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STRUCTURE AND SYNTHESIS OF THE GROWTH INHIBITOR BATATASIN I FROM *DIOSCOREA BATATAS*

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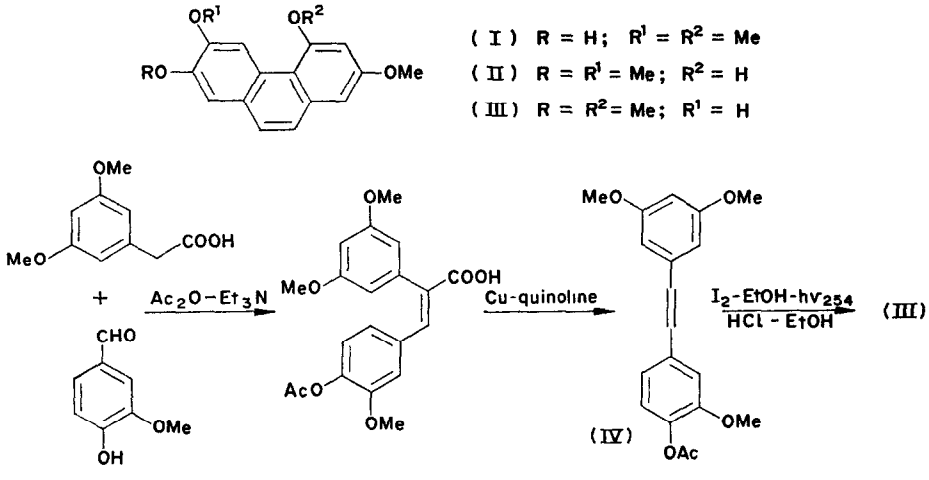
Key Word Index—*Dioscorea batatas*; Dioscoreaceae; yam; batatasin I; 6-hydroxy-2,4,7-trimethoxyphenanthrene.

Abstract—The synthesis of 6-hydroxy-2,4,7-trimethoxyphenanthrene is described and its identity with the growth inhibitor, batatasin I, is confirmed.

RECENTLY Hashimoto *et al.*[1] isolated from dormant yam bulbils (*Dioscorea batatas* Decne.) a phenanthrene, batatasin I (B–I), $(C_{17}H_{16}O_4)$[2] which on methylation[2] gave the known 2,4,6,7-tetramethoxyphenanthrene. This phenanthrol which appears to be a growth inhibitor, has m.p. 148·5-149·6°,[1] and is clearly different from the known 2,4,6,7-substituted trimethoxyphenanthrols (I)[3] and (II)[3] with m.ps of 177–179° and 252–253° respectively.

An examination of the spectral data[1,2] of B–I suggests it to have structure (III), which we have now synthesized (see Scheme 1). A Perkin condensation of 3,5-dimethoxyphenylacetic acid and vanillin gave α-(3,5-dimethoxyphenyl)-4-acetoxy-3-methoxycinnamic acid which on decarboxylation gave the stilbene (IV) from which 6-acetoxy-2,4,7-trimethoxyphenanthrene was obtained as the only product from irradiation in ethanol. Hydrolysis



SCHEME 1. SYNTHESIS OF BATATASIN I.

[1] HASHIMOTO, T., HASEGAWA, K. and KAWARADA, A. (1972) *Planta (Berl.)* **108**, 369.
[2] HASHIMOTO, T. private communication.
[3] LETCHER, R. M. and NHAMO, L. R. M. (1972) *Tetrahedron Letters* 486

yielded 6-hydroxy-2,4,7-trimethoxyphenanthrene m.p. 145–147°, identical (UV,[1,2] IR,[1] NMR[2] and m.p.) with Hashimoto's B–I, which consequently must have structure (III).*

EXPERIMENTAL

General experimental details are described in Ref. 4.

