Oruwal, a Novel Dihydroanthraquinone Pigment from *Morinda lucida* Benth.

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Summary Four known anthraquinones, and a new compound oruwal which was characterized as 9,10-dimethoxyanthracene-2-carbaldehyde from spectroscopic evidence and chemical transformation were isolated from *Morinda lucida* Benth. (Rubiaceae); oruwal is a possible intermediate in the biosynthetic route to some anthraquinones.

Morinda lucida Benth., known in the Western State of Nigeria as Oruwo, is a valuable tree used as a dye, and in native medicine.

The petroleum extract of the stem on deactivated alumina gave some high-boiling hydrocarbons, steroids, and some anthraquinones. Four of the anthraquinones were characterized by their m.p., and i.r., u.v., n.m.r.† and mass spectra as damnacanthal (I), alizarin-1-methyl ether (II), rubiadin-1-methyl ether, (III), and soranjidiol (IV), all of which are known.[1]

In addition, a fluorescent fraction gave in low yield oruwal, a bright yellow solid ($C_{17}H_{14}O_3$), m.p. 157°, M^+ 266. The i.r. spectrum [ν_{max} (Nujol) 1695, 1680, 1620w, and

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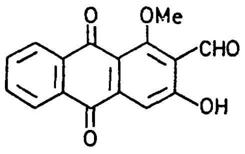
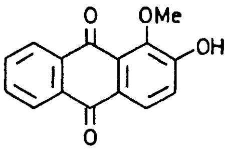
† All n.m.r. spectra were measured at 60 MHz in $CDCl_3$ solutions and chemical shifts are relative to $SiMe_4$.

695 cm^{-1}] shows no band at *ca.* 1580 cm^{-1} characteristic of the other four anthraquinones. The n.m.r. spectrum shows two aromatic methoxy resonances (δ 4·11 and 4·18 p.p.m.), an aldehydic proton (δ 10·2 p.p.m.), and seven aromatic protons of which six resonate between δ 7·5 and 8·47, while the seventh at 8·80 (J = 2 Hz), suggests *para* and/or *meta* coupling, and an adjacent deshielding nucleus. The u.v. absorption: λ_{max} (cyclohexane) 238sh, 243, 272sh, 277, 360, and 375 nm (log ϵ 4·41, 4·43, 4·76, 4·81, 3·63, and 3·75), shows weak absorptions at higher wavelength as in anthracene. All the data can be accommodated by an anthracene but not an anthraquinone nucleus; oruwal could be a dimethoxyanthracene aldehyde.

The structure of oruwal was confirmed by demethylation in sulphuric acid and work-up to give a pale yellow product, m.p. 183—185°; a strong i.r. peak at ν_{max} (Nujol) 1590 cm^{-1} indicates an anthraquinone skeleton while the strong peak at 710 cm^{-1} suggests one of the aromatic rings is unsubstituted. Detailed study of the n.m.r. spectrum (which among other things shows the loss of two OMe groups, the presence of one aldehyde proton and seven aromatic protons) allow the unambiguous assignment of the transformation product as the known anthraquinone-2-carbaldehyde (VI), m.p. 188—189°,[1] whose recorded spectral properties are in good agreement with ours. Oruwal is therefore 9,10-dimethoxyanthracene-2-carbaldehyde (V). The fragmentation pattern in the mass spectrum is in agreement with the assignment.



(I)



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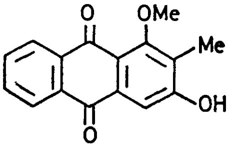

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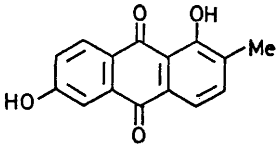

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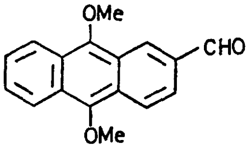
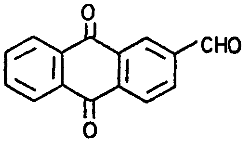
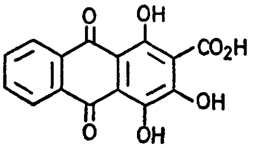


(V)



(VI)



(VII)

As far as we know this is the first isolation of this compound, and we think oruwal is of biogenetic interest. Anthraquinones are biogenetically derivable by the acetate–malonate pathway,[1-3] or by the shikimic acid–mevalonate pathway.[1,2,4,5] The co-occurrence of the five compounds (I)—(V), structurally related to pseudopurpurin (VII) from *Rubia tinctorum* (Rubiaceae), which is known to be derived from shikimate and mevalonate precursors,[5] strongly indicates the operation of this pathway in the biosynthesis of oruwal and its congeners, involving oxidative cyclisation of a prenylated naphthoquinone.

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[1] R. H. Thomson, 'Naturally Occurring Quinones', 2nd edn., Academic Press, London and New York, 1971, and the references therein to individual compounds.

[2] T. A. Geissman and D. H. G. Crout, 'Organic Chemistry of Secondary Plant Metabolism', Freeman, Cooper and Company, San Francisco, 1969, p. 113.

[3] E. Leistner and M. H. Zenk, *Chem. Comm.*, 1969, 210.

[4] E. Leistner and M. H. Zenk, *Tetrahedron Letters*, 1967, 475; 1968, 1395.

[5] A. H. Burnett and R. H. Thomson, *J. Chem. Soc.* (*C*), 1967, 2100; 1968, 2437.