Tetrahedron Letters No. 9, pp 639 - 640, 1973. Pergamon Press. Printed in Great Britain.

THE CRYSTAL STRUCTURE OF (±)-ALTENUIC ACID II

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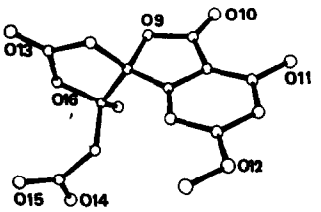
(Received in UK 14 November 1972; accepted for publication 17 January 1973)

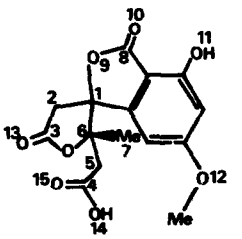
(±)-Altenuic Acid II, $C_{15}H_{14}O_8$, is one of three isomeric acids, interconvertible under basic conditions, which have been isolated from the mould Alternaria tenuis. An X-ray crystallographic study, has now established the structure (I).

The acid crystallises from dioxan as small clear rhombs; triclinic $P\bar{1}$, a = 13.718, b = 6.599, c = 8.177 Å, α = 95.73°, β = 107.88°, γ = 93.72°, 2 mols/cell (1 is D and the other L). Intensities of 2620 reflections were measured on a Siemens diffractometer with Cu-K_α radiation (to θ max. of 70°) and of these, 268 were reckoned unobserved. The structure was solved by the symbolic-addition procedure and refined to a current R value of 0.047. The spatial arrangement and configuration of one enantiomer is illustrated in the figure. The oxygen atoms O(10) and O(11) are joined by pairs of intermolecular bonds (2.76 Å). Pairs of intermolecular hydrogen bonds (2.66 Å) also exist between the carboxylate groups of symmetry-related molecules. This system of hydrogen bonding produces rigid continuous chains of molecules which contribute to the high melting point (245-246°) of this isomer.

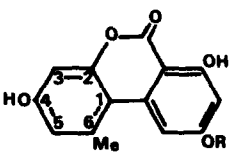
Structural considerations are consistent with the initial suggestion that the altenuic acids may be formed via oxidative ring fission of a product related to alternariol (II) or its methyl ether(III).[2] Additional support for this biosynthetic scheme is afforded by the structure recently proposed for the A. tenuis metabolite altenusin (IV).[3] This could yield (I) following ring cleavage of the catechol moiety in a manner closely analogous to the known metabolic degradation of catechol leading to cis, cis - muconic acid and muconolactone (V).[4]



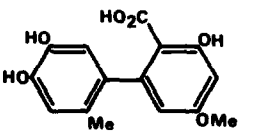
FIGURE



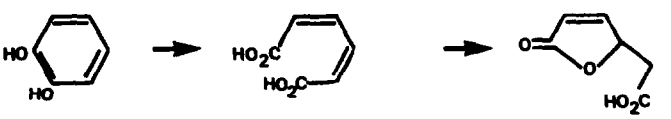
(I)



(II) R = H
(III) R = Me



(IV)



(V)

REFERENCES

1. H. Raistrick, C.E. Stickings, and R. Thomas, Biochem.J., 1953, 55, 421; T. Rosett, R.H. Sankhala, C.E. Stickings, M.E.U. Taylor, and R. Thomas, ibid 1957, 67, 390.

2. R. Thomas, Biochem. J., 1961, 80, 234; R. Thomas, ch.13 in 'Biogenesis of Antibiotic Substances', ed. Z. Vanek and Z. Hostalek, Czechoslovak Academy of Sciences, Prague, 1965.

3. D. Rogers, D.J. Williams and R. Thomas, Chem. Comm., 1971, 393; R.G. Coombe, J.J. Jacobs and T.R. Watson, Austral. J. Chem., 1970, 23, 2343.

4. J.A. Elvidge, R.P. Linstead, B.A. Orkin, P. Sims, H. Baer and D.B. Pattison, J. Chem. Soc., 1950, 2228; W.R. Sistrom and R.Y. Stanier, J. Biol. Chem., 1954, 210, 821.