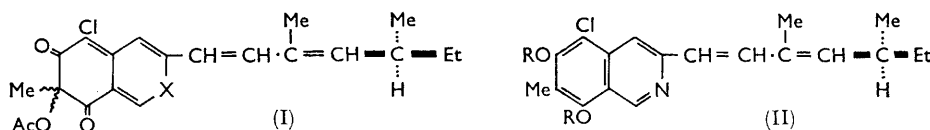


1334. The Chemistry of Fungi. Part LII.¹ (—)-Sclerotiorin

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(—)-Sclerotiorin has been converted into aposclerotioramine (II; R = H) from which it follows that (+)- and (—)-sclerotiorin differ only in the relative configuration at C-7.

FROM a comparison of the C₁₀ dienoic acids formed upon alkaline hydrolysis, it has been concluded² that (—)-sclerotiorin (I; X = O), produced by *Penicillium hirayamae*,³ and (+)-sclerotiorin, isolated as a metabolite of *P. sclerotiorum*,⁴ *P. multicolor*,⁴ and *P. implicatum*, have the same configuration at the asymmetric centre in the side-chain. In view of the relatively low specific rotation associated with the asymmetric centre in this side-chain it seemed desirable to provide collateral evidence for this conclusion.



Thus, we have converted (—)-sclerotiorin successively into (—)-sclerloramine (I; X = NH) and thence into aposclerotioramine (II; R = H). This was characterised as

¹ Part LI, preceding Paper.

² E. M. Gregory and W. B. Turner, *Chem. and Ind.*, 1963, 1625.

³ S. Udagawa, *Chem. and Pharm. Bull. (Japan)*, 1963, **11**, 366.

⁴ F. M. Dean, J. Staunton, and W. B. Whalley, *J.*, 1959, 3004, and references cited therein.

the di-*O*-acetate (II; R = Ac) which was identical (m. p., mixed m. p., infrared spectrum, and o.r.d. curve) with a specimen prepared from (+)-sclerotiorin. Hence, in agreement with the work of Gregory and Turner,² (+)- and (–)-sclerotiorin differ only in the relative configuration at C-7.

Since ozonolysis of (+)-sclerotiorin yields (+)- α -methylbutyraldehyde which has the same absolute configuration as (–)-2-methylbutanol (cf. Birkinshaw⁵), and this has been shown⁶ to possess the (*S*) absolute configuration, it follows that the absolute configurations of (+)- and (–)-sclerotiorin and of aposclerotioramine are as shown in (I; X = O) and (II), respectively.

EXPERIMENTAL

(–)-*Sclerotiorin*. This was obtained from the mycelium of *P. hirayamae* when grown upon a modified Czapek–Dox medium as described for the production of (+)-sclerotiorin,⁷ and had m. p. 204–205°, $[\alpha]_D^{26}$ –480° (*c* 0.01 in ethanol). (–)-Sclerotioramine, prepared as for (+)-sclerotioramine,⁷ was reductively aromatised with zinc and alkali to yield aposclerotioramine⁸ which formed the di-*O*-acetate,⁸ m. p. 153° (Found: C, 66.0; H, 6.3; N, 3.4. Calc. for C₂₃H₂₄ClNO₄: C, 66.3; H, 6.3; N, 3.4%).

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⁵ J. H. Birkinshaw, *Biochem. J.*, 1952, **52**, 283.

⁶ *Progr. Stereochem.*, 1954, **1**, 188.

⁷ R. A. Eade, H. Page, A. Robertson, K. Turner, and W. B. Whalley, *J.*, 1957, 4913.

⁸ H. C. Fielding, N. B. Graham, A. Robertson, R. B. Travers, and W. B. Whalley, *J.*, 1957, 4931.