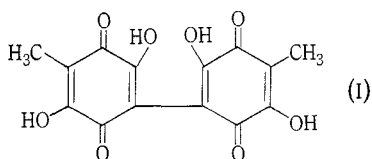


STUDIES IN RELATION TO BIOSYNTHESIS

XXXIX.* OOSPOREIN

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Monomeric methylbenzoquinones are frequently derived by the polyketide route by way of hydroxymethylbenzoic acids¹ in accord with prediction² and some early tracer work in our laboratory.³ A dimeric benzoquinone such as oosporein (I) accordingly probably arises by a

similar route, with an oxidative dimerization stage, e.g.⁴ In order to confirm the polyketide origin, [1-¹⁴C]acetic acid was fed to the organism, grown for 28 days on a modified William Saunders medium,⁵ omitting thallos chloride, ferric chloride, and potassium iodide. The acetic acid (300 μ Ci) was added on the ninth day. The metabolite was extracted with ethyl acetate from the mycelium⁵ and the concentrated medium, the combined yield of product being 350 mg/l. The product, consisting of pale yellow needles, m.p. 300–330°, was not the quinone, but the corresponding hydroquinone. Oxidation with chromic acid gave oosporein as bronze plates, m.p. 260–270° (lit.⁶ 260–275°) (Found: C, 54.9; H, 3.65. Calc. for C₁₄H₁₀O₈: C, 54.9; H, 3.3%). The tetraacetate had m.p. 190–191° (lit.⁶ 191°) (Found: C, 55.7; H, 4.55. Calc. for C₂₂H₁₈O₁₂: C, 55.7; H, 3.8%). The quinone was converted into the leucoacetate, m.p. 265–266° (lit.⁶ 271°) (Found: C, 56.0; H, 4.9. Calc. for C₃₀H₃₀O₁₆: C, 55.75; H, 4.6%). The metabolite from radioactive precursor was oxidized to the quinone, diluted with inactive material, and crystallized to constant radioactivity from dioxan; the incorporation was 4%. The oosporein (r.m.a. 153.2 $\times 10^4$) was submitted to Kuhn–Roth oxidation and the resulting acetic acid degraded in the

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² Birch, A. J., *Fortschr. Chem. org. NatStoffe*, 1957, **14**, 198.

³ Birch, A. J., Fryer, R. I., and Smith, H., *Proc. chem. Soc.*, 1958, 343.

⁴ Dean, F. M., Osman, A. M., and Robertson, A., *J. chem. Soc.*, 1955, 11; Erdtman, H., and Wachtmeister, C. A., "Festschrift A. Stoll," p. 144. (Birkhäuser: Basel 1957.)

⁵ Lloyd, G., Robertson, A., Sankey, G. B., and Whalley, W. B., *J. chem. Soc.*, 1955, 2163.

⁶ Kögl, A., *Recl Trav. chim. Pays-Bas*, 1944, **63**, 5.

usual manner; r.m.a. of BaCO_3 : 18.8×10^4 ; r.m.a. of *N*-methyl-2,4-dinitroaniline: 0.095×10^4 . Radioactive assay was carried out as in previous parts of this series.⁷

There is, therefore, little randomization of label, and the acetic acid represents one-eighth of the r.m.a. of the oosporein (i.e. contains one-quarter of the radioactivity since two moles result from the oxidation). This accords with the expected polyketide origin.

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⁷ Birch, A. J., Massy-Westropp, R. A., Rickards, R. W., and Smith, H., *J. chem. Soc.*, 1958, 360.