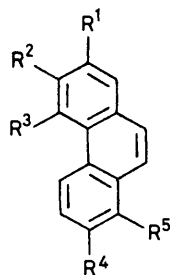


## Structure and Synthesis of the Phenanthrenes Tal and TaV from *Tamus communis*

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Using photochemical syntheses, the structure of TaV has been confirmed as 2,5,6,7-tetramethoxy-1-phenanthrol, and the structure of Tal revised to 1,2-methylenedioxy-5,6,7-trimethoxyphenanthrene. The influence of certain substituents at C-4 on the chemical shift of the C-5 proton in phenanthrenes is demonstrated.

REISCH *et al.* have isolated a number of crystalline products from the rhizomes of *Tamus communis* and to seven of these they have assigned<sup>1,2</sup> simple substituted phenanthrene structures. Apart from the extractive D.C. whose structure (1) was confirmed by synthesis,<sup>3</sup> all



- (1) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = OMe  
 (2) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = OMe, R<sup>5</sup> = OH  
 (2a) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = OMe, R<sup>5</sup> = OAc  
 (3) R<sup>1</sup> = R<sup>4</sup> = R<sup>5</sup> = OMe, R<sup>2</sup>, R<sup>3</sup> = OCH<sub>2</sub>O  
 (4) R<sup>1</sup> = R<sup>4</sup> = R<sup>5</sup> = OMe, R<sup>2</sup> = R<sup>3</sup> = OAc  
 (5) R<sup>1</sup> = R<sup>2</sup> = OAc, R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = OMe  
 (6) R<sup>1</sup>, R<sup>2</sup> = OCH<sub>2</sub>O, R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = OMe  
 (7) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = OMe, R<sup>4</sup>, R<sup>5</sup> = OCH<sub>2</sub>O

other *T. communis* extractives have been assigned structures using non-rigorous methods such as the rate of methylation or from biogenetic considerations. That such methods could result in incorrect structure assignments was shown by Letcher,<sup>4</sup> who revised the structure for TaVI to 7-hydroxy-2,4,6-trimethoxyphenanthrene, using an unambiguous method based on deuteration of phenanthrols followed by n.m.r. spectral analysis. In the present paper, structures (2) and (3) proposed by Reisch *et al.* for TaV<sup>2</sup> and Tal<sup>1</sup> respectively, are considered.

Reisch *et al.* confirmed the oxygenation pattern of the hydroxytetramethoxyphenanthrene TaV, from its ready methylation to (1), but the position of the hydroxy group was less rigorously determined as it followed from an argument based on the position of the methoxy signals which occur over a very narrow range in the n.m.r. spectrum.<sup>2</sup> Structural proof however is readily obtainable from synthesis. The synthesis of 2,5,6,7-tetra-

methoxy-1-phenanthryl acetate (2a) was achieved by the unambiguous photocyclisation of 2-acetoxy-3,3',4',5'-tetramethoxystilbene, prepared by a Wittig reaction, and the product was found to be identical (mixed m.p., i.r., and n.m.r.) with an authentic sample of TaV acetate, thus confirming structure (2) for TaV. An attempt to synthesise (2) by photocyclisation of the expected cinnamic acid from the Perkin condensation of *o*-vanillin and 3,4,5-trimethoxyphenylacetic acid was not possible as the Perkin condensation yielded no cinnamic acid but a new coumarin, 3-(3,4,5-trimethoxyphenyl)-8-methoxycoumarin.

Relatively few reliable spectroscopic methods for the locating of substituents in phenanthrene systems are known. In particular it would be most useful to have a method which does not rely on the deuteration<sup>5</sup> of phenanthrols for cases where no suitably placed hydroxy group is present. In the n.m.r. spectra of phenanthrenes it has been observed<sup>5</sup> that the proton at C-5 (or at C-4) resonates at a lower field than the remaining aromatic protons. Therefore, being readily identifiable, it is possible to study the influence of various substituents at C-4 on the chemical shift of this C-5 proton. Thus in the case of some 26 4,6-disubstituted 5-unsubstituted phenanthrenes exemplified by all the nine 2,3,4,6,7-penta- and 2,4,6,7-tetra-substituted phenanthrenes from the *Combretum* species,<sup>5-8</sup> 3,4-dimethoxy-6-ethoxyphenanthrene (see below), and others,<sup>4,9</sup> together with their derivatives, it is apparent that the 4-methoxy group (and also the 4-hydroxy) is associated with a particularly low-field aromatic proton, H-5 with  $\delta$  8.88–9.40, and in compounds with a 4-acetoxy group the low-field proton resonates appreciably higher, between  $\delta$  8.40 and 8.93. This substituent-dependent trend is even more sharply defined in cases where the influence of the adjacent substituent at C-6 is constant. Table I lists a number of such phenanthrene derivatives in which both positions 5 and 6 are unsubstituted. Apart from (4) and (5), the structures have all been previously established or follow from their synthesis (see below). Table I shows that when C-6 is unsubstituted, 4-hydroxy- and 4-methoxy-phenanthrenes are associated with an H-5 doublet at  $\delta$  9.42–9.52 and 9.20–9.65 respectively,

<sup>5</sup> R. M. Letcher and L. R. M. Nhamo, *J. Chem. Soc. (C)*, 1971, 3070.

