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FURTHER PHENOLIC KETONES FROM *Remirea maritima* Aubl.

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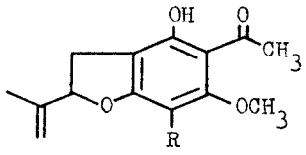
Previous communications[1,2] from this laboratory have reported the isolation of the isoprenoid acetogenins Remirol (I) and iso-Evodionol (II) together with the quinones III - V from the rhizomes of the tropical sea-shore sedge *Remirea maritima* Aubl. The co-occurrence of I and II and the quinones III - V led us to suggest[1] that the 3-methylfuran moiety found in III-V might arise by ring closure of the o-methoxyacetophenone portion of I to a 3-methyl-benzofuran. Remirol (I) should, therefore, be a biogenetic precursor of the cyperaquinones III - V. We now wish to report two further phenolic ketones from *R. maritima* which support this scheme for the biogenesis of the cyperaquinones.

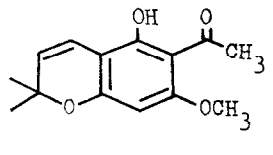
Preremirol (VI), $C_{14}H_{18}O_4$, was obtained from the polar fractions of a chloroform extract of *R. maritima* rhizome. It separated from chloroform-hexane as pale yellow prisms m.p. 173.5 - 174°. The U.V. spectrum ($\lambda_{max}^{ethanol}$ 294 nm (log ε, 4.27), 340 nm (shoulder; log ε, 3.59) was closely similar to that of I.

The 100 MHz n.m.r. spectrum in deuteropyridine showed signals corresponding to 18 protons as follows: τ 8.30 (3H, singlet); τ 8.10 (3H, singlet); τ 7.43 (3H, singlet); τ 6.40 (3H, singlet); τ 6.33 (2H, doublet J = 7 Hz); τ 4.35 (1H, triplet J = 7 Hz); τ 3.85 (1H singlet); τ 0.2 (1H, singlet) and τ -4.7 (1H, singlet). The last two peaks disappear on addition of deuterium oxide. This data is in accord with structures VI and VII for preremirol and is supported by the 70 e.v. mass spectrum which showed a molecular ion m/e 250 (95%) and main fragment ions at 235 (70%), 207 (56%), 195 (100%) and 179 (56%).

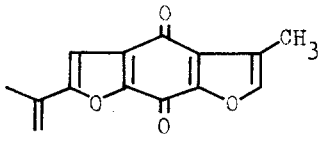
Conclusive evidence for VI as the structure of preremirol came from acid cyclisation to two products. The first of these (35% yield), m.p. 90°, was identical in all respects to the dihydro-derivative of II. The second product (55% yield), m.p. 184.5 - 185° showed non-hydrogen bonded phenol and a non-hydrogen bonded carbonyl in the i.r. spectrum and may be formulated as VIII. Compound VII, acronylin, m.p. 128 - 129°, has recently been reported.[3]



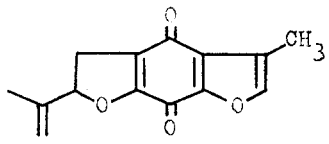
I R = H
IX R = OH



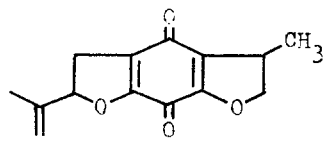
II



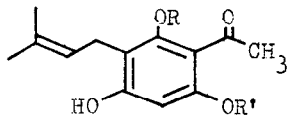
III



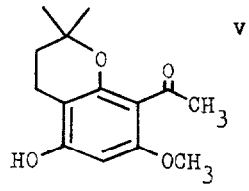
IV



V



VI R = H, R' = CH_3
VII R = CH_3, R' = H



VIII

Remiridiol (IX), $C_{14}H_{16}O_5$, crystallised from hexane as pale yellow needles m.p. 97 - 97.5°, $[\alpha]_D^{CHCl_3}$ + 62.6°. The u.v. spectrum showed λ_{max}^{EtOH} 218 (log ε 4.22), 296 (log ε 4.16), 350 (log ε 3.68). The 100 MHz n.m.r. in $CDCl_3$ showed signals characteristic[2] of a 2,3 dihydro 2-isopropenyl benzo-furan grouping [τ 8.12 (3H, broad singlet); τ 4.91 (1H, broad singlet); τ 5.06 (1H, broad singlet); τ 4.66 (1H, triplet, J = 8.5 Hz); τ 6.83 (2H, octet, J_{AB} 15 Hz, J_{AX} 8 Hz, J_{BX} 9 Hz)]. The remainder of the spectrum consisted of a methoxyl (τ 6.08; 3H, singlet), CH_3CO (τ 7.35; 3H, singlet) and two hydroxyl singlets at τ -3.08 and τ 5.0 disappearing on deuterium exchange. The 70 e.v. mass spectrum showed a molecular ion m/e 264 (50%) and main fragment ions at 249 (100%) 234 (11%) and 231 (15%). Structure IX is proposed for remiridiol.

An attractive scheme, therefore, emerges for the biosynthesis of the cyperaquinones i.e. VI → II + I → IX → IV → III + V.

REFERENCES

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(2) R.D. Allan, R.L. Correll and R.J. Wells, Tetrahedron Letters, 4673 (1969).

(3) G.K. Biswas and A. Chatterjee, Chem. and Ind., 654 (1970).