m/e* 288 (base peak) and 273 (Found: C, 66·3; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%). For u.v. and n.m.r. data see Tables 1 and 2.

2,6-*Dihydroxy*-3,4,7-*trimethoxy*-9,10-*dihydrophenanthrene* [*Phenol* (*B*)].—2,6-*Diacetoxy*-3,4,7-*trimethoxy*-9,10-*dihydrophenanthrene* [*phenol* (*B*) *acetate*] crystallised as prisms, m.p. 172—175° (from ethanol), $\nu_{max.}$ 1760, 1620, and 1520 cm^{-1}, *m/e* 386, 344, and 302 (base peak) (Found: C, 65·0; H, 5·8. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%). Alkaline hydrolysis gave 2,6-*dihydroxy*-3,4,7-*trimethoxy*-9,10-*dihydrophenanthrene* as prisms, m.p. 155—156° (from benzene–light petroleum), $\nu_{max.}$ 3430, 2900, 1620, 1597, and 1520 cm^{-1}, *m/e* 302 (base peak) and 287 (Found: C, 67·7; H, 6·1. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%). This phenol exhibits a negative response to Gibbs test. Dehydrogenation of phenol (B) acetate gave 2,6-*diacetoxy*-3,4,7-*trimethoxyphenanthrene* as prisms, m.p. 135—136° (from ethanol), $\nu_{max.}$ 1755, 1615, and 1515 cm^{-1}, *m/e* 384, 342, 300 (base peak), and 285 (Found: C, 65·3; H, 5·7. $C_{21}H_{20}O_7$ requires C, 65·6; H, 5·2%). Alkaline hydrolysis gave 2,6-*dihydroxy*-3,4,7-*trimethoxyphenanthrene*, m.p. 182—185° (from ethanol), $\nu_{max.}$ 3280, 2900, 1620, 1585, and 1530 cm^{-1}, *m/e* 300 (base peak) and 285 (Found: C, 68·45; H, 5·7. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·4%). Methylation gave a product, m.p. 134—136°, identical (mixed m.p., i.r., and n.m.r.) with 2,3,4,6,7-pentamethoxyphenanthrene.[1] For u.v. and n.m.r. data see Tables 1 and 2.

3,4′-*Dihydroxy*-4,5-*dimethoxybibenzyl* [*Phenol* (*C*)].—3,4′-*Diacetoxy*-4,5-*dimethoxybibenzyl* [*Phenol* (*C*) *acetate*] was obtained as an oil, $\nu_{max.}$ (film) 1755, 1610, 1590, and 1515 cm^{-1}, *m/e* 358, 316, 274, 209, 167 (base peak), and 107 (M^+, 358·1451. $C_{20}H_{22}O_6$ requires *M*, 358·1415; base peak 167·0684. $C_9H_{11}O_3$ requires base peak, 167·0708). Alkaline hydrolysis gave 3,4′-*dihydroxy*-4,5-*dimethoxybibenzyl* as prisms, m.p. 128—130° (from chloroform–light petroleum), $\nu_{max.}$ 3500—3300, 1600, and 1522 cm^{-1}, *m/e* 274, 167 (base peak), and 107 (Found: C, 69·45; H, 6·9. $C_{16}H_{18}O_4$ requires C, 70·05; H, 6·6%). This phenol gives a positive response to the Gibbs test. Methylation gave 3,4,4′,5-*tetramethoxybibenzyl* as a gum, which solidifies under high vacuum at 0° to give a solid, m.p. *ca.* 15°, $\nu_{max.}$ (film) 2950, 1600, and 1525 cm^{-1}, *m/e* 302, 181 (base peak), and 121 (Found: C, 71·4; H, 7·7. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3%). Dehydrogenation of phenol (C) acetate during 10 days gave 3,4′-*diacetoxy*-4,5-*dimethoxystilbene* as a gum, $\nu_{max.}$ (film) 1765, 1610, 1590, and 1520 cm^{-1}, *m/e* 356, 314, 272 (base peak), and 257. For u.v. and n.m.r. data see Tables 1 and 3.

