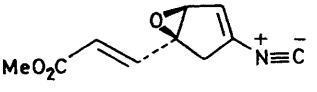
Isonitrile Acids from Cultures of the Fungus *Trichoderma hamatum* (Bon.) Bain. aggr., *X*-Ray Structure†

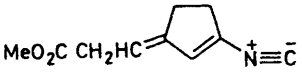
By DONALD BREWER, ERIC J. GABE, ALFRED W. HANSON, and ALAN TAYLOR*
(*National Research Council of Canada, Atlantic Regional Laboratory, Halifax, Nova Scotia*)
JOHN W. KEEPING and VIKTOR THALLER
(*The Dyson Perrins Laboratory, Oxford University, South Parks Road, Oxford* OX1 3QY)
and BHUPESH C. DAS
(*Centre National de la Recherche Scientifique, Institut de Chimie des Substances Naturelles*, 91190, *Gif-sur-Yvette, France*)

Summary Two acids have been isolated from cultures of the above fungus as the corresponding methyl esters; one is shown by *X*-ray crystallographic analysis to be methyl 3-(3-isocyano-6-oxabicyclo[3.1.0]hex-2-en-5-yl) acrylate (**1**), the other is probably methyl 3-(3-isocyanocyclopent-2-enylidine) propionate (**2**).

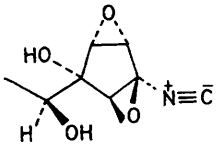
SEVERAL groups of workers[1,2] have reported the presence of unstable metabolites in cultures of *Trichoderma* spp. On the basis of their strong absorption at *ca.* 2150 cm^{-1}, these metabolites have variously been considered to be nitriles or acetylenes. We have reported[3] that *Trichoderma* spp. constitute an important part of the microflora of permanent pasture where poor ruminant growth is a problem. Examination of isolates of *Trichoderma hamatum* (Bon.) Bain. aggr.[4] from these pastures showed that 30% produced metabolites in culture that absorbed at 2150 cm^{-1}. Cultures from one such typical isolate (HLX 1360‡) produced two acids (20 and 30 mg l^{-1} respectively) which were isolated as the corresponding methyl esters. For the first, the epoxy-ester structure [(**1**) or its enantiomer] was established by *X*-ray diffraction analysis; for the second, structure (**2**) is a reasonable interpretation of the data available. Whilst this work was in progress, the structure of the neutral *Trichoderma* metabolite trichoviridine[2] was established as (**3**).[5]



(1)



(2)



(3)

The epoxy-ester (**1**) was obtained as crystals, m.p. 70—71 °C, $[\alpha]_D^{20}$ + 115°, (*c*, 0·31, Et_2O), λ_{max} (MeOH) 225 nm (ϵ 15,600), *m/e* 191·057 ($C_{10}H_9NO_3$ requires 191·072), 132·047, and 105·035 (m* *ca.* 83·5 = $C_8H_6NO^+ \rightarrow C_7H_5O$ + HCN), δ (^1H) (CCl_4) 6·81 (1H, *J* 16 Hz), 6·28 (1H, *J* 1·9 and 1·9 Hz), 6·08 (1H, *J* 16 Hz), 3·74 (1H, d, *J* 1·9 Hz), 3·73 (3H), and 2·89 (2H, *J* 1·9 Hz), δ(^{13}C) (CCl_4–$C^2H_2Cl_2$, 1 : 1) 171·4, 164·9, 141·8 (J_{CH} 161·7, $^2J_{CH}$ −1·7 Hz), 132·3, 129·1 (J_{CH} 176·2, $^2J_{CH}$ 8·8, $^3J_{CH(2)}$ 4·5 Hz), 122·9 (J_{CH} 165·4, $^2J_{CH}$ −4·4 Hz), 64·9 (J_{CH} 192·0 $^2J_{CH}$ 7·7 Hz), 62·4, 51·4 ($J_{CH(3)}$ 147 Hz), and 38·0 p.p.m. ($J_{CH(2)}$ 134·4,

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‡ Accession number to the culture collection held at the Atlantic Regional Laboratory.

$J_{CH(2)}$ 140·9, ^3J 2·9 Hz), which were monoclinic, space group $C2$, $a = 14{\cdot}50$ (1), $b = 5{\cdot}288$ (4), $c = 14{\cdot}17$ (1) Å, $\beta = 112{\cdot}56$ (5)°, $Z = 4$. The structure was solved by direct methods (MULTAN) and refined by block-diagonal least-squares. The present R index is 0·07 for 803 independent reflections. Refinement of a model representing the corresponding nitrile resulted in poorer agreement, an anomaly in the residual electron density, and improbable thermal-motion parameters for the presumed C and N atoms.§

The ester (**2**) crystallised in unstable prisms, $[\alpha]_D^{20}$ 0° (*c*, 0·76, CCl_4), λ_{max} (Et_2O) 270 nm (ϵ 12,000), *m/e* 177·079 ($C_{10}H_{11}NO_2$ requires 177·079), 118·066, 91·055 (m* *ca.* 70·2 = $C_8H_8N^+ \rightarrow C_7H_7^+ + HCN$), ν_{max} (CCl_4) 2110 and 1740 cm^{-1}, δ (^1H) (CCl_4) 6·49 (1H, br), 5·42 (1H, J 7·5 Hz), 3·66 (3H), 3·05 (2H, J 7·5 Hz), and 2·68 (2H, br), δ (^{13}C) (CCl_4–$C^2H_2Cl_2$, 1:1) 171·2, 170·9, 144·0, 132·9, 128·6 (J_{CH} 170 Hz), 114·9 (J_{CH} 160 Hz), 51·7 ($J_{CH(3)}$ 146·9 Hz), 34·5 ($J_{CH(2)}$ 129 Hz), 32·8 ($J_{CH(2)}$ 135·6, $J_{CH(2)}$ 3·8, J_{CH} 7·8 Hz), and 28·5 p.p.m. ($J_{CH(2)}$ 136 Hz). Like the isonitrile (**1**) the ^{13}C resonances at δ 170·9 and 132·9 were broad and of low intensity. A brown polymer was obtained when this metabolite was treated with a trace of nickel chloride.[6] It reacted with ammonium formate and phenylacetaldehyde[7] to give a yellow oil which did not absorb at 2110 cm^{-1} and which gave DL-phenylalanine after acid hydrolysis. These factors may be interpreted in terms of structure (**2**).

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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