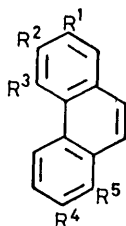


## Structure and Synthesis of the Phenanthrenes TaIV and TaVIII from *Tamus communis*

By Roy M. Letcher\* and Kum-Moon Wong, Department of Chemistry, University of Hong Kong, Hong Kong

By use of photochemical syntheses, TaIV and TaVIII have been identified as 3-hydroxy-2,4-dimethoxy-7,8-methylenedioxyphenanthrene and 3,7-dihydroxy-2,4-dimethoxyphenanthrene, respectively; earlier assignments are thus shown to be incorrect.

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> substituted phenanthrene structures. The structures were, however, assigned by non-rigorous methods, and already two have been revised.<sup>3,4</sup> In the present paper, structures (1) and



- (1) R<sup>1</sup> = R<sup>5</sup> = OMe, R<sup>4</sup> = OH, R<sup>2</sup>R<sup>3</sup> = OCH<sub>2</sub>O
- (2) R<sup>1</sup> = R<sup>2</sup> = OMe, R<sup>3</sup> = R<sup>4</sup> = OH, R<sup>5</sup> = H
- (3) R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = R<sup>5</sup> = OMe
- (4) 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
- (5) 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
- (6) R<sup>1</sup> = OH, R<sup>2</sup> = R<sup>3</sup> = OMe, R<sup>4</sup>R<sup>5</sup> = OCH<sub>2</sub>O
- (7) R<sup>1</sup> = R<sup>2</sup> = OMe, R<sup>3</sup> = OH, R<sup>4</sup>R<sup>5</sup> = OCH<sub>2</sub>O
- (8) R<sup>1</sup> = R<sup>3</sup> = OMe, R<sup>2</sup> = OH, R<sup>4</sup>R<sup>5</sup> = OCH<sub>2</sub>O
- (9) R<sup>2</sup> = R<sup>3</sup> = OMe, R<sup>1</sup> = R<sup>4</sup> = OAc, R<sup>5</sup> = H
- (10) R<sup>1</sup> = R<sup>3</sup> = OMe, R<sup>2</sup> = R<sup>4</sup> = OAc, R<sup>5</sup> = H
- (11) R<sup>3</sup> = R<sup>4</sup> = OMe, R<sup>1</sup> = R<sup>2</sup> = OAc, R<sup>5</sup> = H

(2) proposed by Reisch *et al.* for TaIV<sup>1</sup> and TaVIII,<sup>2</sup> respectively, are considered, and also data (m.p., <sup>1</sup>H n.m.r., i.r., and u.v.) not previously available are reported for one of the extractives (DC) whose structure (3) is known from synthesis.<sup>5</sup>

Compound	M.p. (°C)	$\delta$ Values (J in Hz) <sup>a</sup>	$\lambda_{\max.}/\text{nm}$ (log $\epsilon$ ) <sup>b</sup>
TaIV <sup>1,7</sup>	160—161	4.0 (3 H, s), 4.1 (3 H, s), 6.21 (2 H, s), 7.13 (1 H, s), 7.3 (1 H, d, J 9), 7.67 (2 H, br, s), 9.1 (1 H, d, J 9)	373 (3.75), 355 (3.66), 339 (3.86), 308 (3.98)
(8)	159—161	3.93 (3 H, s), 4.03 (3 H, s), 6.14 (2 H, s), 7.05 (1 H, s), 7.22 (1 H, d, J 9.5), 7.60 (2 H, br, s), 9.05 (1 H, d, J 9.5) (irradiation at $\delta$ 9.05 caused the d at $\delta$ 7.22 to collapse to s)	373 (3.62), 356 (3.59), 308sh (4.01), 267 (4.71)
TaVIII <sup>2</sup>	157—158	2.3 (3 H, s), 2.4 (3 H, s), 3.9 (3 H, s), 3.95 (3 H, s), 7.13 (1 H, s), 7.37 (1 H, dd, J 9, 2.5), 7.58 (1 H, d, J 2.5), 7.62 (2 H, s), 9.45 (1 H, d, J 9)	301 (3.91), 288 (4.10), 280 (4.22), 260 (4.83)
(10)	152—154	2.34 (3 H, s), 2.42 (3 H, s), 3.92 (3 H, s), 3.96 (3 H, s), 7.14 (1 H, s), 7.30 (1 H, dd, J 10, 3), 7.59 (1 H, d, J 3), 7.64 (2 H, s), 9.45 (1 H, d, J 10) (irradiation at $\delta$ 9.45 caused the dd at $\delta$ 7.30 to collapse to d, J 3 Hz)	300 (3.94), 288sh (4.12), 280sh (4.23), 259 (4.93)