Synthesis of 6,7-*Diacetoxy*-2,3,4-*trimethoxyphenanthrene* [*Phenol* (*D*) *acetate*].—A mixture of 3,4-dihydroxybenzaldehyde[11] (0·5 g), 3,4,5-trimethoxyphenylacetic acid[1] (0·7 g), acetic anhydride (1 ml), and triethylamine (0·5 ml) was heated under reflux for 2 h. The solution was evaporated under reduced pressure to leave a gum, which was warmed with dilute ammonia solution and charcoal. The solution was filtered, washed with chloroform, and acidified with dilute hydrochloric acid to give a solid (1·0 g). This was filtered off and crystallised from aqueous ethanol to give needles of α-(3,4,5-*trimethoxyphenyl*)-3,4-*dihydroxycinnamic acid* (V), m.p. 238—240°, $\nu_{max.}$ 3500—2500br, 1675, 1595, and 1520 cm^{-1}, $\lambda_{max.}$ 240sh (log ε 4·43) and 329 nm (4·38) (Found: C, 62·3; H, 5·45. $C_{18}H_{18}O_7$ requires C, 62·4; H, 5·2%). After treating the acid (V) with acetic anhydride–pyridine for 2 h at 90°, the solution was evaporated and the resulting gum (0·4 g) was mixed with quinoline (5 ml) and copper chromite (0·1 g), and heated under reflux for 15 min under nitrogen. Ethyl acetate was added and the product was filtered off through Celite. The filtrate was washed with dilute hydrochloric acid, water, dried ($MgSO_4$), and evaporated to leave a residue, which was also treated with acetic anhydride–pyridine for 2 h at 90°. This solution was evaporated under reduced pressure and the residue was purified by t.l.c. [methanol–chloroform (2 : 100)] yielding 3′,4′-*diacetoxy*-3,4,5-*trimethoxystilbene* (0·2 g) (VI) as an oil, $\nu_{max.}$ 1770, 1590, and 1510 cm^{-1}, $\lambda_{max.}$ 320 (log ε 4·41), τ 2·8 (3H, m, $w_{\frac{1}{2}}$ 7 Hz), 3·16 (2H, s), 3·39 (2H, s), 6·16 (9H, s), and 7·74 (6H, s) (Found: C, 65·2; H, 5·55. $C_{21}H_{22}O_7$ requires C, 65·3; H, 5·7%). A stirred solution of the diacetate (VI) (0·2 g) and iodine (0·02 g) in ethanol (400 ml) in an open beaker was irradiated for 4 h with a 125 W medium-pressure lamp situated 20 cm directly above the liquid surface. The reaction was followed by measurement of the u.v. absorption spectrum of the solution, which showed a gradual decrease in $\lambda_{max.}$ for stilbene at 320 nm with simultaneous increase in the very strong phenanthrene absorption at 261 nm. The solution was evaporated under reduced pressure and the residue purified by t.l.c. Only one dark band was detected on the plates under u.v. light (254 nm), and extraction of that band followed by crystallisation of the product gave 6,7-diacetoxy-2,3,4-trimethoxyphenanthrene (30 mg) as prisms, m.p. 121—123°, identical (mixed m.p., i.r., and n.m.r.) with phenol (D) acetate above and with phenol (C′) acetate from *Combretum apiculatum*.[1]

Synthesis of 3,4,4′,5-*Tetramethoxybibenzyl*.—A mixture of 4-methoxybenzaldehyde (1·0 g), 3,4,5-trimethoxyphenylacetic acid[1] (1·0 g), acetic anhydride (2 ml), and triethylamine (1 ml) was heated under reflux for 3 h. After acidification with concentrated hydrochloric acid (3 ml), the product (800 mg) was filtered off and crystallised from aqueous ethanol yielding laths of α-(3,4,5-*trimethoxyphenyl*)-4-*methoxycinnamic acid* (XIII), m.p. 198—202°, $\nu_{max.}$ 3000—2500br, 1670, 1610, 1590, and 1520 cm^{-1}, $\lambda_{max.}$ 225sh (log ε 4·31) and 308 (4·21) nm, τ 2·19 (1H, s), 3·00 (2H, d, *J* 9 Hz), 3·33 (2H, d, *J* 9 Hz), 3·58 (2H, s), 6·13 (3H, s), and 6·25 (9H, s) (Found: C, 66·2; H, 6·05. $C_{19}H_{20}O_6$ requires C, 66·3; H, 5·85%). A mixture of acid (XIII) (0·25 g), quinoline (5 ml), and basic copper carbonate (0·3 g) was heated under reflux for 1·5 h, cooled, and extracted with ether (50 ml). The ethereal solution was washed with dilute hydrochloric acid, followed by saturated sodium chloride solution, dried ($MgSO_4$), and evaporated. The product was purified by t.l.c. (developed with chloroform) to give 3,4,4′,5-*tetramethoxystilbene* (XIV) (85 mg) as a gum, $\nu_{max.}$ (film), 2950, 2820, 1515, 1585, and 1520 cm^{-1}, τ 3·1 (8H, m, $w_{\frac{1}{2}}$ 28 Hz) and 6·25 (12H, m, $w_{\frac{1}{2}}$ 30 Hz), *m/e* 300 (base peak) and 285. Hydrogenation of (XIV), as before, yielded 3,4,4′,5-tetramethoxybibenzyl (XII) as a gum, identical (i.r. and n.m.r.) with the product obtained above.

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