Portentol:[1] A Novel Polypropionate from the Lichen *Roccella portentosa*

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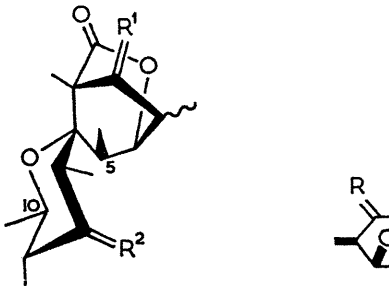
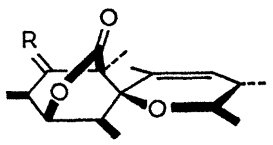
WE have isolated from *Roccella portentosa* (Mont.) Darb. and related lichens a novel polyketide lactone which we name portentol and formulate as (I) on the basis of the following and much additional evidence to be reported elsewhere.

Portentol (I), $C_{17}H_{26}O_5$,† m.p. 260—261°, $[\alpha]_D$ +21° ($CHCl_3$ throughout) and the naturally occurring acetate (from *R. fuciformis* DC.) (Ia), $C_{19}H_{28}O_6$, m.p. 223—224°, $[\alpha]_D$ +35°, showed the expected bands in the i.r. [ν_{max} (CCl_4) (I) 1776 (boat δ-lactone[2]), 1725 (cyclohexanone), and 3629 (OH) cm.$^{-1}$; (Ia) 1787, 1735, and 1753 (acetate) cm.$^{-1}$]. Portentol was oxidised readily to portentone (II), $C_{17}H_{24}O_5$, m.p. 153—154°, $[\alpha]_D$ +50°, but acetylated only with difficulty. Anhydroportentol (III), $C_{17}H_{24}O_4$, m.p. 195—197°, $[\alpha]_D$ +92° was formed very readily by heating portentol above its melting point or by keeping the acetate at 20° in H_2SO_4–AcOH (1 : 19). The n.m.r (Figure) and n.m.d.r. spectra (HA 100) of portentol acetate identify the functional sequences X and Y of the Figure which account for all but the ringed fragments.



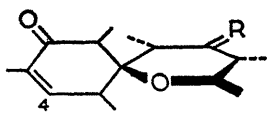
A

	R^1	R^2
(I)	O	α-OH, H
(Ia)	O	α-OAc, H
(II)	O	O
(V)	OH, H	α-OH, H
(VI)	OH, H	α-OAc, H



B

(III) R = O
(VII) R = OH, H

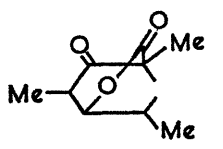


C

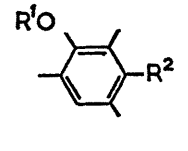
(IV) R=α-OH, H
(IX) R = O

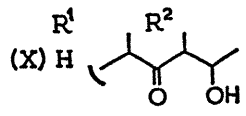
Portentol, or its acetate, on being heated with KOH (1N, EtOH) under reflux gave decarboxyportentol (IV), $C_{16}H_{26}O_3$, b.p. 120°/0·1 mm, $[\alpha]_D$ + 177°. Portentone (II) and anhydroportentol (III) similarly decarboxylated but the alcohols (V), m.p. 269—271°, $[\alpha]_D$ +67°, (VI), m.p. 193—194°, $[\alpha]_D$ +78°, and (VII), m.p. 202—204°, $[\alpha]_D$ +30° did not. The ketonic carbonyl is therefore necessary for decarboxylation. This requirement and the spectroscopic properties of decarboxyportentol (IV) [λ_{max} 242 nm. (ε 5500); ν_{max} (CCl_4) 1675 cm.$^{-1}$; τ 3·35 (d of qu, 1H, H-4) and 8·82 (s, 3H; vinyl Me)] lead uniquely to the fragment (VIII), derivable from the part structure X in the Figure. When (VIII) is joined to fragment Y of the Figure through the remaining carbon atom, this leads unambiguously to the constitution (I) for portentol.

