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A NEW CLASS OF QUINONES FROM CERTAIN MEMBERS OF THE FAMILY *Cyperaceae*

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Chemical examination of the *Cyperaceae* has been cursory although the family contains about 3200 species within 75 genera. We wish to report the isolation of five new quinones from the roots and rhizomes of some tropical Australian representatives. These pigments, for which we propose the name Cyperaquinones, contain the [1,2-b: 5,4-b'] benzodifuran ring system (I) and, to our knowledge, are the first representatives of this class of compound found in nature.

Four of the 35 species (representing 10 genera of *Cyperaceae*) screened to date have been found to contain quinones. These quinones were extracted with cold ether and separated by a combination of column and thin layer chromatography on silica gel.

Their origin is tabulated below.

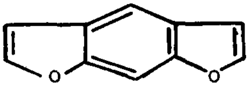
Quinone	Formula	Origin	% dry wt. of root and rhizome
Cyperaquinone (II)	$C_{14}H_{10}O_4$	*Cyperus haspan* L.	0.1
		Remirea maritima Aubl.	0.01
		Fimbristylis dichotoma[a], L.	0.05
Dihydrocyperaquinone (III)	$C_{14}H_{12}O_4$	*Remirea maritima* Aubl.	1.5
		Fimbristylis dichotoma[a], L.	0.05
Tetrahydrocyperaquinone (IV)	$C_{14}H_{14}O_4$	*R. maritima*, Aubl.	0.1
Hydroxycyperaquinone (V)	$C_{14}H_{10}O_5$	*C. haspan* L.	0.4
Demethylcyperaquinone (VI)	$C_{13}H_8O_4$	*Cyperus compressus* L.	0.001

[a] The plants from which collection was made have not been observed in flower.

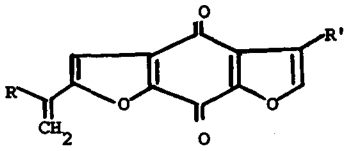
Dihydrocyperaquinone (III) $C_{14}H_{12}O_4$, $[\alpha]_D^{CHCl_3}$ - 35°, separated from hexane as orange needles mp. 113-4°. The U.V. spectrum ($\lambda_{max}^{ethanol}$; 463 (log ε 2.75), 334 (log ε 3.93), 275 (log ε 4.28) suggested a conjugated quinone. This was supported by reduction with sodium bisulphite to the colourless dihydroxy derivative, from which the quinone could be regenerated by aerial oxidation. The failure of (III) to form a phenazine derivative with o-phenylene diamine and the I.R. absorption ($\nu_{max}^{C=O}$ 1675, 1640 cm.$^{-1}$)$^{(1)}$ indicate a para-quinone.

The 100 MHz nmr spectrum shows signals corresponding to 12 protons as follows: τ 8.20 (3H, singlet); τ 7.74 (3H, singlet); τ 6.9 (2H, octet); τ 5.03 (1H, broad singlet); τ 4.91 (1H, broad singlet); τ 4.62 (1H, triplet); τ 2.54 (1H, singlet). The signals at τ values 8.2, 6.9, 5.03, 4.91 and 4.62 are almost identical in chemical shift and splitting pattern with those shown by the 2-isopropenyl 2,3-dihydrofuran portion of the nmr spectrum of remirol$^{(2)}$. The two remaining signals at τ 7.74 and τ 2.54 are satisfied by a 3-methylfuran moiety. The structure III is therefore proposed for dihydrocyperaquinone. The 2,6 dioxygenation pattern about the p-benzoquinone ring is preferred to the alternative 2,5 oxygenation pattern on biogenetic grounds.

The 70 ev mass spectrum$^{(*)}$ of III, showing a molecular ion m/e 244 (66%) and major fragment ions at m/e 229 (40%), 216 (90%), 214 (40%), 201 (100%), 144 (20%), 137 (23%) and 109 (68%), is in accord with the proposed structure.



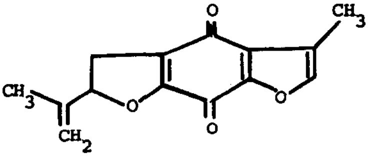
I



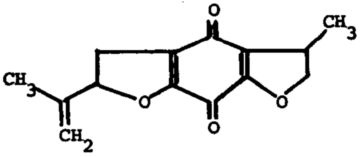
II R = R' = CH_3

V R = CH_2OH R' = CH_3

VI R = CH_3 R' = H



III



IV

Tetrahydrocyperaquinone, IV, $C_{14}H_{14}O_4$, $[\alpha]_D^{CHCl_3}$ +210°, crystallised from benzene:hexane as small maroon prisms mp. 138-140°; U.V. $\lambda_{max}^{ethanol}$ 480 (log ε 2.50), 323 (log ε 4.36), 264 (log ε 3.66). The 100 MHz nmr spectrum showed signals at τ 8.22 (3H singlet); τ 7.00 (2H, octet); τ 5.05 (1H, broad singlet); τ 4.94 (1H, broad singlet) and τ 4.68 (1H, triplet) characteristic of the 2-isopropenyl dihydrofuran moiety. In addition, signals at τ 8.67

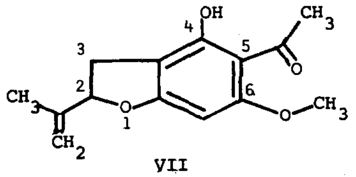
(3H, doublet); τ 6.5 (1H, multiplet); τ 5.75 (1H, quartet) and τ 5.23 (1H, triplet) conforms to the transformation of the 3 methylfuran portion of III to a 3-methyl 2,3-dihydrofuran, demanding IV as the structure of tetrahydrocyperaquinone.

