A New Pentaketide, Diplodialide-D, from *Diplodia pinea*

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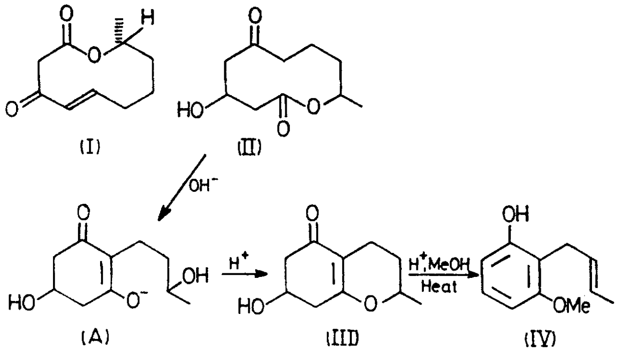
Summary The isolation from *Diplodia pinea* and structural elucidation of a minor pentaketide, diplodialide-D, is reported.

DURING an investigation of the production of a steroid hydroxylase inhibitor, diplodialide-A (I), by *D. pinea*,[1] a new related metabolite, diplodialide-D (II) was discovered in the culture, and we now report its structure elucidation.

Diplodialide-D (II) is a colourless oil, $C_{10}H_{16}O_4$; M^+, *m/e* 200·1050;[†] $[\alpha]_D^{25}$ +0·8° ($CHCl_3$); ν ($CHCl_3$) 3450, 1730, and 1700 cm^{-1}; δ ($CDCl_3$) 1·23 (3H, d, *J* 6 Hz, >CMe), 2·57 (2H, d, *J* 5 Hz, $-CH_2C:O$), 2·60 (1H, q, *J* 14 and 4 Hz) and 2·90

[†] Mass spectrum of (II): *m/e* 200·1050 ($C_{10}H_{16}O_4$; 19%), 182·0925 ($C_{10}H_{14}O_3$; 10%), 167·0715 ($C_9H_{11}O_3$; 7%), 164·0811 ($C_{10}H_{12}O_2$; 9%), 156·0761 ($C_8H_{12}O_3$; 4%), 115·0755 ($C_6H_{11}O_2$; 54%), and 113·0244 ($C_5H_5O_3$; 100%).

(1H, q, J 14 and 3Hz) ($-CH_2C:O$), 3·23 (1H, m, CHO*H*, disappears on D_2O addition), 4·37 (1H, m, CHOH), and 4·56 (1H, m, O–CH); no other signals below δ 4·0. Irradiation of the signal at δ 4·37 simplified the two CH_2 signals to a singlet (δ 2·52) and a four-line signal (δ 2·67, J 14 Hz), indicating that (II) has the partial structure $-CO-CH_2-CH(OH)-CH_2-CO-$. The partial structure $Me-CH(OCO-)-CH_2-$ was confirmed by irradiation of the signal at δ 1·23, which caused the signal at δ 4·56 to become a double doublet (J 6 and 2 Hz). The single additional unsaturation shown by the empirical formula of (II) was thus attributable to the presence of a ring.



The u.v. spectrum of (II) in MeOH showed no absorption, but an absorption maximum (λ_{max} 290 nm, ε 9000) appeared after addition of 0·1 N-NaOH which shifted irreversibly to 263 nm upon acidification. Treatment of (II) with KOH in $MeOH-H_2O$ (1:2) (room temp; 2 h) followed by acidification gave an αβ-unsaturated ketone (III) as a viscous oil, $C_{10}H_{14}O_3$ (M^+ 182·0938). The i.r. (3400, 1650, and 1615 cm^{-1}) and u.v. (MeOH, 263 nm, ε 11,800) spectra of (III) show the formation of an αββ'-trisubstituted αβ-unsaturated ketone group[2] and the disappearance of the ester function of (II). The n.m.r. spectrum ($CDCl_3$) of (III) showed signals at δ 1·36 (3H, d, J 6 Hz, *Me*CH–O–), 1·3—1·8 (2H, m, $-CH_2-$), 2·0—3·0 (6H, m, allylic-H and $-CH_2C:O$), and 4·16 and 4·30 (each 1H, m, –CH–O–), confirming the assignment of structure (III). Accordingly, the changes in the u.v. spectrum of (II) on addition of base and acid are presumed to be due to the formation of a 1,3-dicarbonyl intermediate (A) by transannular cyclization of (II) and dehydration of the enolate ion (A) to (III) with acid. Furthermore, (III), when heated under reflux in 1·75% HCl in MeOH for 1 h, gave a phenolic compound (IV), $C_{11}H_{14}O_2$, [m/e 178 (M^+), 137 ($M - C_3H_5$), and 136 ($M - C_3H_6$); λ_{max} 273 (ε 1000) and 281 (ε 1000) nm]. From these results, we assign structure (II) to diplodialide-D. The high-resolution mass spectrum of (II)† is also compatible with structure (II) for diplodialide-D.

The presence of (II) in the culture filtrate of *D. pinea* suggests that diplodialides may be derived from a partially reduced pentaketide.[3]

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[1] T. Ishida and K. Wada, *J.C.S., Chem. Comm.*, 1975, 209.

[2] K. Nakanishi, 'Infrared Absorption Spectroscopy—Practical,' Holden-Day, San Francisco and Nankodo, Tokyo, 1962, p. 69; A. I. Scott, 'Interpretation of the Ultraviolet Spectra of Natural Products,' Pergamon Press, Oxford, 1964, p. 58.

[3] W. B. Turner, 'Fungal Metabolites,' Academic Press, London, 1971, p. 116.