<sup>6</sup> R. M. Letcher, L. R. M. Nhamo, and I. T. Gumiro, *J.C.S. Perkin I*, 1972, 206.

<sup>7</sup> R. M. Letcher and L. R. M. Nhamo, *J.C.S. Perkin I*, 1972, 2941.

<sup>8</sup> R. M. Letcher and L. R. M. Nhamo, *J.C.S. Perkin I*, 1973, 1179.

<sup>9</sup> R. M. Letcher, *Phytochemistry*, 1973, 2789.

<sup>1</sup> J. Reisch, M. Báthory, K. Szendrei, E. Minker, and I. Novák, *Tetrahedron Letters*, 1969, 67.

<sup>2</sup> J. Reisch, M. Báthory, K. Szendrei, I. Novák, and E. Minker, *Phytochemistry*, 1973, 228.

<sup>3</sup> J. Reisch, M. Báthory, I. Novák, and K. Szendrei, *Herba Hungarica*, 1970, 9, 43.

<sup>4</sup> R. M. Letcher and L. R. M. Nhamo, *Tetrahedron Letters*, 1972, 4869.

the two being readily distinguished by a marked shift (*ca.* 0.6 p.p.m.) of H-5 to higher field on acetylation, shown only by 4-hydroxyphenanthrenes. The 4-acetoxypheanthrenes listed exhibit H-5 at  $\delta$  8.96 and 8.62.

TABLE 1  
Low-field  $^1\text{H}$  n.m.r. spectra ( $\delta$  values;  $J$  in Hz) for  $\text{CDCl}_3$  solutions

Substituted phenanthrene	H-5 ( $J$ )
7-Acetoxy-4-methoxy <sup>a</sup>	9.65 (9.5)
7-Hydroxy-4-methoxy <sup>a</sup>	9.53 (10)
4-Acetoxy-7-methoxy <sup>a</sup>	8.96 (10)
4-Hydroxy-7-methoxy <sup>a</sup>	9.52 (10)
7-Acetoxy-2,4-dimethoxy <sup>b</sup>	9.46 (10)
7-Hydroxy-2,4-dimethoxy <sup>b</sup>	9.37 (11)
1-Acetoxy-2,5,6,7-tetramethoxy	9.40 (10)
3,4-Diacetoxy-2,7,8-trimethoxy (4)	8.62 (9.5)
3,4-Dihydroxy-2,7,8-trimethoxy	9.42 (9.5)
2,3-Diacetoxy-4,7,8-trimethoxy (5)	9.20 (9.5)
2,3-Dihydroxy-4,7,8-trimethoxy	9.34 (9.5)
7,8-Diacetoxy-2,3,4-trimethoxy	9.45 (9.5)
2,4-Dimethoxy	9.50 (8.0, 3.0)
3,4-Methylenedioxy-7,8-dimethoxy	8.81 (9.5)

<sup>a</sup> See ref. 10. <sup>b</sup> R. M. Letcher and L. R. M. Nhamo, *J.C.S. Perkin I*, 1973, 1263.

Table 1 also suggests that the influence of the 3,4-methylenedioxy-group on the chemical shift of H-5 is much less pronounced, the relevant signal appearing at  $\delta$  8.81. It is interesting to note that in cases of alkoxy-substituted phenanthrenes having no 4- and 5-substituents, particularly low-field signals are absent with H-4 and -5 resonating at  $\delta$  7.77—8.45, *i.e.* close to or in the region where the other aromatic signals appear (see Table 2).

TABLE 2  
Low-field  $^1\text{H}$  n.m.r. spectra ( $\delta$  values;  $J$  in Hz) for  $\text{CDCl}_3$  solutions

Substituted phenanthrene	H-4, H-5, or aryl-H
2-Methoxy-7-acetoxy <sup>a</sup>	8.4 (1 H, d, $J$ 10), 8.45 (1 H, d, $J$ 9.5)
2,3-Methylenedioxy-7,8-dimethoxy	7.93 (1 H, s), 8.17 (1 H, s, $J$ 9.5)
2,3-Dimethoxy-6-ethoxy	7.05—7.9 (7 H, m)
1,2-Dimethoxy-6-ethoxy	8.30 (1 H, d, $J$ 9.5), 7.1—8.1 (6 H, m)
1-Methoxy-6-ethoxy	6.85—8.30 (8 H, m)
3-Methoxy-6-ethoxy	7.81 (2 H, d, $J$ 2.5)
2,3-Methylenedioxy-6-ethoxy	7.88 (1 H, s), 7.77 (1 H, d, $J$ 2.5)

<sup>a</sup> See ref. 10.

