

An Antifungal Acetylenic Keto-ester from a Plant of the Papilionaceae Family

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THE resistance to fungal infection exhibited by certain plants might have a chemical basis, and the compounds responsible could perhaps function as systemic fungicides when applied to other plants. This hypothesis instigated the examination of a number of plants for their fungitoxic properties and led¹ to the detection of three active principles in the

shoots of the broad bean, *Vicia faba* L. (Fam. Papilionaceae).

One of these [m.p. 63.5—64.5°; λ_{\max} (in EtOH) 3510 Å; ϵ 27,000] was isolated in 0.001% yield from seedlings (grown for 8 days in the dark) by extraction with benzene, chromatography on silica gel using ultraviolet light absorption and inhibition of

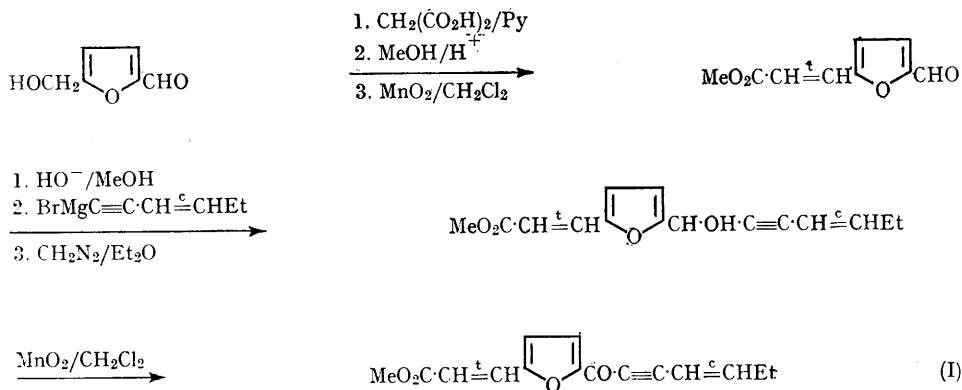
¹ R. L. Wain, D. M. Spencer, and C. H. Fawcett, "Fungicides in Agriculture and Horticulture," Society of Chemical Industry Monograph No. 15, pp. 109—131. London, 1961, See also *Chem. and Ind.*, 1961, 343.

spore germination of *Alternaria brassicicola* as criteria of purity, and low temperature crystallisation from hexane.

The formation of a 2,4-dinitrophenylhydrazone and the strong infrared peak at 2195 cm^{-1} , which disappeared almost completely on sodium borohydride reduction and was regenerated on manganese

(the lower homologue was also obtained by using *cis*-pentyne).

The natural and synthetic compounds were identical in m.p. and in infrared, nuclear magnetic resonance, and mass spectra and they showed similar activities against several fungal cultures. Compound (I) shows high fungicidal activity



dioxide oxidation, pointed to a conjugated acetylenic carbonyl compound. The nuclear magnetic resonance spectrum suggested the presence of the methyl ester, *trans*-ethylenic and *cis*-butenyl ($\text{CH}=\text{CH}\cdot\text{CH}_2\cdot\text{Me}$) groups, as well as the disubstituted furan system. Mass spectroscopy supported a $\text{C}_{15}\text{H}_{14}\text{O}_4$ formula, but the precise sequence of the various unsaturated centres could not be discerned, and structure (I) and two other $\alpha\beta$ -acetylenic ketone formulations seemed equally probable. Differentiation between them only became possible after suitable model compounds had been made and their light-absorption properties measured; the keto-ester (I) was then synthesised from 5-hydroxymethylfurfural as indicated

against a range of fungi¹ and in both structure and activity it is comparable with the naturally-occurring capillin ($\text{Ph}\cdot\text{CO}\cdot\text{C}\equiv\text{C}\cdot\text{C}\equiv\text{C}\cdot\text{Me}$) and related synthetic compounds.² It is of considerable interest however, that a much lower activity is observed against *Botrytis* species which are well known pathogens of *Vicia faba* in which the keto-ester is found.

The present isolation of an acetylenic compound from a plant of the Papilionaceae family emphasises their widespread distribution and brings to a total³ of ten the plant families known to elaborate such compounds.

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¹ K. Tanaka, I. Iwai, Y. Okajima, and T. Konotsune, *Antibiotics and Chemotherapy*, 1959, **9**, 151; B. W. Nash, D. A. Thomas, W. K. Warburton, and T. D. Williams, *J. Chem. Soc.*, 1965, 2983.

² J. D. Bu'Lock (*Progr. Org. Chem.*, 1964, **6**, 86) mentions eight, and K. E. Schulte, J. Reisch, and J. Rheinbay (*Phytochemistry*, 1965, **4**, 481) have reported the isolation of acetylenic hydrocarbons from *Gramineae* species.