The decarboxylation products are, predictably, easily aromatised. Thus, for example, decarboxyportentone,

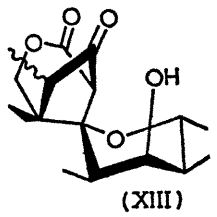


(VIII)

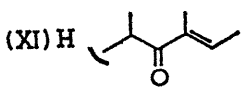




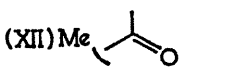
(X) H



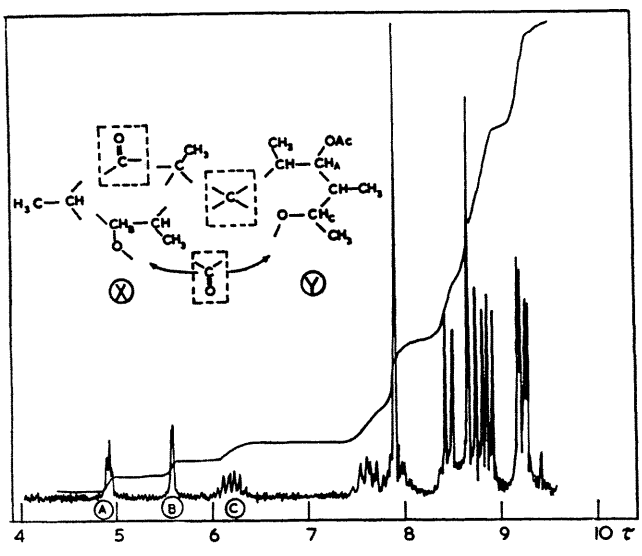
(XIII)



(XI) H



(XII) Me



FIGURE

† The composition of all compounds is based on high resolution (MS9) mass spectrometry and/or combustion analyses. Full spectroscopic support has been obtained for all compounds even where this is not specifically stated.

(IX), $C_{16}H_{24}O_3$, m.p. 98—100°, $[\alpha]_D$ + 167° gives at 100° with H_2SO_4–H_2O–EtOH (1 : 4 : 5) [*via* the intermediate (X)] the mesitol (XI), $C_{16}H_{22}O_2$, m.p. 126—127°, $[\alpha]_D$ ±0°, $[\alpha]_{227nm.}$ −4880°; ν_{max} (CCl_4) 3615, 3500, and 1670 cm.$^{-1}$ λ_{max}(MeOH) 223(!) nm. (ϵ 15,400), 285 nm. (2000), moving to 295 nm. (3600) in base; n.m.r. signals at τ 3·19 (1H, s, ArH), 3·67 (1H, qq, vinyl H), and 5·32 (1H, s, phenolic H; D_2O exchangeable). Methylation of (XI) and a three-stage oxidative degradation (OsO_4, $NaIO_4$, H_2O_2–OH^-; all intermediates characterized) afforded the acetophenone (XII), identical with an authentic specimen (obtained from the known[3] phenol).

The absolute configuration of portentol (I) derives from the following considerations: (*a*) detection of a strong (30% in $CDCl_3$) NOE[4] between H-10 and the C-5 methyl group in (Ia); (*b*) the magnitudes of coupling constants in (I) and (Ia) show that the methyl groups borne by the tetrahydropyran ring must all be equatorial, the hydroxyl axial; (*c*) the vinyl methyl signals in anhydroportentol (III) and its reduction product (VII) are at τ 8·51 and 8·08 respectively, so that[5] the tetrahydropyran ring must be attached at the spiro-centre as shown and not in the diastereomeric sense; (*d*) the absolute configuration at C-10 [determined by the Horeau method[6] applied to (X) and its phenolic methyl ether; optical yields 18 and 29%] is *R*. Of the two configurational alternatives (I) and (XIII) for portentol permitted by this evidence, the observed strongly positive ($[\Phi]_{227nm.}$ + 4060°) Cotton Effect of the dihydroxylactone (V), points[7] to (I). An *X*-ray structure analysis of the *p*-bromobenzoate, m.p. 212—214°, $[\alpha]_D$ +51, of the alcohol (VI) is in progress.

The *in vivo* formation of portentol apparently *via* a linear polyketide assembled from one acetate and five propionate units (as is the aglycone portion of the macrolide methymycin[8]), raises interesting questions as to its biosynthesis. Preliminary studies suggest that this may, in some important respects, differ from that of the macrolides.[8]

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