Rotenoid Synthesis, by One-carbon Insertion, from 2'-Hydroxyisoflavones using Dimethylsulphoxonium Methylide

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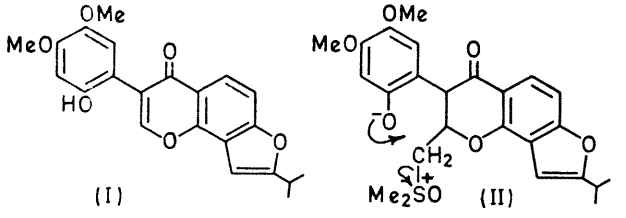
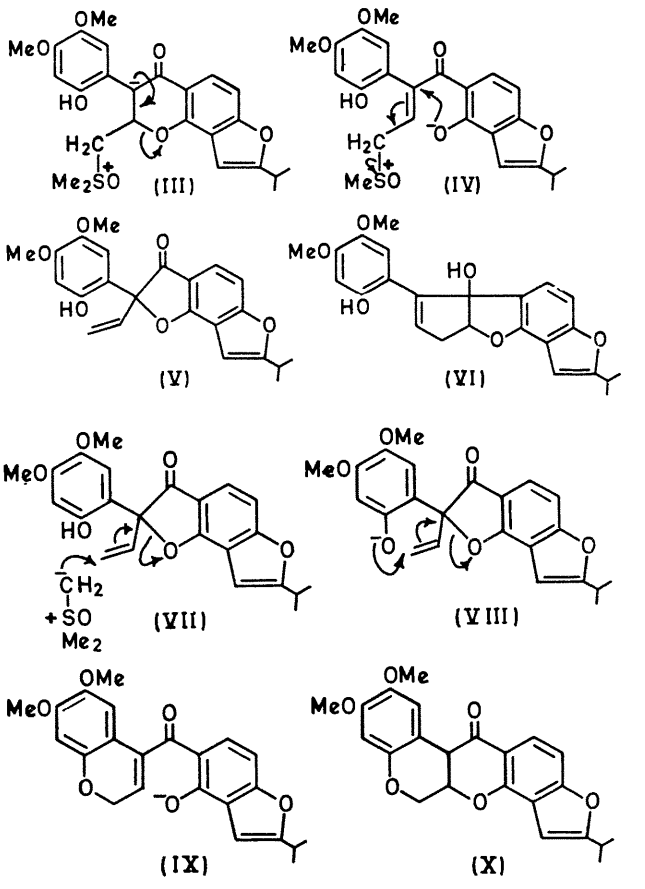
Summary The vinylcoumaranone (V) formed when isoderritol isoflavone (I) reacts with dimethylsulphoxonium methylide (1 mol) is isomerised by pyridine to isorotenone (X): the new rotenoid synthesis has similarities to the biosynthetic route.

THE possibility that a 2'-hydroxyisoflavone might react with dimethylsulphoxonium methylide to give a rotenoid has been envisaged in more than one laboratory, but the product is in fact reported to be a 2-vinylcoumaran-3-one.[1] In agreement, isoderritol isoflavone (I) reacts with dimethylsulphoxonium methylide (1 mol) not as in (II) but as in (III)—(IV) to give the 2-vinylcoumaran-3-one (V).[2] Reaction with further dimethylsulphoxonium methylide gives (VI), initiated as in (VII).[2] It seems reasonable to



conclude that the vinylcoumaranone (V) might be susceptible to intramolecular base-catalysed rearrangement as in (VIII) to give (IX) which is known to equilibrate with the corresponding rotenoid in a basic medium.[3]

Heating (V) in pyridine at 100° for 48 h gave isorotenone, isolated (80% yield) by preparative-layer chromatography, m.p. and mixed m.p. 163° after crystallisation (methanol). Identity was verified by spectral comparison. The objective of devising a rotenoid synthesis patterned on biosynthetic lines and using dimethylsulphoxonium methylide is thus attained.



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[1] G. A. Caplin, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc.* (*C*), 1968, 2302.
[2] L. Crombie, J. S. Davies, and D. A. Whiting, *Chem. Comm.*, 1970, 535.
[3] L. Crombie, P. J. Godin, D. A. Whiting, and K. S. Siddalingaiah, *J. Chem. Soc.*, 1961, 2876.