Photocyclisation of 3,4-diacetoxy-2',3',5-trimethoxystilbene yielded two products both exhibiting low-field *ortho*-coupled (d,  $J$  9.5 Hz) proton signals in their n.m.r. spectra. These must be (4) and (5). Structural assignments to the two products can be made using the previously observed feature<sup>5</sup> that the 4-(or 5)-acetoxy proton signals appear at a somewhat different chemical shift from all other phenanthrene acetoxy protons. The product with the larger difference in chemical shift between the acetoxy protons is therefore assigned the 4-acetoxy structure, *viz.* (4). This was further confirmed

<sup>10</sup> R. M. Letcher and K. M. Wong, *J.C.S. Perkin I*, 1977, 178.

<sup>11</sup> J. Reisch, K. Szendrei, E. Minker, and I. Novák, *Herba Hungarica*, 1969, 8, 139.

<sup>12</sup> H. Pauly, K. Schübel, and K. Lockemann, *Annalen*, 1911, 383, 312.

on hydrolysing the acetates, when only the latter diphenol exhibited a considerable change in chemical shift of the low field proton (H-5) (from  $\delta$  8.62 to 9.42), when compared with its diacetate.<sup>10</sup>

When considering the proposed structure (3) for TaI which was based on biogenetic considerations,<sup>1,11</sup> and comparing the reported n.m.r. data (which includes a doublet at  $\delta$  9.17)<sup>1</sup> with the conclusions from Table 1, it is apparent that a reinvestigation of this structure is necessary. With this in mind (3) was synthesised. Photocyclisation of 3,4-methylenedioxy-2',3',5-trimethoxystilbene gave the two expected products, (3) and (6), whose structures were assigned on the basis of the conclusions from Table 1: the substance with m.p. 188—189° and which exhibited a low-field signal at  $\delta$  8.54 is (3), whilst the other with m.p. 120—122° and  $\delta$  9.23 is (6); both the low-field signals in (3) and (6) show *ortho*-coupling ( $J$  9.5 Hz). Neither of these two products is TaI since TaI is reported to have m.p. 151—152°.<sup>1</sup> However, we have now synthesised (7) *via* the unambiguous photocyclisation of 2,3-methylenedioxy-3',4',5'-trimethoxystilbene, and have found the product to be identical with TaI (by mixed m.p. and i.r. with an authentic sample, and see Table 3 for a comparison of n.m.r. and u.v. spectra with published data<sup>1,11</sup>).

## EXPERIMENTAL

Details of general techniques and physical measurements are described in ref. 10. N.m.r. spectra were recorded using a Perkin-Elmer R20 spectrometer.

**8-Methoxy-3-(3,4,5-trimethoxyphenyl)coumarin.**—A mixture of 3,4,5-trimethoxyphenylacetic acid (3 g), *o*-vanillin (1.5 g), acetic anhydride (10 ml), and triethylamine (1 ml) was heated overnight at 90°. After acidification with concentrated hydrochloric acid (5 ml) the product was filtered and crystallised yielding 8-methoxy-3-(3,4,5-trimethoxyphenyl)coumarin (2 g), m.p. 172—174° (methanol),  $\nu_{\text{max}}$  1 700 and 1 570  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  335 nm ( $\log \epsilon$  4.38),  $\delta$  3.89 (3 H, s), 3.92 (6 H, s), 3.98 (3 H, s), 6.93 (2 H, s), 7.13—7.25 (3 H, m), and 7.76 (1 H, s), *m/e* 342 ( $M^+$ , base peak), 327, and 299 (Found: C, 66.65; H, 5.6.  $\text{C}_{19}\text{H}_{18}\text{O}_6$  requires C, 66.65; H, 5.3%).

**Preparation of Benzenoid Starting Materials.**—Acetylation of 2,3-dihydroxybenzaldehyde, m.p. 107—108° (lit.,<sup>12</sup> 108°), gave 2,3-diacetoxybenzaldehyde, m.p. 98—99° (benzene),  $\delta$  2.21 (3 H, s), 2.29 (3 H, s), 7.30—7.90 (3 H, m), and 10.0 (1 H, s) (Found: C, 59.4; H, 4.3.  $\text{C}_{11}\text{H}_{10}\text{O}_5$  requires C, 59.45; H, 4.55%), and methylenation [methylene bromide, anhydrous potassium carbonate, and copper(II) oxide in deoxygenated anhydrous dimethylformamide] gave 2,3-methylenedioxybenzaldehyde as an oil (lit.,<sup>13</sup> m.p. 34°),  $\nu_{\text{max}}$  1 680, 1 630, 1 600, and 1 500  $\text{cm}^{-1}$ ,  $\delta$  6.60 (2 H, s), 6.80—7.30 (3 H, m), and 10.05 (1 H, s), *m/e* 150 ( $M^+$ ), 149 (base peak), and 135.