<sup>a</sup> Solvent CDCl<sub>3</sub>. <sup>b</sup> Solvent CHCl<sub>3</sub>.

Reisch *et al.*<sup>1</sup> found that on methylation the monohydric phenol TaIV gave TaI, and in the light of biogenetic considerations, which were not discussed, they proposed structure (1) for TaIV. More recently,<sup>4</sup> it has been found that the structure (4) of TaI used in their argument was incorrect; TaI in fact has the structure (5), and on this basis<sup>4</sup> TaIV can be (6), (7), or (8). Preliminary synthetic studies<sup>6</sup> excluded both (6) and (7), and (8) was therefore synthesised by unam-

biguous photocyclisation of 4-acetoxy-3,5-dimethoxy-2',3'-methylenedioxy stilbene, followed by hydrolysis. The published <sup>1</sup>H n.m.r. spectrum<sup>6</sup> of TaIV<sup>1,7</sup> was identical with that of (8), and the u.v. spectra were also identical (see Table).

TaVIII was isolated<sup>2</sup> as the diacetate, and from an analysis of its <sup>1</sup>H n.m.r. spectrum Reisch *et al.*<sup>2</sup> showed it to be a 2,3,4,7-tetrasubstituted phenanthrene. One hydroxy group was placed at C-7 in view of the chemical shift of H-8, and the other at C-4 from the methoxy-chemical shifts, giving structure (2) for TaVIII. However, in view of a report<sup>4</sup> that 5,6-unsubstituted 4-methoxyphenanthrenes are associated with an H-5 doublet at  $\delta$  9.20—9.65, and 4-acetoxyphenanthrenes with an H-5 chemical shift appreciably lower at  $\delta$  8.96 and 8.62, it seems that this structure (2) requires further scrutiny, as the reported chemical shift of H-5 ( $\delta$  9.45) of TaVIII acetate is consistent with a 4-methoxy- and not a 4-acetoxy-structure. Consequently TaVIII acetate is (9), (10), or (11). Preliminary syntheses<sup>6</sup> excluded (9), and also (2). The synthesis of (10) was achieved by oxidative photochemical cyclisation of 3',4-diacetoxy-3,5-dimethoxystilbene. In this reaction only one product, (10), was isolated, its <sup>1</sup>H n.m.r. spectrum (particularly the characteristic low-field doublet) showing it to be the 2,3,4,7- and not the alternative 2,3,4,5-tetrasubstituted phenanthrene. In such oxidative photochemical cyclisations the more hindered 4,5-substituted

phenanthrenes are often not observed, or are produced in very low yields. The isolated product, however, exhibits m.p. and i.r., n.m.r., and u.v. spectra identical with those reported<sup>2</sup> for TaVIII (see Table).

Unfortunately no authentic samples of TaIV and TaVIII are available † for direct comparison; neverthe-

† It appears that TaIV and TaVIII were isolated in very small amounts (personal communication), and that insufficient is now available for comparison.

less the above data appear to be conclusive in favour of structures (8) and (10), respectively.

#### EXPERIMENTAL

Details of general techniques and physical measurements are described in ref. 4.

