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QUINONE METHIDES DERIVED FROM 5-OXA AND 5-AZA-9-PHENYL-1-PHENALENONE IN THE FLOWERS OF LACHNANTHES TINCTORIA (HAEMODORACEAE)[1].

J. M. Edwards

School of Pharmacy, University of Connecticut, Storrs, Conn., 06268 USA.

Ulrich Weiss

National Institutes of Health, Bethesda, Maryland, 20014 USA.

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Roots[2] and fruit capsules[3] of L. tinctoria Ell. have proved to be rich sources of the 9-phenylphenalenone pigments (e.g., lachnanthocarpone (1)[3]) characteristic[4] of the family Haemodoraceae. In addition, the roots of this plant also contain compounds formally derivable from 9-phenylphenalenones by removal of C-5. They are exemplified by the naphthalide (2)[2].

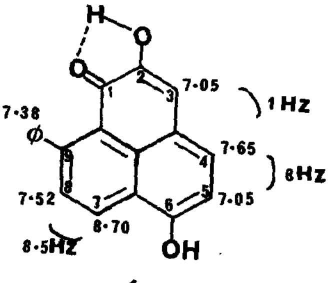
We now find that the inconspicuous yellow flowers of the plant contain two major pigments similarly lacking C-5, and exhibiting unusual modifications of the ring system. Both pigments were readily isolated from acetone extracts of the flowers by column chromatography over silica with benzene/ethyl acetate as eluant.

The less polar pigment, $C_{18}H_{10}O_4$ (high resolution mass spec.) forms large yellow crystals from benzene, mp 222-225°; it gives a mono-acetate and a yellow-fluorescing monomethyl ether with CH_2N_2 in ether. The brownish-yellow color of the solution of the pigment in aqueous NaOH changes slowly to light yellow on addition of $Na_2S_2O_4$; the pigment is thus quinonoid. In contrast to NaOH, ammonia and primary amines give intense brown-red colors. The ir spectrum (KBr) (ν 1725s, 1655w, 1632 m.cm^{-1}) suggests the presence of an α-pyrone grouping[5] (ν 1727s, 1706w, 1640w, cm^{-1}) and of a hydrogen-bonded carbonyl similar to that of (1)[3] (ν CO1625, changed to 1642 and 1655 cm^{-1} in the methyl ether and acetate). A strong $(M-1)^+$ peak in the mass spectrum, characteristic of 9-phenyl-1-phenalenones[3], and the loss of four molecules of CO from the molecular ion, support these conclusions; α-pyrones are known[6] to lose two molecules of CO, and the other two molecules come from the oxygenated carbons 1 and 2 (also observed in the mass spectrum of (1)). All these observations are readily accommodated by formula (3) for the yellow pigment, for which we propose the name lachnanthopyrone. The nmr spectrum of (3) is similarly in excellent agreement (see δ and J values indicated on structures (1), (2), and (3)).

Methylation of (3) with diazomethane in methanol gave a yellow, intensely green-fluorescing dimethyl ether, for which ir (νCO 1725 cm^{-1}) and nmr spectroscopy established structure (4). Absence of the ir carbonyl band at 1632 cm^{-1}, and an $(M-1)^+$ peak in the mass spectrum, show that the compound has lost the hydrogen-bonded carbonyl of ring A, and that it has thus been formed by a 1,6-addition commonly encountered in quinone methides[7]. Conclusive evidence for the correctness of structure (3) is provided by the ready oxidation (MnO_2, $CHCl_3$) of (4) to the known[8] anhydride (5) whose structure is unequivocally established. In contrast to (4) the monomethyl ether and acetate already mentioned, are, from spectroscopic and analytical evidence, normal derivatives of the C-2 hydroxyl group of (3).