Acetylation of 3,4-dihydroxy-5-methoxybenzaldehyde, m.p. 131—133° (lit.,<sup>13</sup> 132—134°) gave 3,4-diacetoxy-5-methoxybenzaldehyde, m.p. 97—98° (lit.,<sup>14</sup> 98—99°), and methylenation gave 3,4-methylenedioxy-5-methoxybenzaldehyde, m.p. 130—131° (lit.,<sup>15</sup> 128—129°).

<sup>13</sup> W. H. Perkin and V. M. Trikojus, *J. Chem. Soc.*, 1926, 2931.

<sup>14</sup> W. Bradley, R. Robinson, and G. Schwarzenbach, *J. Chem. Soc.*, 1930, 793.

<sup>15</sup> A. T. Shulgin, *Canad. J. Chem.*, 1968, 75.

*Synthesis of Phenanthrenes.*—Unless otherwise stated all stilbenes were prepared from Wittig reactions of the appropriate aldehyde and benzyltriphenylphosphonium chloride using *n*-butyl-lithium in sodium dried benzene solution. The benzyl chlorides for preparing the phosphonium chlorides were obtained from the corresponding benzyl alcohols using thionyl chloride, and the benzyl alcohols in turn were prepared by sodium borohydride reduction or catalytic reduction [Adams catalyst together with a catalytic amount of iron(II) chloride] of the corresponding aldehydes. Unless otherwise stated the stilbenes were isolated only as mixtures of *cis*- and *trans*-isomers and in yields of 50–70%. Irradiations were carried out in cyclohexane solutions containing 0.005% iodine, using either aerial photolysis<sup>6</sup> or a Hanovia photochemical reactor (1 l) fitted with a 100 W medium pressure mercury arc surrounded by a quartz envelope. Similar results were obtained from either method, and the products were isolated as described in ref. 6.

(a) *Photolysis of 2-acetoxy-3,3',4',5'-trimethoxystilbene.* 3,4,5-Trimethoxybenzyl alcohol<sup>16</sup> and 2-acetoxy-3-methoxybenzaldehyde<sup>17</sup> gave *trans*-2-acetoxy-3,3',4',5'-tetramethoxystilbene, m.p. 131–133° (methanol),  $\nu_{\max}$  1760 and 1580  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  312 (log  $\epsilon$  4.45) and 235 nm (4.36),  $\delta$  2.34 (3

264 nm (log  $\epsilon$  4.81),  $\delta$  3.97 (6 H, s), 4.06 (3 H, s), 5.98 (2 H, s), 6.93 (1 H, s), 7.24 (1 H, d, *J* 9.5 Hz), 7.47 (1 H, d, *J* 9 Hz), 7.96 (1 H, d, *J* 9 Hz), and 9.23 (1 H, d, *J* 9.5 Hz), *m/e* 312 ( $M^+$ , base peak), 252, and 198 (Found: C, 69.1; H, 5.2.  $\text{C}_{18}\text{H}_{16}\text{O}_5$  requires C, 69.2; H, 5.15%), the latter being the least soluble in methanol.

(c) *Photolysis of 2,3-methylenedioxy-3',4',5'-trimethoxystilbene.* 3,4,5-Trimethoxybenzyl alcohol and 2,3-methylenedioxybenzaldehyde gave 2,3-methylenedioxy-3',4',5'-trimethoxystilbene as an oil,  $\lambda_{\max}$  310 nm (log  $\epsilon$  4.30), *m/e* 314 ( $M^+$ , base peak) and 299. Irradiation gave 1,2-methylenedioxy-5,6,7-trimethoxyphenanthrene (7) (60%), m.p. 145–146° (methanol), *m/e* 312 ( $M^+$ , base peak), 297, 267, and 254. An authentic sample of TaI, m.p. 144–146°, showed no depression when mixed with (7).

(d) *Photolysis of 3,4-diacetoxy-2',3',5'-trimethoxystilbene.* 2,3-Dimethoxybenzyl alcohol and 3,4-diacetoxy-5-methoxybenzaldehyde gave 3,4-diacetoxy-2',3',5'-trimethoxystilbene as an oil,  $\nu_{\max}$  1770 and 1600  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  301 nm (log  $\epsilon$  4.20), *m/e* 386 ( $M^+$ ), 344, and 302 (base peak). Irradiation gave two products (4) and (5) separable by fractional crystallisation (methanol), 3,4-diacetoxy-2,7,8-trimethoxyphenanthrene (4) (10%), m.p. 177–179° (methanol),  $\nu_{\max}$

