

C₁₅ QUINONES FROM CYPERUS SPECIES

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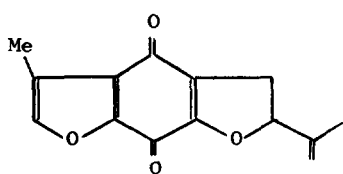
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It has previously been reported⁽¹⁾ that the roots and rhizomes of many species of the genus Cyperus contain quinones. The major quinone, (1), of Remirea maritima was accompanied by compounds (2), (3) and 4 and the biosynthesis of 1 from 2 by the route 2→3→4→1 was postulated. This scheme involved the formation of a 3-methylfuran by the ring closure of a 2-methoxyacetophenone moiety.

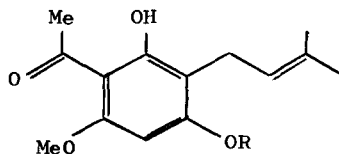
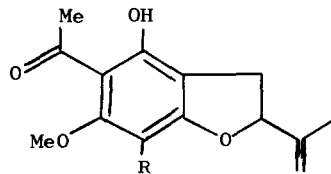
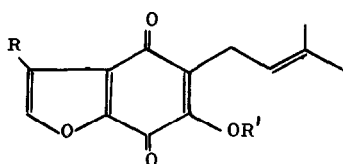
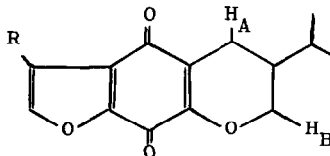
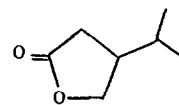
The rhizomes of Cyperus brevibracteatus yielded two C₁₅ quinones; breviquinone C₁₅H₁₆O₄ (5) and hydroxybreviquinone, C₁₅H₁₆O₅ (6). The u.v. spectrum of breviquinone [λ_{\max} 498, 318, and 265 nm (log ϵ 3.06, 3.74 and 4.11)] was almost identical to that of (1). The n.m.r. spectrum showed the presence of a 3-methylfuran [τ 7.72 (3H,d; J=1Hz) and 2.60 (1H,q; J=1Hz)], an isopentenyl substituent [τ 8.24 (3H,s), 8.32 (3H,s), 6.81 (2H,d; J=8Hz) and 4.94 (1H,t; J=8Hz)]. This suggested that breviquinone was (5). Reduction of (1) by lithium in liquid ammonia, followed by aerial oxidation of the intermediate quinol, gave the hydroxyquinone (7) in high yield which, on treatment with diazomethane, gave (5) identical with natural breviquinone.

The formulation of hydroxybreviquinone as (6) followed from the n.m.r. spectrum which showed replacement of the 3-methylfuran signals by resonances attributable to a 3-hydroxymethylfuran grouping.

The rhizomes of C.scaber and C.distans yield four quinones; scabequinone (8), dihydroscabequinone (10), hydroxyscabequinone (11) and scabequinol (12).



(1)

(2) R=H
(14) R=Me(3) R=H
(4) R=OH(5) R=Me R'=Me
(6) R=CH₂-OH R'=Me
(7) R=Me R'=H(8) R=Me,
(11) R=CH₂OH

(9)

Scabequinone (C₁₅H₁₄O₄) had a u.v. spectrum almost identical to (1) and (5). The n.m.r. spectrum revealed the presence of a 3-methylfuran group [τ 7.74 (3H,d) and 2.56 (1H,q)] and resonances [τ 8.98 (6H,d; J=6Hz), 5.53 (1H, sextet) 6.22 (1H,t), 7.30 (1H, octet), 7.84 (1H,q) and 8.36 (2H,m) attributed to a 3-isopropylchroman moiety. Such data demands (8) as the structure of scabequinone. A feature of the n.m.r. spectrum is the strong W coupling (J=2.2Hz) between equatorial protons H_A and H_B on the isopropylchroman ring. All assignments were verified by double resonance experiments.

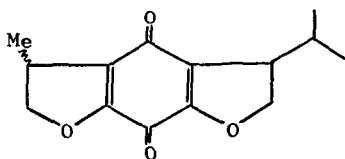
Exhaustive ozonolysis of 8 ($[\alpha]_D^{20} + 166^\circ$ (CHCl₃)) followed by reductive workup gave the lactone 9 ($[\alpha]_D^{20} + 12^\circ$) which was prepared independently from (-) isopropylsuccinic acid thus establishing the absolute configuration of (8) as "R".

Scabediol (13) was also isolated from *C.scaber* and its occurrence is analogous to the presence of (4) in *R.maritima*. (13) is an attractive biosynthetic precursor of (8) and supports the postulated biosynthesis of (1).

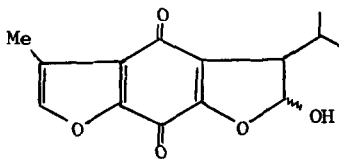
The presence of quinones (5) and (8) in botanically closely related species suggests that the biosynthetic precursor of the 3-isopropylchroman ring system found in (8) is a methoxyisopentenyl moiety. Thus, all the cyperaquinones of type (1) could be derived from preremirol (2) and the C₁₅ quinones, described above, could be derived from O-methylpreremirol (14).

Hence twenty-four of the twenty-nine new compounds isolated from Cyperus^{1,2} seem to be derived from the single precursor (2).

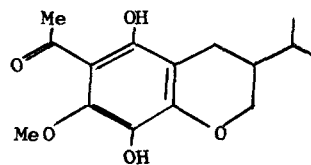
Attempts to effect ring closure of the quinol (13) or the quinone derived from it (oxidation by DDQ) by photochemical means have not been successful.



(10)



(11)



(13)

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References

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- c) R. D. Allan, J. M. MacLeod and R. J. Wells, *Tetrahedron Letters* 3945 (1970)
- 2 R. D. Allan, J. K. MacLeod and R. J. Wells Unpublished results