

Structure of the Lichen Depsidone Pannarin

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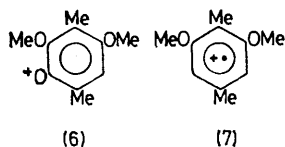
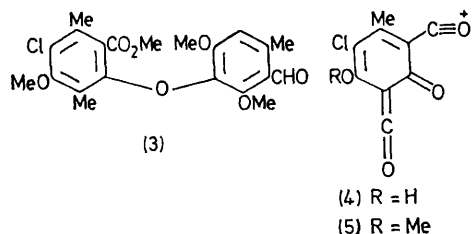
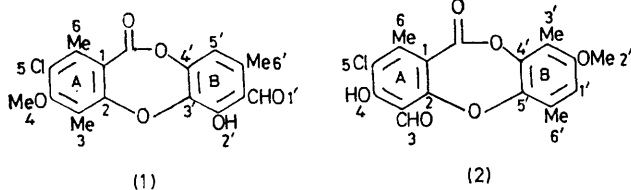
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Summary The structure of the lichen depsidone pannarin is revised to 5-chloro-3-formyl-4-hydroxy-2'-methoxy-3',6,6,'-trimethyldepsidone (**2**)

THE depsidone, pannarin, was assigned structure (**1**) by Yosioka after a sequence of classical degradations.¹ It is unusual in that the diaryl ether linkage is at the 3'-position of ring B.² We now present evidence for the revised

structure (2) for pannarin, which is biogenetically more normal.



Methylation of pannarin followed by methanolysis of the depside linkage and further methylation gave a diaryl ether, m.p. 94–96°, which must have structure (3) were Yosioka's structure for pannarin correct. A synthetic specimen of the diaryl ether (3) was secured by standard reactions from 4-methoxy-2,5-dimethylbenzoic acid³ and

3,4,5-trimethoxytoluene,⁴ and was different from the degradation product.

Pannarin is an *o*-hydroxyaldehyde since the i.r. spectrum exhibits a band at 1650 cm⁻¹ and the n.m.r. spectrum (CDCl₃; 90 MHz) shows sharp singlets at τ - 2.77 (OH) and - 0.66 (CHO). Its mass spectrum exhibits a peak at *m/e* 210.9798 (¹²C₉¹H₄³⁵Cl¹⁶O₄) due to a ring A fragment,⁵ now ascribed structure (4). In the mass spectrum of *O*-methylpannarin, m.p. 192–194°, the ring A fragment, ascribed structure (5), occurs at *m/e* 225. In view of the biogenesis of depsidones these data are best accommodated by the ring A of structure (2).

The nature of ring B of pannarin is evident from its n.m.r. spectrum which, in addition to the features mentioned above, exhibits resonances at τ 3.56 (1H, br s, *W*₁ 2.0 Hz, ArH), 6.21 (3H, sharp s, OMe), 7.44 (3H, sharp s, 6-Me), 7.64 (3H, br s, *W*₁ 2 Hz, 6'-Me), and 7.80 (3H, br s, *W*₁ 2 Hz, 3'-Me). Irradiation at τ 7.80 caused sharpening of the aromatic proton (*W*₁ 1.7 Hz), and irradiation at τ 7.64 caused greater sharpening of the aromatic proton (*W*₁ 1.0 Hz). In addition irradiation at τ 3.56 caused the broad singlets at 7.64 and 7.80 to collapse to two apparent doublets. We interpret⁶ these results in terms of the biogenetically reasonable *para*-arrangement of the methyl groups on ring B, which also bears a methoxy-group and an aromatic proton as shown in structure (2). This is confirmed by the presence of prominent peaks in the mass spectrum of the degradation product, m.p. 94–96°, at *m/e* 181 and 166 to which structures (6) and (7) are ascribed.

We therefore propose on the basis of this evidence and from biogenetic considerations that pannarin has structure (2). Huneck and Lamb have since reached the same conclusions on different grounds.⁷

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¹ I. Yosioka, *Yakagaku Zasshi*, 1941, **61**, 332.

² C. F. Culberson, 'Chemical and Botanical Guide to Lichen Products,' University of North Carolina Press, Chapel Hill, 1969, p. 43.

³ G. R. Clemo, R. D. Haworth, and E. Walton, *J. Chem. Soc.*, 1929, 2368.

⁴ H. Sugihara, M. Watanabe, Y. Kawamatsu, and H. Morimoto, *Annalen*, 1972, **763**, 109.

⁵ S. Huneck, C. Djerassi, D. Becher, M. Barber, M. von Ardenne, K. Steinfelder, and R. Tümmeler, *Tetrahedron*, 1968, **24**, 2707.

⁶ See J. B. Rowbotham and T. Schaefer, *Canad. J. Chem.*, 1974, **52**, 589, and refs. therein.

⁷ S. Huneck and I. M. Lamb, unpublished results; S. Huneck, personal communication to M.V.S. (18.5.74).