Structure of Victoxinine

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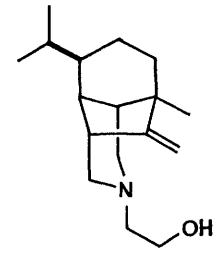
Summary The structure of victoxinine, a toxic base from *Helminthosporium victoriae*, has been established as (**1**) by partial synthesis from prehelminthosporol (**2**).

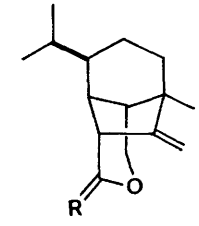
VICTOXININE, $C_{17}H_{29}NO$, hydrochloride m.p. 172—173°, is a component of victorin, a most potent host-specific toxin from *Helminthosporium victoriae*.[1] The compound also occurs as the free base in culture filtrates from non-toxin-producing isolates of the same organism.[2] Previous investigations had indicated a tricyclic structure containing a terminal methylene unit as well as a methyl and an isopropyl group, whereas the exact nature of the two heteroatoms remained veiled.[3]

Victoxinine has now been isolated in amounts of 8—12 mg l^{-1} from the culture filtrate of *Helminthosporium sativum*.† In contrast to a previous report,[3] victoxinine was readily converted into an oily *O*-acetyl derivative, $[\alpha]_D^{25}$ −56° ($CHCl_3$), $\nu_{C=O}$ ($CHCl_3$) 1730 cm^{-1}, from which the parent compound could be regenerated with MeOH–KOH. This, together with the assignment of 21 protons in the n.m.r. spectrum of the metabolite and a suspected biogenetic relationship to other terpenoid metabolites from *H. sativum*, *e.g.* (**2**),[4] suggested (**1**) as the most plausible structure for victoxinine.

Unequivocal evidence for the correctness of this proposal was obtained through partial synthesis of (**1**). Prehelminthosporol (**2**) was converted into the known[4] lactone (**3**) and hence with $LiAlH_4$ into the diol (**4**), $[\alpha]_D^{25}$ −17° ($CHCl_3$). In the presence of acids (**4**) underwent easy cyclisation to the saturated isomer (**6**), m.p. 83—84°, $[\alpha]_D^{25}$ +36° ($CHCl_3$), δ ($CDCl_3$) 0·94 (Me), 1·19 (Me) p.p.m. Compounds (**4**) and (**6**) were subsequently found as major metabolites in culture filtrates of *H. victoriae*. Conversion of (**4**) into the dimethanesulphonate (**5**), m.p. 106°, $[\alpha]_D^{25}$ −2° ($CHCl_3$), followed by treatment with ethanolamine in dioxan, gave (**1**) as an oily base, $[\alpha]_D^{25}$ −78° (EtOH), identical in every respect with an authentic sample of victoxinine.

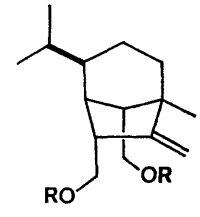


(1)



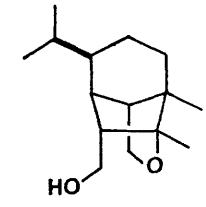
(2) R = H, OH

(3) R = O



(4) R = H

(5) R = $MeSO_2$



(6)

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The biogenetic combination of a mevalonoid precursor and an ethanolamine unit implied by the structure of victoxinine is not without precedent.[5]

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[1] R. B. Pringle and A. C. Brown, *Nature*, 1958, **181**, 1205.
[2] R. B. Pringle and A. C. Brown, *Phytopathology*, 1960, **50**, 324.
[3] R. B. Pringle, in 'Phytotoxins in Plant Diseases,' eds. R. K. S. Wood, A. Ballio, and A. Graniti, Academic Press, New York, 1972, p. 141.
[4] P. de Mayo, R. E. Williams, and Y. E. Spencer, *Canad. J. Chem.*, 1965, **43**, 1357.
[5] K. Wiesner, R. Armstrong, M. F. Bartlett, and J. A. Edwards, *J. Amer. Chem. Soc.*, 1954, **76**, 6068; T. Okamoto, M. Natsume, T. Onaka, F. Uchimaru, and M. Shimizu, *Chem. Pharm. Bull. (Tokyo)*, 1966, **14**, 672: T. Tokuyama, J. Daly, B. Witkop, I. L. Karle, and J. Karle, *J. Amer. Chem. Soc.*, 1968, **90**, 1917.