TABLE 3

Compound	M.p. (°C)	<sup>1</sup> H N.m.r. spectra ( $\delta$ values; <i>J</i> in Hz) for $\text{CDCl}_3$ solutions		$\lambda_{\max.}/\text{nm}$ (log $\epsilon$ ) in $\text{CHCl}_3$	
TaI	151–152 (ethyl acetate)	4.0 (6 H, s), 7.1 (1 H, s), 7.58 (1 H, s), 7.63 (1 H, s), 9.17 (1 H, d, <i>J</i> 9)	4.07 (3 H, s), 7.3 (1 H, d, <i>J</i> 9), 7.63 (1 H, s), 9.17 (1 H, d, <i>J</i> 9)	375 (3.70), 306 (4.15)	357 (3.64), 342 (3.37), 317 (3.98)
(7)	145–146 (methanol)	3.98 (6 H, s), 7.0 (1 H, s), 7.50 (1 H, d, <i>J</i> 8.5), 9.08 (1 H, d, <i>J</i> 9)	4.01 (3 H, s), 7.18 (1 H, d, <i>J</i> 9), 7.64 (1 H, d, <i>J</i> 8.5), 9.08 (1 H, d, <i>J</i> 9)	364 (3.46), 305 (4.00), 270 (4.62)	358 (3.49), 342 (3.37), 317 (3.87)

H, s), 3.80 (3 H, s), 3.84 (3 H, s), 3.88 (6 H, s), 6.55 (2 H, s), and 6.80–7.20 (5 H, m), *m/e* 358 ( $M^+$ ) and 316 (base peak) (Found: C, 67.25; H, 6.2.  $\text{C}_{20}\text{H}_{22}\text{O}_6$  requires C, 67.0; H, 6.2%). Irradiation gave 2,5,6,7-tetramethoxy-1-phenanthryl acetate (2a) (50%), m.p. 175–176° (methanol),  $\nu_{\max}$  1760, 1620, and 1560  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  263 (log  $\epsilon$  4.94), 275 (4.22), and 306.5 nm (4.00),  $\delta$  2.45 (3 H, s), 3.95 (6 H, s), 3.97 (3 H, s), 4.00 (3 H, s), 7.20 (1 H, s), 7.33 (1 H, d, *J* 10 Hz), 7.60 (2 H, s), and 9.40 (1 H, d, *J* 10 Hz), *m/e* 356 ( $M^+$ ) and 314 (base peak) (Found: C, 67.2; H, 5.45.  $\text{C}_{20}\text{H}_{20}\text{O}_6$  requires C, 67.4; H, 5.65%). Acid hydrolysis gave 2,5,6,7-tetramethoxy-1-phenanthrol (2),  $\delta$  3.98 (6 H, s), 3.99 (6 H, s), 5.98br (1 H, exchanges with  $\text{D}_2\text{O}$ ), 7.00 (1 H, s, H-8), 7.29 (1 H, d, *J* 9 Hz, H-3), 7.50 (1 H, d, *J* 9 Hz, H-9 or -10), 8.00 (1 H, d, *J* 9 Hz, H-9 or -10), and 8.98 (1 H, d, *J* 9 Hz, H-4).

(b) *Photolysis of 3,4-methylenedioxy-2',3',5'-trimethoxystilbene.* 2,3-Dimethoxybenzyl alcohol<sup>12</sup> and 3,4-methylenedioxy-5-methoxybenzaldehyde gave 3,4-methylenedioxy-2',3',5'-trimethoxystilbene as an oil,  $\lambda_{\max}$  344 nm (log  $\epsilon$  4.20), *m/e* 314 ( $M^+$ , base peak) and 299. Irradiation gave two products separable by fractional crystallisation (methanol), 3,4-methylenedioxy-2,7,8-trimethoxyphenanthrene (3) (10%), m.p. 188–189° (methanol),  $\lambda_{\max}$  267.5 nm (log  $\epsilon$  4.78),  $\delta$  4.00 (9 H, s), 6.22 (2 H, s), 6.91 (1 H, s), 7.24 (1 H, d, *J* 9.5 Hz), 7.52 (1 H, d, *J* 9 Hz), 7.90 (1 H, d, *J* 9 Hz), and 8.54 (1 H, d, *J* 9.5 Hz), *m/e* 312 ( $M^+$ , base peak), 297, 269, and 254 (Found: C, 68.85; H, 5.4.  $\text{C}_{18}\text{H}_{16}\text{O}_5$  requires C, 69.2; H, 5.1%), and 2,3-methylenedioxy-4,7,8-trimethoxyphenanthrene (6) (20%), m.p. 120–122° (methanol),  $\lambda_{\max}$

