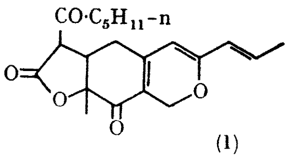
The Structure of Monascin

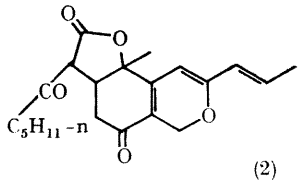
By F. C. CHEN,† P. S. MANCHARD, and W. B. WHALLEY*
(*The School of Pharmacy, The University, London, W.C.*1)

THE fungal metabolite, monascin, elaborated *inter alia* by *Monascus purpureus Went.*, has been assigned the structure (1),[1] although an alternative (2) has not been entirely excluded.[2] Unequivocal definition of structure (1) is now reported.

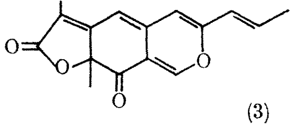
Thus, oxidation of mass spectrometrically pure monascin with dichlorodicyanobenzoquinone in benzene at room temperature gave a mixture which was purified by chromatography on Celite followed by t.l.c., on silica to give rubropunctatin[3] (3) (*ca.* 10% yield) identical [elementary analysis, m.p. and mixed m.p., t.l.c., n.m.r., i.r., u.v., specific rotation, and mass spectrum (M^+, 354·14671; Calc. for $C_{21}H_{22}O_5$, M^+, 354·146713)] with an authentic specimen.



(1)



(2)



(3)

This structure (1) is also in accord with the mass spectrum of monascin which has a molecular ion peak at *m/e* 358 ($C_{21}H_{26}O_5$) and a base peak at *m/e* 162, corresponding (accurate mass measurement) to $C_{10}H_{10}O_2{}^+$. A plausible

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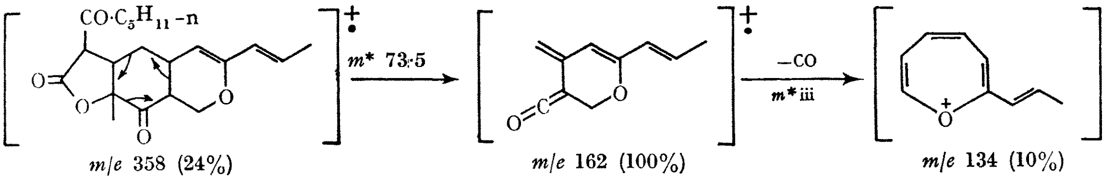
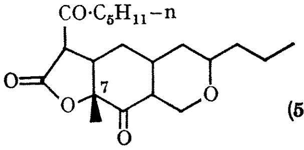
† On leave of absence from the National Taiwan University.

mechanism for the production of this base peak involves a retro-Diels-Alder cleavage of the molecular ion as follows:



(4)



(5)

The ion corresponding to the base-peak loses carbon monoxide (as seen from a metastable peak at *m/e* 111) to give the rearranged ion *m/e* 134, possibly the oxepinoid (4). The formation of the base peak *m/e* 162 is not readily explicable on the basis of the structure (2) for monascin.

An examination of the n.m.r. spectrum[1] of perhydromonascin (5) in benzene and in deuteriochloroform shows that the signal corresponding to the C-7 methyl group exhibits a shift $\delta(C_6H_6) - \delta(CDCl_3) = 11$ c./sec., thus indicating that in (5) [and hence in (1)], this methyl group is axial to the plane of the cyclohexanone ring.

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[1] B. C. Fielding, J. S. E. Holker, D. F. Jones, A. D. G. Powell, K. W. Richmond, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 1961, 4579.

[2] Y. Inouye, K. Nakanishi, H. Nishikawa, M. Ohashi, A. Terahara, and S. Yamamura, *Tetrahedron*, 1962, **18**, 1195.

[3] E. J. Haws, J. S. E. Holker, A. Kelly, A. D. G. Powell, and A. Robertson, *J. Chem. Soc.*, 1959, 3598.