Viridiol, a Steroid-like Product from Trichoderma viride

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Summary Viridiol, a new fungal metabolite, is shown to be a dihydro-derivative of viridin.

We report the characterization of a new fungal metabolite as a dihydro-derivative of the known product viridin (I), for which the structure (II) and the name viridiol are suggested From a batch of crude (I), which also contained gliotoxin and which was produced from cultures of Gliocladium virens Miller, Giddens and Foster ACC213, a small proportion of the new metabolite was isolated by chromatography. Again, in analysing culture filtrates of Trichoderma viride Pers. ex Fr. NRRL 1828† for gliotoxin we encountered a major u.v.-absorbing material with characteristic t.l.c. behaviour [λ_{max} 250, 317 nm (log ϵ 4.47, 4.07);

 $R_{\rm F}$ 0·36 on silica gel G in 9:1 CHCl₃-MeOH; green fl. under u.v.; red-brown with AgNO₃]. Preparative extraction and chromatographic purification gave a product $C_{20}H_{18}O_6$, m.p. 198—201° (decomp), M^+ 354 with losses of 18, 33, 46, and 74 mass units, $v_{\rm max}$ 1680, 1695 cm.⁻¹ (Nujol); 1673,

1712 cm.⁻¹ (CHCl₃). The compound was unstable in aqueous ethanolic alkali, giving $\lambda_{\rm max}$ 290, 500 nm changing reversibly to 275 nm. on acidification. Comparison with viridin (I)¹⁻² M 352, $\lambda_{\rm max}$ 300 nm. (log ϵ 4·22) suggested that the new product was a dihydroviridin. The significant differences between the n.m.r. spectrum of the new compound and that of (I) as recorded by Grove *et al.*² are that:—

- (a) the singlet due to the proton at C-4 is now at τ 2·23, instead of at τ 1·55 as in (I).
- (b) there are signals (doublets, sharpened in D_2O) due to two CHOH groups, one at τ 5·7 (J 6) similar to that at C-1 in (I) (τ 5·55, J 5) and one not paralleled in (I) at τ 4·85 (J 4·5).
- (c) the proton at C-2 [in (I), τ 6·05, d (J 5)] now gives a more complex signal at ca. τ 6·2—6·3 and is shown by double irradiation to be coupled to both of the above CHOH protons.

All three of these observations (together with the general similarity of the remainder of the n.m.r. spectrum) require structure (II), viridiol, for the new product. In the light of the known stereochemistry of viridin² the coupling constant of 4.5 c./sec. between the protons at C-2 and C-3 in viridiol suggests, but does not rigidly prove, the stereochemistry shown. Viridiol is a major metabolite of T. viride NRRL 1828, especially on C-rich, N-limited media.

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† This is the Weinding G-1 strain ("Gliocladium sp.," CMI-101,525), also described as Gliocladium fimbriatum Gilman and Abbott, but cf. P. W. Brian, Nature, 1944, 154, 667.

¹ J. F. Grove, J. S. Moffatt, and E. B. Vischer, *J. Chem. Soc.*, 1965, 3803; the coincidence of names between *T. viride* and *G. virens* is convenient but fortuitous.

² J. F. Grove, P. McCloskey, and J. S. Moffatt, *J. Chem. Soc.* (C), 1966, 743.