Natalenone, a Novel Quinone Dimer from *Euclea Natalensis*

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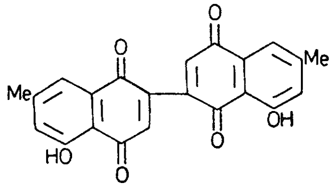
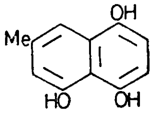
Summary Natalenone (V) is a dehydro dimer of 7-methyljuglone in which the two halves are linked by two carbon–carbon bonds to give a fused tetracyclic structure in which one ring carries a methylene bridge.

Binaphthoquinones of the conventional type, *e.g.* rotundiquinone (I),[1] occur frequently in *Diospyros* and *Euclea* (Ebenaceae) heartwoods,[2] presumably formed by phenolic coupling of (II) (or an equivalent) and further oxidation. We report here an unconventional dimer extracted from the roots of *Euclea natalensis*.[3]

Natalenone, m.p. 229—231 °C, $C_{22}H_{16}O_6$, [(I) is $C_{22}H_{14}O_6$)], is optically inactive (c.d.), shows λ_{max} (EtOH) 266, 294sh 324sh, and 440 nm (log ϵ 4·18, 3·83, 3·68, and 3·66), (EtOH–OH^-) 568 nm (log ϵ 3·79), and ν_{max} (KBr) 3523, 1670, 1640, and 1610 cm^{-1} consistent with a structure of type (I), as is the mass spectrum except that the base peak falls at *m/e* 358 ($M^+ - H_2O$). The ^1H n.m.r. spectrum ($CDCl_3$) includes four singlets for two aromatic methyl and two *peri*-hydroxy groups, and four doublets for *meta*-coupled aromatic protons [*cf.* (I)], and in addition a hydroxy singlet at δ 4·69 (1H, exchanges with D_2O) and a methine proton signal at δ 4·17(m) coupled to a methylene resonance at 3·02 (2H, d, *J* 3 Hz). The third hydroxy group is evidently tertiary although the pigment forms a monoacetate (warming with $HOAc–H_2SO_4$) and a triacetate ($Ac_2O–H_2SO_4$, 8 days at room temperature). This is confirmed by ^{13}C n.m.r. data ($CDCl_3$); the off-resonance decoupled spectrum includes a singlet at 82 p.p.m., together with a CH_2 triplet at 54 and a CH doublet at 52 p.p.m., and signals for two methyl, two vinyl (singlets), twelve aromatic, and three carbonyl (198, 188 and 181 p.p.m.) carbon atoms. The combined evidence suggests the presence of the groupings (III) and (IV) linked together by $>CH–CH_2–$ and $\geqslant COH$ fragments. As several structures are possible


(I)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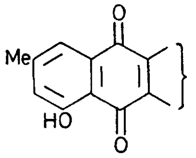
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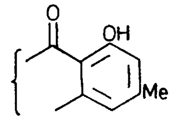
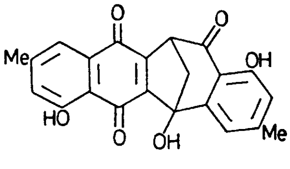
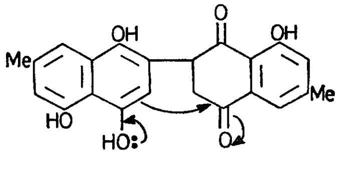
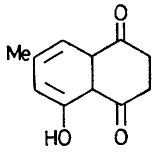
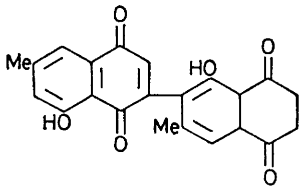

(IV)


(V)


(VI)


(VII)


(VIII)

the final solution was obtained by *X*-ray crystallographic analysis which defined natalenone as (V).

The crystals were triclinic, $P\bar{1}$, with $a = 14{\cdot}311(2)$, $b = 5{\cdot}956(1)$, $c = 10{\cdot}754(2)$ Å, $\alpha = 93{\cdot}87(5)$, $\beta = 106{\cdot}65(5)$, $\gamma = 94{\cdot}39(5)^\circ$. A total of 3707 reflections were measured on a Hilger-Watt four circle diffractometer using Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å) out to $\theta = 27{\cdot}5^\circ$, of these 2195 with a net count $>3\sigma$ were deemed observed. The structure was solved, with difficulty, in the acentric space group $P1$ using MULTAN, and refined in the centric space group using all observed reflections. In the final stages hydrogens were included and allowed to refine isotropically, the other atoms anisotropically. The variables were refined in two blocks and at convergence the maximum positional shift was $0{\cdot}13\sigma$ and R was $0{\cdot}045$. Bond lengths and angles were normal with calculated e.s.d.'s of *ca.* 0·004 Å and 0·25° for parameters not involving hydrogen. The molecule consists of two essentially planar parts folded about the bridgehead carbons, the fold angle being 106°.

Presumably (V) arises *in vivo* by coupling of (II) to give an unsymmetrical dehydro dimer, followed by formation of a second internuclear bond as indicated (VI), one half of the molecule reacting in the diketo tautomeric form (*cf.* the naphthocyclinones[4]). Stable diketo tautomers of 1,4,5-trihydroxynaphthalenes are known,[5] and both (VII)[6] and (VIII)[7] are natural examples found in *Diospyros* spp.

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