A Polychloro Quinone from Green Soils

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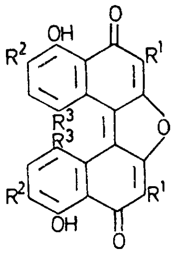
Summary A polychloro pigment, $C_{20}H_4Cl_6O_5$, isolated from certain green soils, has been shown to be the binaphthofuran quinone (**1**).

Polychlorinated aromatic compounds have been implicated in environmental matters. A naturally occurring example was reported briefly in 1964.[1] It has been obtained (5 mg per kg) from green coastal soils in southern Australia, including remote areas of National Park land. We have chromatographed CH_2Cl_2 extracts to obtain a major pigment, $C_{20}H_4Cl_6O_5$. It formed purple solutions (λ_{max} 400 and 555 nm; ν_{max} 1620 cm^{-1}). With boroacetic anhydride it had λ_{max} 750 nm.

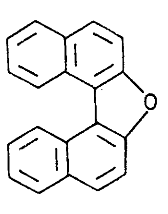
The pigment showed redox behaviour. Its ^{1}H n.m.r. spectrum ($CDCl_3$) exhibited two singlets (δ 7·75 and 13·70), the former corresponding to two aromatic protons, the latter, exchangeable with D_2O, to two H-bonded hydroxy-groups. Reductive acetylation of the pigment or of its derived diacetate gave a dihydrotetra-acetate (acetate resonances at δ 2·46 and 2·48). Both this product and the diacetate were reconverted into the original pigment by treatment with formic acid in air. On zinc dust distillation the pigment cleanly gave perylene, accounting for all 20 carbon atoms.

These data are compatible with structure (**1**) which was confirmed as follows. The electronic absorption spectrum of the dihydrotetra-acetate had fine structure identical with that of the binaphthofuran (**2**)[2] and was bathochromically shifted by *ca.* 45 nm owing to the acetoxy- and chloro-groups.

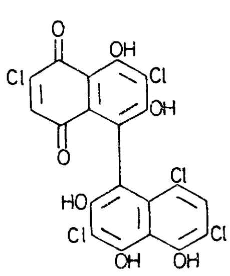
Treatment of the pigment with zinc in ethanol gave penta-, tetra-, tri-, and di-chloro-analogues after atmospheric reoxidation. The tetrachloro-compound (**3**) showed an additional quinonoid singlet resonance (2H) at δ 6·47. For the dichloro-analogue (**4**) the benzenoid region of the spectrum formed an AB system (δ 7·75 and 7·19, J 8 Hz). All three compounds (**1**), (**3**), and (**4**) underwent concerted loss of Cl_2 as their major mass spectrometric fragmentation.



(1) $R^1 = R^2 = R^3 = Cl$
(3) $R^1 = H, R^2 = R^3 = Cl$
(4) $R^1 = R^2 = H, R^3 = Cl$



(2)



(5)

Ring opening of the cyclic ether was effected by mild treatment with methanolic NaOH. Loss of Cl$^-$ from the presumed intermediate extended quinone gave the coupled napthoquinone (**5**). Like the protoaphins[3] it underwent reductive cleavage, alkaline stannite concomitantly removing the chloro-groups to give a mixture of naphthalene-1,3,8-triol and naphthalene-1,3,5,8-tetraol both of which were unstable in air. They were isolated as their triacetate (m.p. 118—120 °C, 10%) and tetra-acetate (m.p. 179—80 °C, 40%) respectively. The former was synthesised independently,[4] the latter from 5,7-dihydroxy-1,4-naphthoquinone.[5]

Structure (**1**) suggests that the pigment is formed by coupling of naphthalenic monomers. So too are common constituents of wood-rotting fungi.[6] The parent soils are invariably associated with stringybark eucalypts and pigment production is greatest along the lines of decomposing roots.

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