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SYNTHESIS OF A NATURAL POLYCHLORO DINAPHTHOFURAN QUINONE

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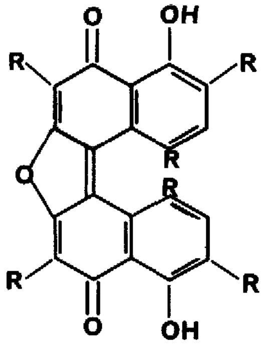
Summary. The hexachloro dinaphthofuran quinone (1), the only natural example of this ring system has been synthesised for the first time.

This communication reports the first synthesis of the dinaphthofuran quinone (1),isolated from green coastal soils in southern Australia[1]. As the only natural example of this ring system it has interesting affinity with environmentally hazardous polychlorinated biphenyls and dibenzofurans[2]. The molecule is particularly unusual in showing considerable deviation from planarity as a result of interaction between the two inner chloro substituents[3].

Synthesis of (1) proceeded through the ester (2). This was formed by Stobbe reaction between 3,5-dimethoxybenzaldehyde and dimethyl succinate followed by cyclisation and methylation of the product. Treatment of (2) with iodine in the presence of mercuric acetate[4] gave (3). On heating to 120° in the solid phase this underwent Ullmann coupling with extrusion of iodine to give the diester (4) (80%). Its 'H n.m.r. spectrum ($CDCl_3$) contained a singlet benzenoid resonance at δ6.90 and meta-coupled doublets at 7.22 and 7.40. The extraordinary mildness of this coupling reaction suggests the involvement of topochemical phenomena[5].

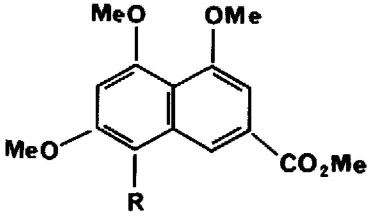
Treatment of the diester (4) with concentrated hydrobromic acid and remethylation of the crude product with alkaline dimethyl sulphate gave the dinaphthofuran (5) (57%). The benzenoid region of its n.m.r. spectrum qualitatively resembled that of (4); however one of the meta-coupled signals was considerably deshielded (δ9.04), as would be expected for protons in the inner positions of the dinaphthofuran system[1].

Alkaline hydrolysis of (5) gave the diacid (6). This was then decarboxylated by heating with a mixture of cupric carbonate and copper bronze to give the tetramethoxy dinaphthofuran(7) (55%). Its electronic absorption resembled that of dinaphtho[2,1-b:1',2'-d]furan itself[1] with a bathochromic shift of 32 nm in the long wavelength region associated with the effect of the four methoxy groups.



1 R=Cl

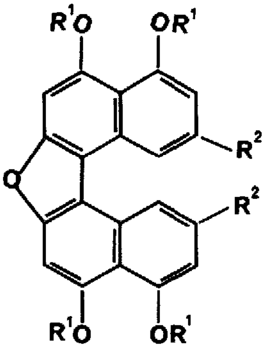
9 R=H



2 R=H (ArH)

3 R=I (ArI)

4 R=Ar(ArAr)



	R'	R^2
5	Me	CO_2Me
6	Me	CO_2H
7	Me	H
8	H	H

Demethylation of (7) with boron tribromide and oxidation of the resulting tetrol (8) with lead tetraacetate gave the extended quinone (9) (75%), the basic chromophore of (1). Its electronic spectrum (λ_{max} 383 and 541nm) was hypsochromically shifted by 18nm relative to (1). *Its n.m.r. spectrum was amenable to first order analysis, containing a singlet at δ6.37, broad* doublets (J8Hz) at 7.19 and 8.26, a triplet (J8Hz) at 7.55, and a sharp singlet (OH) at 13.20.

Treatment of (8) or (9) with chlorine gave a mixture of di-,tri-,tetra-,penta-, and hexachloro quinones separable by chromatography. Further chlorination of the lower members increased the yield of the hexachloro compound but competing decomposition processes restricted its optimum recovery to 9%. The product was identical with the natural pigment (1) in n.m.r., electronic, i.r., and mass spectra and in chromatographic behaviour, its isomeric homogeneity being explicable in terms of complete chlorination of the predictably reactive positions in the dinaphthofuran quinone system.

Satisfactory elemental analyses and spectra have been obtained for all new compounds reported in this work. Preliminary experiments were carried out by Mr. P. Craig. We acknowledge an Australian Postgraduate Research Award (to L.J.H.P).

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