1780 and 1620  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  263 nm (log  $\epsilon$  4.62),  $\delta$  2.35 (3 H, s), 2.47 (3 H, s), 3.89 (3 H, s), 3.95 (6 H, s), 7.20 (1 H, s), 7.24 (1 H, d, *J* 9.5 Hz), 7.55 (1 H, d, *J* 9.5 Hz), 8.05 (1 H, d, *J* 9.5 Hz), and 8.62 (1 H, d, *J* 9.5 Hz), *m/e* 384 ( $M^+$ ), 342, 300 (base peak), and 285 (Found: C, 65.4; H, 5.15.  $\text{C}_{21}\text{H}_{20}\text{O}_7$  requires C, 65.6; H, 5.25%), which on hydrolysis gave the diphenol as a gum,  $\delta$  3.96 (9 H, s), 6.9–8.1 (4 H, m), and 9.42 (1 H, d, *J* 9.5 Hz) and 2,3-diacetoxy-4,7,8-trimethoxyphenanthrene (5) (10%), m.p. 157–159° (methanol),  $\nu_{\max}$  1770, 1600, and 1570  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  264 nm (log  $\epsilon$  4.64),  $\delta$  2.35 (3 H, s), 2.40 (3 H, s), 3.90 (3 H, s), 4.00 (6 H, s), 7.32 (1 H, d, *J* 9.5 Hz), 7.50 (1 H, s), 7.60 (1 H, d, *J* 8.5 Hz), 8.12 (1 H, d, *J* 8.5 Hz), and 9.20 (1 H, d, *J* 9.5 Hz), *m/e* 384 ( $M^+$ ) 342, 300 (base peak), and 285 (Found: C, 65.5; H, 5.25.  $\text{C}_{21}\text{H}_{20}\text{O}_7$  requires C, 65.6; H, 5.25%), which on hydrolysis gave the diphenol as a gum,  $\delta$  4.0 (9 H, s), 7.1–8.15 (4 H, m), and 9.34 (1 H, d, *J* 9.5 Hz).

(e) *Photolysis of 2,3-diacetoxy-3',4',5'-trimethoxystilbene.* 3,4,5-Trimethoxybenzyl alcohol and 2,3-diacetoxybenzaldehyde gave 2,3-diacetoxy-3',4',5'-trimethoxystilbene as an oil,  $\nu_{\max}$  1750 and 1580  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  305 nm (log  $\epsilon$  4.24), *m/e* 386 ( $M^+$ ), 344, 302 (base peak), and 265. Irradiation gave 7,8-diacetoxy-2,3,4-trimethoxyphenanthrene (20%), m.p. 160–162° (methanol),  $\nu_{\max}$  1770 and 1620  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  260 nm (log  $\epsilon$  4.91),  $\delta$  2.32 (3 H, s), 2.44 (3 H, s), 3.99 (3 H, s), 4.01 (6 H, s), 7.06 (1 H, s), 7.42 (1 H, d, *J* 9.5 Hz), 7.64 (2 H, s), and 9.45 (1 H, d, *J* 9.5 Hz), *m/e* 384 ( $M^+$ ), 342, and 300 (base

<sup>16</sup> W. Graham, A. Cohen, R. W. Lapsley, and C. A. Lawrence, *J. Chem. Soc.*, 1944, 322.

<sup>17</sup> E. Rupp and M. Beyer, *Arch. Pharm.*, 1915, 253, 379.

peak) (Found: C, 65.7; H, 5.25.  $C_{21}H_{20}O_7$  requires C, 65.6; H, 5.25%).

(f) *Photolysis of 3,5-dimethoxystilbene*. Benzyltriphenylphosphonium bromide and 3,5-dimethoxybenzaldehyde gave 3,5-dimethoxystilbene as an oil,  $\lambda_{\max}$  290 nm (log  $\epsilon$  4.34),  $m/e$  240 ( $M^+$ , base peak). Irradiation gave 2,4-dimethoxyphenanthrene (35%), m.p. 76–77° (lit.,<sup>18</sup> 75.5–76.5°),  $\lambda_{\max}$  265 nm (log  $\epsilon$  4.66),  $\delta$  3.92 (3 H, s), 4.06 (3 H, s), 6.70–7.88 (7 H, m), and 9.50 (1 H, dd,  $J$  8.0, 3.0 Hz),  $m/e$  238 ( $M^+$ , base peak) and 223.

