Tetrahedron Letters No.53, pp. 4673-4674, 1969. Pergamon Press. Printed in Great Britain

TWO NEW PHENOLIC KETONES FROM *Remirea maritima (Cyperaceae)*

R.D. Allan, R.L. Correll and R.J. Wells

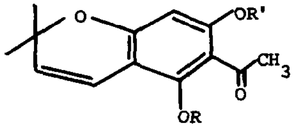
Department of Chemistry, University College of Townsville, Queensland, Australia.

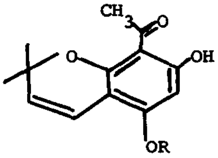
(Received in UK 1st October 1969; accepted for publication 16th October 1969)

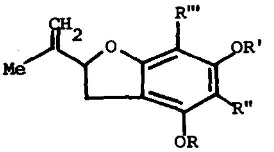
Remirea maritima (Cyperaceae) is a small perennial which is common on the sea shores of northern Australia and a cosmopolitan tropical species. Ether extraction of the rhizomes of this plant gives a deep orange gum from which two new phenolic ketones can be obtained by chromatography on silica gel, together with a new series of quinones which will be discussed in the following paper. We propose the names iso-evodionol and remirol for the phenolic ketones.

Iso-Evodionol (II), $C_{14}H_{16}O_4$, separated from hexane as large yellow needles mp. 128.5-129°, dinitrophenylhydrazone mp. 179-180°, and represents 0.4% of the dried rhizome. Hydrogenation gave a dihydro derivative mp. 90° and methylation with potassium carbonate:dimethyl sulphate gave methyl iso-evodionol (IV) mp. 76.5-77°. Attempted methylation with diazomethane failed thus indicating a hydrogen bonded phenol.

The 70 ev mass spectrum* of iso-evodionol shows a molecular ion m/e 248 (21%) and only two significant fragment ions at m/e 233 (100%) and m/e 215 (21%) reminiscent of the behaviour of 2,2-dimethylchromenes(1). The 100 MHz nmr* showed signals at τ 8.56 (6H, singlet); τ 7.42 (3H, singlet); τ 6.17 (3H, singlet); τ 4.57 (1H, doublet, J = 10 c.p.s.); τ 4.13(1H, singlet); τ 3.35 (1H, doublet J = 10 c.p.s.) and τ -4.24 (1H, singlet disappearing after deuterium exchange). The results were in accord with the structure of iso-evodionol being I, II, or III. The non-identity of iso-evodionol with the known compounds evodionol (I)(2) or allo-evodionol III(3) demands II as its structure, further confirmed by the complete identity of the methyl ethers (IV) of I and II. The U.V. spectrum of II (λ_{max}^{EtOH}: 350 nm [log ε 3.74], 306 nm (sh) [log ε 4.31], 294 nm (sh) [log ε 4.38], 272 nm [log ε 4.81]) is almost identical with that reported for evodionol.(2)







I R = Me R' = H

II R = H R' = Me

IV R = R' = Me

III

V R = R''' = H, R' = Me, R'' = $\overset{O}{\overset{\|}{C}}$ - Me

VI R' = R''' = H, R = Me, R'' = $\overset{O}{\overset{\|}{C}}$ - Me

VII R = Me, R' = R'' = H, R''' = $\overset{O}{\overset{\|}{C}}$ - Me

VIII R = R' = Me, R''' = H, R'' = $\overset{O}{\overset{\|}{C}}$ - Me

Remirol (V) $C_{14}H_{16}O_4$, $[\alpha]_D^{25}$ 66.5°, separated from hexane as pale yellow prisms mp. 76.5-77°. Hydrogenation gave dihydroremirol, $C_{14}H_{18}O_4$, mp. 61.5-62° $[\alpha]_D^{25}$ 61° and methylation with potassium carbonate:dimethyl sulphate (but not with diazomethane) gave methyl remirol (VIII) as an oil, indicating the presence of an olefin and hydrogen bonded phenol.

The 100 MHz nmr shows signals at τ 8.24 (3H, broad singlet); τ 7.42 (3H, singlet); τ 6.9 (2H, octet); τ 6.16 (3H, singlet); τ 5.1 (1H, broad singlet); τ 4.94 (broad singlet); τ 4.74 (1H, triplet), τ 4.05 (1H, singlet) and τ -4.02 (1H, singlet exchangeable with D_2O). Double resonance experiments showed that the two broad singlets at τ 5.1 and 4.94 were coupled to the broad methyl singlet at τ 8.24 and also coupled to the triplet at τ 4.74 indicative of an isopropenyl grouping. Further the octet at τ 3.9 and triplet at 4.74 make up the AB and X portions of an ABX system. This data, in conjunction with chemical shift values suggests that remirol has structures V, VI or VII.

Support for V comes by analogy with iso-evodionol II and also from a positive Gibbs test obtained with remirol indicative of a proton para to a free phenol. The U.V. spectrum (λ_{max}^{EtOH}: 294 nm (log ε 4.26), 239 (log ε 3.98), 216 (log ε 4.22) and mass spectrum (M^+, m/e 248, main fragment ions 233 (100%), 218, 109) are in accord with this structure.

Acknowledgement

*We wish to thank Dr. J.K. MacLeod, Australian National University, Canberra, for mass spectra, and Dr. R. Bramley, also of A.N.U. for n.m.r. and double resonance experiments.

References

(1) C.S. Barnes and J.L. Occolonitz, Aust.J.Chem. 17, 975 (1964).

(2) F.N. Lahey, Chem.Abstracts. 37, 3432 (1943).

(3) M.D. Sutherland, Chem.Abstracts. 44, 1230 (1950).