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A REVISED STRUCTURE FOR THE TETRA-SUBSTITUTED PHENANTHRENE FROM TAMUS COMMUNIS

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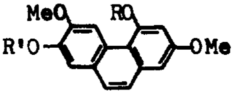
Recently Reisch et al. isolated from the rhizomes of Tamus communis a 2,4,6,7-tetra-substituted phenanthrene (Ta VI) to which they gave the structure (I), [1,2] the placing of the hydroxyl-group following merely from its apparent slow rate of methylation with diazomethane. This non-rigorous structure elucidation prompted us to examine its structure.

We have now synthesised (I) and found it to have different characteristics from that reported[1] for (Ta VI) and furthermore, we have previously isolated[3] from the heartwood of Combretum psidiodes, a compound with characteristics identical to that reported for (Ta VI) (see Table 1), and to which we have given the structure (II),[3] established unambiguously by synthesis and also by chemical and physical methods employing specific deuteriation of the phenol. Consequently a revised structure for (Ta VI) is necessary, and it appears almost certainly to have the structure (II). Unfortunately no sample of (Ta VI) was available for direct comparison.[4]

Table 1

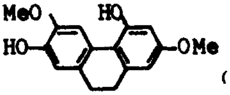
Compound	m.p.	^{1}H N.m.r spectra (τ values; J in Hz) in $CDCl_3$	λ_{max}/nm(log ϵ) in $CHCl_3$
(Ta VI)[1]	175-8	1.0(1H,s), 2.5(2H,s), 2.7(1H,s), 3.15(1H,d,J 2), 3.3(1H,d,J 2), 5.85(6H,s), 6.0(3H,s). Recorded on Varian A60; TMS as external standard.	362 (3.70), 345 (3.58), 328 (3.36), 306 (3.86), 293 (4.03).
(II)[3]	177-9	1.01(1H,s), 2.54(2H,s), 2.77(1H,s), 3.18(1H,d,J 2), 3.33(1H,d,J 2), 4.2* (1H,s), 5.97(6H,s), 6.11(3H,s). Recorded on Perkin-Elmer R12; TMS internal standard.	357 (3.75), 346 (3.65), 330 (3.40), 306 (3.86), 295 (4.03).

*Removed on shaking with D_2O.



(I) R = H; R' = Me

(II) R = Me; R' = H



(III)

Partial methylation of (III) with a methanolic etheral diazomethane solution (2 hrs) gave 4-hydroxy-2,6,7-trimethoxy-9,10-dihydrophenanthrene (see Table 2), the predicted product (steric grounds), which was acetylated before dehydrogenating with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to give 4-acetoxy-2,6,7-trimethoxyphenanthrene which on acid hydrolysis gave (I).

Compound (III) which occurs in *Combretum psidiodes*[3] and in *Combretum apiculatum*[5] and whose structure has been unambiguously established could theoretically yield (II) on partial methylation followed by dehydrogenation, but as (II) is known and is different from the isolated product, this is not the case. Confirmation of the structure (I) followed from the reaction of its 9,10-dihydro-derivative with D_2O under basic conditions,[5] in which the protons at C-1 and C-3 exchanged with deuterium. Furthermore, a pronounced upfield shift of about 0.6 and 0.5 ppm was exhibited by the C-5 proton (in all cases the signal at lowest field) of the phenanthrene (I) and its 9,10-dihydro-derivative respectively, on changing the substituent at C-4 from methoxyl to acetoxyl (see Ref. 5 for the n.m.r. spectra of the respective tetra-methoxyl-derivatives). This diagnostic test, first employed to indicate the presence of a C-1 acetoxyl-group in the aporphine alkaloids,[6] is equally useful in suggesting the presence of the analogous C-4 acetoxyl-group in phenanthrenes and 9,10-dihydrophenanthrenes.[3,5,7]

Table 2 : Data of new compounds**

Compound	m.p.	^{1}H N.m.r. spectra (τ values; J in Hz) in $CDCl_3$
4-hydroxy-2,6,7-trimethoxy-9,10-dihydrophenanthrene	204-7	2.25(1H,s), 3.28(1H,s), 3.62(1H,d,J 2), 3.71(1H,d,J 2), 4.36* (1H, broad), 6.14(6H,s), 6.27(3H,s), 7.30(4H,s).
4-acetoxy-2,6,7-trimethoxy-9,10-dihydrophenanthrene	140-1	2.58(1H,s), 3.34(1H,s), 3.37(1H,d,J 2), 3.54(1H,d,J 2), 6.14 (6H,s), 6.23(3H,s), 7.28(4H,s), 7.72(3H,s).
$[1,3\text{-}^2H_2]$-4-acetoxy-2,6,7-trimethoxy-9,10-dihydrophenanthrene	140-1	2.58(1H,s), 3.34(1H,s), 6.14(6H,s), 6.23(3H,s) 7.28(4H,s), 7.72(3H,s).
4-acetoxy-2,6,7-trimethoxy-phenanthrene	150-2	1.60(1H,s), 2.53(2H,s), 2.90(1H,s), 2.93(1H,d,J 2), 3.15 (1H,d,J 2), 6.02(3H,s), 6.07(3H,s), 6.15(3H,s), 7.54(3H,s).
4-hydroxy-2,6,7-trimethoxy-phenanthrene (I)	252-3	1.03(1H,s), 2.56(2H,s), 2.90(1H,s), 3.23(1H,d,J 2), 3.51 (1H,d,J 2), 6.02(3H,s), 6.04(3H,s), 6.16(3H,s).

**All compounds gave satisfactory spectra and elemental analysis. *Removed on shaking with D_2O.

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