(g) *Photolysis of 3,4-methylenedioxy-2',3'-dimethoxystilbene*. 2,3-Dimethoxybenzyl alcohol and 3,4-methylenedioxybenzaldehyde gave *trans*-3,4-methylenedioxy-2',3'-dimethoxystilbene, m.p. 128–130° (benzene),  $\lambda_{\max}$  326 (log  $\epsilon$  4.34) and 299 nm (4.29),  $\delta$  3.85 (6 H, s), 5.91 (2 H, s), and 6.55–7.85 (8 H, m),  $m/e$  284 ( $M^+$ , base peak), 277, and 261 (Found: C, 71.9; H, 5.75.  $C_{17}H_{16}O_4$  requires C, 71.8; H, 5.65%). Irradiation gave two products which were readily separable by fractional crystallisation (methanol), the more insoluble product being 2,3-methylenedioxy-7,8-dimethoxyphenanthrene (40%), m.p. 177–179° (methanol),  $\lambda_{\max}$  258 (log  $\epsilon$  4.89) and 283 nm (4.32),  $\delta$  4.00 (6 H, s), 6.05 (2 H, s), 7.19 (1 H, s, H-1), 7.35 (1 H, d,  $J$  9.5 Hz, H-6), 7.61 (1 H, d,  $J$  9.5 Hz, H-9 or -10), 7.93 (1 H, s, H-4), 7.99 (1 H, d,  $J$  9.5 Hz, H-9 or -10), and 8.17 (1 H, d,  $J$  9.5 Hz, H-5), irradiation at  $\delta$  8.17 caused the doublet at  $\delta$  7.35 to collapse to a singlet,  $m/e$  282 ( $M^+$ , base peak), 267, and 239 (Found: C, 72.2; H, 5.25.  $C_{17}H_{14}O_4$  requires C, 72.35; H, 5.0%), and the more soluble, 3,4-methylenedioxy-7,8-dimethoxyphenanthrene (10%), m.p. 102–104° (ethanol),  $\lambda_{\max}$  258 (log  $\epsilon$  4.88), 271 (4.83), and 291 nm (4.51),  $\delta$  4.03 (3 H, s), 4.05 (3 H, s), 6.26 (2 H, s), 7.2 (1 H, d,  $J$  9.5 Hz, H-1), 7.35 (1 H, d,  $J$  9.5 Hz, H-6), 7.46 (1 H, d,  $J$  9.5 Hz, H-2), 7.68 (1 H, d,  $J$  9.5 Hz, H-9 or -10), 7.95 (1 H, d,  $J$  9.5 Hz, H-9 or -10), and 8.81 (1 H, d,  $J$  9.5 Hz, H-5), irradiation at  $\delta$  8.81 caused the doublet at  $\delta$  7.35 to collapse to a singlet,  $m/e$  282 ( $M^+$ , base peak), 267, and 239 (Found: C, 72.2; H, 5.2%).

(h) *Photolysis of 3,4-dimethoxy-4'-ethoxystilbene*. 4-Ethoxybenzyl alcohol and 3,4-dimethoxybenzaldehyde gave *trans*-3,4-dimethoxy-4'-ethoxystilbene, m.p. 138–140° (ethanol),  $\lambda_{\max}$  330 (log  $\epsilon$  4.31) and 303 nm (4.24),  $\delta$  1.40 (3 H, t,  $J$  7 Hz), 3.89 (3 H, s), 3.45 (3 H, s), 4.04 (2 H, q,  $J$  7 Hz), and 6.7–7.5 (9 H, m),  $m/e$  284 ( $M^+$ , base peak) (Found: C, 76.15; H, 7.05.  $C_{18}H_{20}O_3$  requires C, 76.05; H, 7.1%). Irradiation gave two products, first 2,3-dimethoxy-6-ethoxyphenanthrene (35%), m.p. 143–144° (ethanol),  $\lambda_{\max}$  255 nm (log  $\epsilon$  4.76),  $\delta$  1.50 (3 H, t,  $J$  7 Hz), 4.02 (3 H, s), 4.19 (3 H, s), 4.25 (2 H, q,  $J$  7 Hz), and 7.05–7.9 (7 H, m),  $\delta$  ( $[^2H_6]$ acetone) 7.12 (1 H, dd,  $J$  8.5, 2.5 Hz, H-7), 7.32 (1 H, s, H-1), 7.54 (2 H, s, H-9 and -10), 7.81 (1 H, d,  $J$  8.5 Hz, H-8), 8.01 (1 H, d,  $J$  2.5 Hz, H-5), and 8.07 (1 H, s, H-4),  $m/e$  282 ( $M^+$ , base peak) (Found: C, 76.35; H, 6.7.  $C_{18}H_{18}O_3$  requires C, 76.55; H, 6.45%), the more insoluble product (methanol), and from the mother liquors 3,4-dimethoxy-6-ethoxyphenanthrene (5%), m.p. 81–83° (ethanol) (lit.,<sup>19</sup> 85°),  $\delta$  1.48 (3 H, t,  $J$  7 Hz), 3.94 (6 H, s), 4.23 (2 H, q,  $J$  7 Hz), 7.0–7.9 (6 H, m), and 9.23 (1 H, d,  $J$  3 Hz, H-5),  $m/e$  282 ( $M^+$ , base peak).