Synthesis of 6-hydroxy-2,4,7-trimethoxyphenanthrene. A Perkin condensation[5] of 3,5-dimethoxyphenylacetic acid and vanillin gave in 70% yield α-*(3,5-dimethoxyphenyl)-4-acetoxy-3-methoxycinnamic acid* as needles, m.p. 190–192° (from EtOH), $IR\nu_{max}^{KBr}$: 3750–2400, 1760, 1680, 1605 and 1595 cm^{-1}, NMR ($CDCl_3$): τ2·25 (1H, *s*), 3·18 (2H, *bs*), 3·37 (1H, *bs*), 3·63 (3H, *s*), 6·28 (6H, *s*), 6·57 (3H, *s*), and 7·74 (3H, *s*), (Found: C, 64·3; H, 5·55. Calc. for $C_{20}H_{20}O_7$: C, 64·5; H, 5·4%). Decarboxlyation[5] gave, in 30% yield, 4-acetoxy-3,3′,5′-trimethoxystilbene as an oil, NMR ($CDCl_3$): τ2·9–3·8 (8H, *m*), 6·26 (9H, *s*), and 7·23 (3H, *s*). Irradiation[5] in ethanol (containing 0·005% iodine) with a Hanovia medium pressure mercury arc submerged in the solution in quartz apparatus, gave in 30% yield, *6-acetoxy-2,4,7-trimethoxyphenanthrene* as large prisms, m.p. 175–177° (from EtOH), $UV\lambda_{max}^{EtOH}$: 352sh (log ε4·64), 359·5 (4·80), 280sh (4 17), 290sh (4 04), and 300sh nm (3 77), $IR\nu_{max}^{KBr}$: 2950, 1750 and 1620 cm^{-1}, NMR ($CDCl_3$) τ0 86 (1H, *s*, H-5), 2·47 (2H, *s*, H-9 and H-10), 2 82 (1H, *s*, H-8), 3·22 (1H, *d*, *J* 2Hz, H-1 or H-3), 3·33 (1H, *d*, *J* 2Hz, H-3 or H-1), 6·0 (3H, *s*, OMe), 6·11 (3H, *s*, OMe), 6·14 (3H, *s*, OMe), and 7·62 (3H, *s*, OAc), (Found: C, 69·75; H, 5·7. Calc. for $C_{19}H_{18}O_5$: C, 69 9; H, 5·55%). Acid hydrolysis[5] gave 6-hydroxy-2,4,7-trimethoxyphenanthrene as needles, m.p. 145–147° (from C_6H_6–light petrol.), (lit.,[1] 148·5–149·6°), $UV\lambda_{max}^{EtOH}$: 362 (log ε4 03), 344 (3·85), 328 (3 64), 307 (3·96), 295sh (4·02), 283 (4·22), 261 (4 94), and 252sh nm (4·77), $IR\nu_{max}^{KBr}$: 3490 (*b*), 2910 (*b*), 1625, 1615, 1580 and 1510 cm^{-1}, NMR ($CDCl_3$): τ1·01 (1H, *s*, H-5), 2·55 (2H, *b s*, H-9 and H-10), 2·93 (1H, *s*, H-8), 3·24 (1H, *d*, *J* 2·5Hz, H-1 or H-3), 3·38 (1H, *d*, *J* 2·5Hz, H-3 or H-1), 6·02 (3H, *s*, OMe), 6·08 (3H, *s*, OMe), and 6·16 (3H, *s*, OMe), MS *m/e* 284 (base peak), 269. A Gibbs test[4] on this synthetic phenol was negative.

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* A mixture of Batatasin I and 6-hydroxy-2,4,7-trimethoxyphenanthrene showed no depression of m.p.

[4] LETCHER, R. M. and NHAMO, L. R. M. (1971) *J. Chem. Soc.* C, 3070.
[5] LETCHER, R. M., NHAMO, L. R. M. and GUMIRO, I. T. (1972) *J. Chem. Soc. Perkin I* 206.