The Structure of Portentol: X-Ray Analysis of a Heavy-atom Derivative

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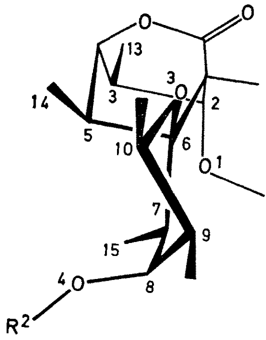
Summary The constitution and absolute configuration of the lichen substance portentol have been established by X-ray analysis of the p-bromobenzoate (I).

THE lichen substance portentol from *Roccella fuciformis*, formulated as (II)[1,2] on the basis of chemical and spectroscopic evidence, is of biosynthetic interest, because it is assembled *in vivo* by an unexpected pathway (see preceding communication). In order to put the biosynthetic work on a firm basis, an X-ray analysis of the p-bromobenzoate (I)[2] was undertaken. The results fully confirm the constitution and absolute configuration (II) of portentol and establish the previously unsupported configuration at C(3).



	R¹	R²
FIGURE.	(I) p-Br·C_6H_4·CO⁻	Ac
	(II) C(2) Ketone	H

The crystals are orthorhombic, space group $P2_12_12_1$ with four molecules of $C_{26}O_7H_{33}Br$, M = 536·9, in a unit cell of dimensions a = 8·704(6), b = 11·065(8), and c = 26·932(18) Å. A total of 2252 intensity data, of which 1327 were unique, were collected on a Hilger and Watts four-circle diffractometer from a crystal mounted about the a axis. The structure was solved by Patterson and Fourier methods and refinement by block-diagonal least-squares techniques

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with anisotropic temperature factors for all atoms has reduced *R* to 10·1%, which is the limit of convergence with this data set due to the effects of crystal decomposition in the later stages of the data collection. The absolute configuration was established by Bijvoet's anomalous dispersion method and this confirms the prediction made previously.[2]

The details of the structure of (I) (Figure) indicate how the conformation of a crowded molecule adjusts itself to minimise unfavourable non-bonded interactions. These are centred in two regions and arise from compression between (i) O(1) and C(15), and (ii) C(14), C(10), C(5), and O(4).

Both sets of interactions are minimised by a flattening of the tetrahydropyran ring at the spiro-carbon atom, such that C(6) is displaced by 0·45 Å and C(9) by −0·65 Å from a mean plane passing through O(3), C(10), C(8), and C(7). In addition, the C(2), O(1) bond rotates in an *exo*-direction to compress the dihedral angle O(1), [C(2), C(3)], C(13) to 73°.

In consequence of these two conformational adjustments, (i) C(15) becomes equidistant from C(2) and C(3) at 3·60 Å, and (ii) the C(14) to C(10) distance increases to 3·25 Å and the C(5) to O(4) distance to 3·19 Å.

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[2] D. J. Aberhart, K. H. Overton, and S. Huneck, *J. Chem. Soc.* (*C*), 1970, in the press.