(i) *Photolysis of 2,3-dimethoxy-4'-ethoxystilbene*. 2,3-Dimethoxybenzyl alcohol and 4'-ethoxybenzaldehyde gave *trans*-2,3-dimethoxy-4'-ethoxystilbene, m.p. 112° (ethanol),

$\lambda_{\max}$  305 nm (log  $\epsilon$  4.43),  $\delta$  1.40 (3 H, t,  $J$  7 Hz), 3.87 (3 H, s), 3.92 (3 H, s), 4.03 (2 H, q,  $J$  7 Hz), and 6.4–7.5 (9 H, m),  $m/e$  284 ( $M^+$ , base peak) (Found: C, 75.85; H, 7.1.  $C_{18}H_{20}O_3$  requires C, 76.05; H, 7.1%). Irradiation gave 1,2-dimethoxy-6-ethoxyphenanthrene (40%), m.p. 133–134° (methanol),  $\lambda_{\max}$  268 (log  $\epsilon$  4.72) and 261 nm (4.75),  $\delta$  1.48 (3 H, t,  $J$  7 Hz), 4.02 (6 H, s), 4.25 (2 H, q,  $J$  7 Hz), 7.1–8.1 (6 H, m), and 8.30 (1 H, d,  $J$  9.5 Hz),  $m/e$  282 ( $M^+$ , base peak) (Found: C, 76.5; H, 6.45.  $C_{18}H_{18}O_3$  requires C, 76.55; H, 6.45%).

(j) *Photolysis of 2-methoxy-4'-ethoxystilbene*. 2-Methoxybenzyl alcohol and 4-ethoxybenzaldehyde gave *trans*-2-methoxy-4'-ethoxystilbene, m.p. 70–71° (lit.,<sup>20</sup> 70°),  $\lambda_{\max}$  325 (log  $\epsilon$  4.26) and 305 nm (4.26). Irradiation gave 1-methoxy-6-ethoxyphenanthrene, m.p. 94–95° (ethanol),  $\lambda_{\max}$  258 nm (log  $\epsilon$  4.71),  $\delta$  1.48 (3 H, t,  $J$  7 Hz), 3.98 (3 H, s), 4.22 (2 H, q,  $J$  7 Hz), and 6.85–8.30 (8 H, m) (Found: C, 80.85; H, 6.2.  $C_{17}H_{16}O_2$  requires C, 80.9; H, 6.4%).

(k) *Photolysis of 4-methoxy-4'-ethoxystilbene*. 4-Methoxybenzyl alcohol and 4-ethoxybenzaldehyde gave *trans*-4-methoxy-4'-ethoxystilbene, m.p. 165–167° (ethanol),  $\lambda_{\max}$  324 (log  $\epsilon$  4.20),  $\delta$  1.38 (3 H, t,  $J$  7 Hz), 3.80 (3 H, s), 4.00 (2 H, q,  $J$  7 Hz), and 6.4–7.5 (10 H, m) (Found: C, 80.15; H, 6.95.  $C_{17}H_{18}O_2$  requires C, 80.3; H, 7.15%). Irradiation gave 3-methoxy-6-ethoxyphenanthrene, m.p. 85–86° (ethanol),  $\lambda_{\max}$  254 nm (log  $\epsilon$  4.69),  $\delta$  1.50 (3 H, t,  $J$  7 Hz), 3.98 (3 H, s), 4.21 (2 H, q,  $J$  7 Hz), 7.20 (2 H, dd,  $J$  8.5, 2.5 Hz), 7.50 (2 H, s), 7.71 (2 H, d,  $J$  8.5 Hz), and 7.81 (2 H, d,  $J$  2.5 Hz) (Found: C, 80.95; H, 6.35.  $C_{17}H_{16}O_2$  requires C, 80.9; H, 6.4%).

(l) *Photolysis of 3,4-methylenedioxy-4'-ethoxystilbene*. 4-Ethoxybenzyl alcohol and 3,4-methylenedioxybenzaldehyde gave *trans*-3,4-methylenedioxy-4'-ethoxystilbene, m.p. 138–139° (ethanol),  $\lambda_{\max}$  328 nm (log  $\epsilon$  4.28),  $\delta$  1.40 (3 H, t,  $J$  7 Hz), 4.02 (2 H, q,  $J$  7 Hz), 5.93 (2 H, s), and 6.8–7.5 (9 H, m) (Found: C, 75.95; H, 5.85.  $C_{17}H_{16}O_3$  requires C, 76.1; H, 6.0%). Irradiation gave only one isolable product, 2,3-methylenedioxy-6-ethoxyphenanthrene, m.p. 152–153° (ethanol),  $\lambda_{\max}$  253 nm (log  $\epsilon$  4.80),  $\delta$  1.49 (3 H, t,  $J$  7 Hz), 4.21 (2 H, q,  $J$  7 Hz), 6.04 (2 H, s), 7.13 (1 H, dd,  $J$  8.5, 2.5 Hz, H-7), 7.15 (1 H, s, H-1), 7.44 (1 H, d,  $J$  8.5 Hz, H-9 or -10), 7.53 (1 H, d,  $J$  8.5 Hz, H-9 or -10), 7.73 (1 H, d,  $J$  8.5 Hz, H-8), 7.77 (1 H, d,  $J$  2.5 Hz, H-5), and 7.88 (1 H, s, H-4),  $m/e$  266 ( $M^+$ , base peak) (Found: C, 76.4; H, 5.55.  $C_{17}H_{14}O_3$  requires C, 76.65; H, 5.3%).

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