A New Metabolite of *Pithomyces chartarum* related to the Sporidesmins

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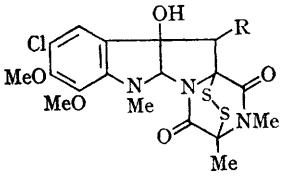
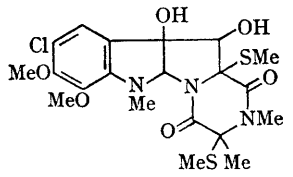
WE report the isolation of a new metabolite of *Pithomyces chartarum* and a new method for the conversion of disulphides into the corresponding dithiomethyl compounds.

Further examination of crude aqueous-methanol extracts of cultures of *Pithomyces chartarum* on *Secale cereale* has shown that sulphur-containing metabolites other than sporidesmin (I; R=OH),[1] sporidesmin-B (I; R=H),[2] and sporidesmin-C[3] are produced. One of these has now been isolated by chromatography of the residue from the methanol–water phase of the partition described previously,[2] on silica gel using the solvent benzene–diethyl ether–acetic acid (44 : 6 : 1). Fractions from the column were monitored by thin-layer chromatography on silica gel using the same solvent and sulphur compounds were detected by spraying the dried plates with a solution (100 ml.) of silver nitrate (5 g.) in water. The new metabolite (called sporidesmin-D) was eluted after sporidesmin, and separated from ether as colourless plates of the etherate. The latter was recrystallised from ethanol, giving the ethanol solvate, m.p. 105—107°, $[\alpha]_D^{20}$ 58° (*c* 0·1, $CHCl_3$), *m/e* 503·0931 ($C_{20}H_{26}{}^{35}ClN_3O_6S_2$ requires 503·0951). Its nuclear magnetic resonance spectrum was similar to that of sporidesmin but in addition two signals, each equivalent to three protons of two *S*-Me groups were observed at τ 7·58, 7·66 p.p.m. Acetylation gave a diacetate [m.p. 202—204°, $[\alpha]_D^{20}$ + 67°, (*c* 0·1, $CHCl_3$)] which was converted into anhydrodethiosporidesmin[4] with boron trifluoride in ether. The presence of two *S*-Me groups in sporidesmin-D was confirmed by treating sporidesmin in pyridine with methyl iodide and a solution of sodium borohydride in methanol. The product obtained in 70% yield was identical to sporidesmin-D. These results are consistent with the expression (II) for the new metabolite. Satisfactory analyses have been obtained for the new compounds.



(I)



(II)

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