The more polar pigment forms bright orange crystals from ethyl acetate; mp 155°. High-resolution mass spectroscopy establishes the molecular formula as $C_{20}H_{15}NO_4$. The compound is non-basic and stable to warm dilute HCl and NaOH. Its wine-red solution in NaOH becomes yellow-brown on addition of $Na_2S_2O_4$. The ir spectrum (KBr) shows strong bands at 1650, 1625, 1614, 1420, and 1055 cm^{-1}. The mass spectrum has the molecular ion (333) as base peak, but shows a prominent (88%) peak at $(M-1)^+$. Strong peaks at 289 ($C_{18}H_{11}NO_3$) and 288 ($C_{18}H_{10}NO_3$) indicate the ready loss of C_2H_5O and C_2H_4O, presumably from M^+ and $(M-1)^+$ respectively. The compound forms a monomethyl ether (CH_2N_2,MeOH) (νCO 1660 and 1640 cm^{-1}), and a diacetate (νCO 1760, 1740, 1670, and 1640 cm^{-1}). The nmr spectrum contains signals closely resembling those from protons at C-7, C-8, and the phenyl ring in (3).

These data indicate a quinonoid system resembling that of (3), and the absence of basicity and the ir spectrum suggest the presence of a lactam. All the data are compatible with formula (6) of an isocarbostyril derived from 5-aza-1-phenalenone. The presence of the $-CH_2-CH_2-OH$ group, initially suggested by the mass spectroscopic loss of C_2H_5O, is supported by the nmr (two triplets at δ 4.43 and 4.31) and the ir spectrum (νCH_2 1420 cm^{-1}). The ir band at 1650 cm^{-1} (1660 in the methyl ether and 1670 cm^{-1} in the diacetate) agrees well with those of authentic isocarbostyrils (1640-1645 cm^{-1}; 1660 cm^{-1}).[9,10] So far no derivatives formed by 1,6-addition to the quinone methide system of (6) have been identified; we feel that this is due to the greater stability of the α-pyridone ring system in contrast to the pyrone ring of (3).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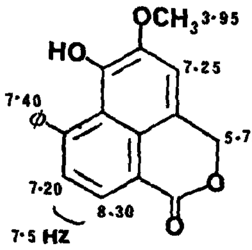
1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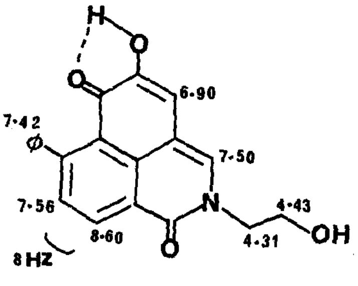
2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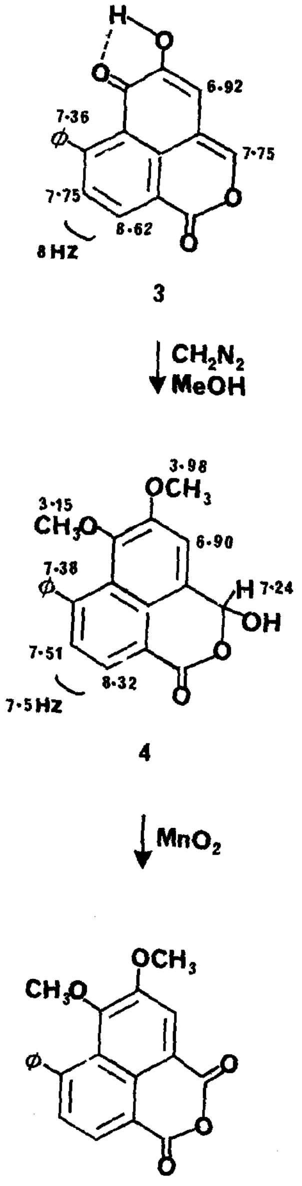
6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7·75
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8 HZ
O
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MeOH
3·98
OCH3
3·15
CH3O
6·90
7·38
φ
H 7·24
OH
7·51
8·32
7·5Hz
MnO2
OCH3
CH3O
φ
O
O
O

3

4

5

We wish to propose the name lachnanthopyridone for the (as yet unknown) N-unsubstituted parent compound of (6); the orange pigment would thus be N-(2-hydroxyethyl)lachnanthopyridone. It is tempting to speculate that (6) may be formed biosynthetically from (3) and ethanolamine (or an equivalent); ample precedent for the probable occurrence of such reactions in the formation of ring systems of natural products is provided by certain diterpenoid alkaloids of the garryine and atisine groups, significantly, atidine and ajaconine contain the grouping $N-CH_2-CH_2OH$[11]. Experiments aimed at converting (3) to lachnanthopyridone and (6) are in hand.

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