*Preparation of DC.*—Catalytic reduction<sup>4</sup> of 3,4,5-trimethoxybenzaldehyde, followed by chlorination<sup>4</sup> and a Wittig reaction<sup>4</sup> with 2,3-dimethoxybenzaldehyde, gave a mixture of *cis*- and *trans*-3,4,5,2',3'-pentamethoxystilbenes as an oil,  $\lambda_{\max}$  319 (log  $\epsilon$  4.09), *m/e* 330 ( $M^+$ , base peak) and 315. Irradiation<sup>4</sup> gave 2,3,4,7,8-pentamethoxyphenanthrene, m.p. 160–162° (methanol),  $\nu_{\max}$  1 600 and 1520  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  264 nm (log  $\epsilon$  5.04),  $\delta$  4.01 (15 H, s, 5 OMe), 7.08 (1 H, s, H-1), 7.33 (1 H, d,  $J$  9.5 Hz, H-6), 7.60 (1 H, d,  $J$  9 Hz, H-9 or H-10), 8.08 (1 H, d,  $J$  9 Hz, H-9 or H-10), and 9.28 (1 H, d,  $J$  9.5 Hz, H-5), *m/e* 328 ( $M^+$ , base peak) and 313 (Found: C, 69.6; H, 6.2.  $\text{C}_{19}\text{H}_{20}\text{O}_5$  requires C, 69.5; H, 6.15%).

*Synthesis of TaIV.*—Methylenation<sup>8</sup> of 2,3-dihydroxybenzaldehyde with methylene bromide, gave 2,3-methylenedioxybenzaldehyde (40%) as an oil (lit.,<sup>9</sup> m.p. 34°),  $\delta$  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, which in a Wittig reaction with (4-acetoxy-3,5-dimethoxybenzylidene)triphenylphosphorane, prepared from syringaldehyde in the usual way,<sup>4</sup> gave a mixture of *cis*- and *trans*-4-acetoxy-3,5-dimethoxy-2',3'-methylenedioxy stilbenes as an oil,  $\lambda_{\max}$  302 nm (log  $\epsilon$  4.16), *m/e* 342 ( $M^+$ ) and 300 (base peak). Irradiation gave 3-acetoxy-2,4-dimethoxy-7,8-methylenedioxyphenanthrene, m.p. 140–143° (ethanol),  $\nu_{\max}$  1 760 and 1 600  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  268 nm (log  $\epsilon$  4.69),  $\delta$  2.44 (3 H, s, Ac), 3.90 (3 H, s, OMe), 3.98 (3 H, s, OMe), 6.14 (2 H, s,  $\text{OCH}_2\text{O}$ ), 7.11 (1 H, s, H-1), 7.22 (1 H, d,  $J$  9 Hz, H-6), 7.55 (1 H, d,  $J$  9 Hz, H-9 or H-10), 7.68

(1 H, d,  $J$  9 Hz, H-9 or H-10), and 9.01 (1 H, d,  $J$  9 Hz, H-5), (irradiation at  $\delta$  9.01 caused the doublet at  $\delta$  7.22 to collapse to a singlet), *m/e* 340 ( $M^+$ ), 298 (base peak), and 253 (Found: C, 66.9; H, 5.05.  $\text{C}_{19}\text{H}_{16}\text{O}_6$  requires C, 67.05; H, 4.75%). Acidic hydrolysis gave 3-hydroxy-2,4-dimethoxy-7,8-methylenedioxyphenanthrene (8) (see Table).

*Synthesis of TaVIII.*—Catalytic reduction of 3-acetoxybenzaldehyde followed by chlorination and Wittig reaction with 4-acetoxy-3,5-dimethoxybenzaldehyde gave a mixture of *cis*- and *trans*-3',4'-diacetoxy-3,5-dimethoxystilbenes as an oil,  $\lambda_{\max}$  301 (log  $\epsilon$  4.04), *m/e* 356 ( $M^+$ ), 314 (base peak), and 272. Irradiation gave only one isolable product, 3,7-diacetoxy-2,4-dimethoxyphenanthrene (10), m.p. 152–154° (methanol),  $\nu_{\max}$  1 760 and 1 610  $\text{cm}^{-1}$ , *m/e* 354 ( $M^+$ ), 312, and 270 (base peak) (Found: C, 67.5; H, 5.0. Calc. for  $\text{C}_{20}\text{H}_{18}\text{O}_6$ : C, 67.8; H, 5.1%) (see also Table).

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