The I.R. spectrum ($\nu_{max}^{C=O}$ 1690, 1642 cm.$^{-1}$) supports a para quinone and the mass spectrum showing a molecular ion at m/e 246 (100%) and major fragment ions at m/e 218 (60%), 203 (92%), 175 (30%), 147 (34%) and 107 (38%) is not inconsistent with structure IV.

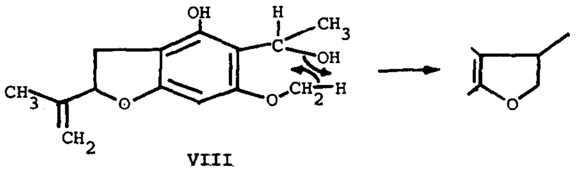
Cyperaquinone, II, $C_{14}H_{10}O_4$ separates from benzene:hexane as small carmine needles mp. 182-83° (dec.); U.V., $\lambda_{max}^{ethanol}$ 473 (log ε 3.63), 347 (log ε 3.50), 259 (log ε 4.46). The 100 MHz nmr shows signals at τ 7.71 (3H, doublet, J = 1 c.p.s.) and τ 2.57 (1H, broad singlet with fine splitting) indicative of a 3-methylfuran and also signals at τ 7.92 (3H, broad singlet); τ 4.72 (1H, broad singlet); τ 4.15 (1H, broad singlet) and τ 3.30 (1H, singlet) indicating a 2-isopropenylfuran. This suggests structure II for cyperaquinone, supported by the 70 ev mass spectrum which shows a molecular ion m/e 242 (100%) with no fragment ions of relative abundance greater than 3% which is in accord with a fully conjugated system.

Hydroxycyperaquinone, V, $C_{14}H_{10}O_5$ crystallises from benzene:hexane as russet plates mp. 166-168° (dec.). The U.V. spectrum ($\lambda_{max}^{ethanol}$ 473 (log ε 3.62), 347 (log ε 3.49), 262 (log 4.62) is virtually identical with that of II. The I.R. shows hydroxyl absorption and the 100 MHz nmr indicates a 3-methylfuran (signals at τ 7.9 (3H, singlet) and τ 2.4 (1H, singlet)) but that the isopropenyl group in II has been converted to $H-O-CH_2-C=CH_2$:[signals at τ 5.3 (2H, very broad singlet); τ 4.7 (1H, broad singlet); τ 4.15 (1H, broad singlet); τ 3.3 (1H, singlet) and τ(6.7 1H, singlet) which disappears after deuterium exchange]. Thus hydroxycyperaquinone has the structure V. As in the case of II the 70 ev mass spectrum shows a very strong molecular ion (m/e 258) with no fragment ions of relative abundance of more than 10%.

Demethylcyperaquinone, VI, $C_{13}H_8O_4$ crystallises from hexane as a small bright red crystal mp. 136-8°. The nmr spectrum (signals at τ 7.9 (3H); τ 4.7 (1H); τ 4.1 (1H); τ 3.3 (1H); τ 3.1 (1H) and τ 2.3 (1H) indicates that demethylcyperaquinone contains a 2-isopropenyl furan and a furan ring and thus has structure VI. The 70 ev mass spectrum shows a molecular ion m/e 228 (100%) and only one significant fragment ion at m/e 115 (16%).



VII



VIII

The occurrence of both 2-isopropenylfuran and 3-methylfuran moieties in the compounds II-V would suggest, from present biogenetic evidence, that the cyperaquinones are built up from two isopentyl units and two acetate units. Any arrangement of these building blocks to give the cyperaquinones, however, seems rather tenuous. The co-occurrence of II, III and IV with the ketone remirol (VII)(2) in *Remirea maritima* lead us to suggest that VII could be the biogenetic precursor of the cyperaquinones. Ring closure of the 5-ketone function of VII (possibly by a radical process after reduction to alcohol) with the CH_3 of the 6-methoxy group to form a 3-methyldihydrofuran, followed by oxidation of the phenolic product to a quinone would lead directly to IV. This would represent a new method for the formation of a 3-methylfuran moiety. Tracer studies will be undertaken to test this suggestion.

The genus *Remirea* contains but one species *R. maritima*. It has been suggested(3) that *Remirea* is co-generic with *Cyperus*. The occurrence of II in both *R. maritima* and *C. haspan* supports this view.

The cyperaquinones appear to be weakly active against some gram positive organisms, also III is highly toxic to fish.

Acknowledgement

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References

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(2) R.D. Allan, R.L. Correll and R.J. Wells, preceding paper.

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