The Synthesis of (±)-Ascochitine

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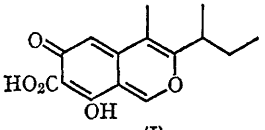
(−)-ASCOCHITINE, a metabolite of *Ascochyta pisi* Lib., and *A. fabae* Speg, has been defined[1] as (I). This represents the first example of the natural occurrence of the pyrono-quinonoid nucleus (II) from which the sclerotiorin group of metabolites[2] is derived. We now record the confirmation of structure (I) by the synthesis of (±)-ascochitine.

Thus, methylation of 3,5-dimethoxybenzyl cyanide[3] with methyl iodide–sodium–liquid ammonia gave 3,5-dimethoxy-α-methylbenzyl cyanide (III). Interaction of the corresponding acid chloride with s-butylmagnesium bromide formed the ketone (IV; R = Me, R′ = H) which was readily demethylated to yield (IV; R = R′ = H). Carboxylation of this at 180° in glycerol–potassium hydrogen carbonate furnished the acid (IV; R = H, R′ = CO_2H) which condensed with ethyl orthoformate to yield (±)-ascochitine (I), m.p. 202° (decomp.), having the same n.m.r. (in $CDCl_3$), infrared (in $CDCl_3$ and CS_2), and ultraviolet (in alcohol) spectra and the same R_f as the natural product.

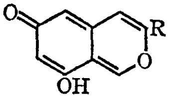
This constitutes the first synthesis of the pyrono-quinonoid system (II).

All new compounds had the requisite spectral and analytical characteristics.

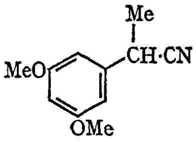
We thank Dr. H. Mishima for a specimen of (−)-ascochitine.



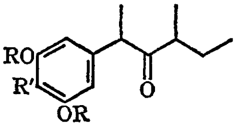
(I)



(II)



(III)



(IV)

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[1] I. Iwai and H. Mishima, *Chem. and Ind.*, 1965, 186.

[2] See: W. B. Whalley, *Pure Appl. Chem.*, 1963, 7, 565, and references cited therein.

[3] R. Adams, S. Mackenzie, and S. Loewe, *J. Amer. Chem. Soc.*, 1948, 70, 664.