THE STRUCTURE OF CHLOROBIUMQUINONE

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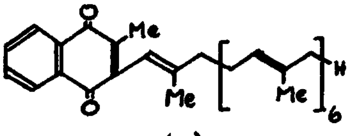
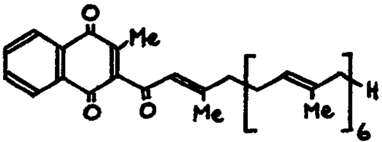
The green photosynthetic bacteria *Chlorobium thiosulphatophilum* and *Chloropseudomonas ethylicum* contain two principle quinones, menaquinone-7 and chlorobiumquinone (Frydman and Rapoport, 1963. Redfearn and Powls, 1967). Frydman and Rapoport suggested for chlorobiumquinone the formula $C_{45}H_{62}O_2$ and a structure (I) in which the first methylene of the normal polyisoprenoid side-chain was omitted in order to explain the unusual features in the u.v. and n.m.r. spectra of the quinone. This structure has always seemed biochemically improbable and we now report that chlorobiumquinone is on fact 1'-oxomenaquinone-7 (II).



(I)

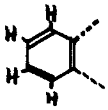
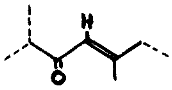
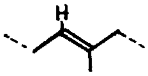
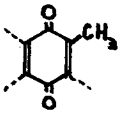
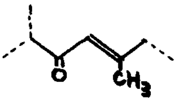
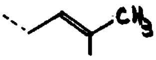
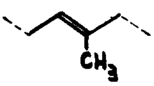


(II)

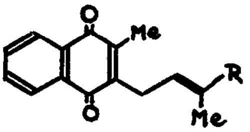
Our sample of chlorobiumquinone, m.p. 48-49° (literature m.p. 50-51°), has u.v. and n.m.r. spectra identical with those reported by Frydman and Rapoport and shows the reported behaviour relative to menaquinone in both adsorption and reverse phase chromatography.

Chlorobiumquinone has the molecular formula $C_{46}H_{62}O_3$ (mass peak at *m/e* 662.4691). As with related quinones (Das et al., 1965), the (M+2) ion increases with time and is often comparable in intensity

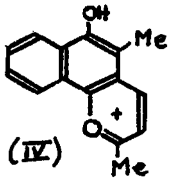
Table. N.m.r. Spectrum (220 Mc./sec.) of Chlorobiumquinone in $CDCl_3$

τ	No. of Hydrogens	Structural Element
1.94(*b*) 2.27(*b*)	4	
3.85(*s*)	1	
4.92(*b*)	6	
7.72(*s*)	3	
7.78(*b*)	3	
7.92 - 8.01(*m*)	24	
8.34(*s*)	3	
8.42(*s*)	18	

with the molecular ion. A major fragment of quinones having the general structure (III) is at *m/e* 225 due to the ion (IV). In the spectrum of chlorobiumquinone this peak is small and the major peak in this region is at *m/e* 241.0856 due to the fragment $C_{15}H_{13}O_3$. Further abundant ions at *m/e* 322 (loss of five isoprene units), 201.0532 ($C_{12}H_9O_3$) and 200.0469 ($C_{12}H_8O_3$) establish that the third



(III)



(IV)

oxygen of chlorobiumquinone is on the first carbon of the side-chain. This oxygen is not hydroxylic for chlorobiumquinone behaves as a relatively non-polar compound on chromatography and its n.m.r. spectrum in deuteriochloroform is not changed on shaking the solution with deuterium oxide. The u.v. spectrum of the quinone ($\lambda_{max.}$ 254 with a shoulder at 265 mμ in ethanol) is very similar to that of 2-acetylnaphthoquinone ($\lambda_{max.}$ 253 with a shoulder at 275 mμ in 95% ethanol) (Eugster and Bosshard, 1963). On reduction with sodium borohydride in buffered ethanol (Lester, White, and Smith, 1964) typical naphthoquinol absorption at 247 mμ remains. Reduction in unbuffered ethanol leaves only a broad inflexion at 251 mμ as reported by Frydman and Rapoport. The n.m.r. spectrum (see Table) fully supports the structure (II) for chlorobiumquinone. As expected the side-chain carbonyl is masked in the i.r. by the quinone carbonyls.

Chlorobiumquinone is the first example of a naturally occurring polyisoprenoid quinone containing a side-chain carbonyl group.

We are indebted to I.C.I. (Petrolchemical & Polymer Laboratories) for the high resolution mass spectra and the 220 Mc. n.m.r. spectra.

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