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LACHNANTHOSPIRONE, A DIMERIC 9-PHENYLPHENALENONE FROM THE SEEDS OF *LACHNANTHES TINCTORIA* ELL. (1).

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ABSTRACT. The structure of lachnanthospirone [4] a novel dimeric pigment from *Lachnanthes tinctoria* has been established from the X-ray crystal structure of a derivative [3] in which the spirolactone present in the natural product has been opened.

Lachnanthes tinctoria Ell. (Haemodoraceae) has proved to be a rich source of pigments containing both intact and modified 9-phenylphenalenone ring systems (2). An investigation of the seeds of the plant has revealed the presence of lachnanthocarpone [1] (3) and haemocorin aglycone [2] (4), and of a novel dimeric compound.

Chromatography (SiO_2, $CHCl_3$) of a benzene extract of defatted seeds of *L. tinctoria* gave 1 and 2, and a less polar yellow pigment, $C_{39}H_{22}O_7$ (high-resolution MS) which formed deep-orange crystals from acetone-water, mp > 310°. A strong $(M-1)^+$ peak seen in the mass spectrum and the loss of two molecules of CO from the parent ion implied the presence of a 9-phenyl-1-phenalenone (3); major fragement ions were seen at m/e 287 ($C_{19}H_{11}O_3$), and 314. The compound, which was stable to hot, dilute acid, but unstable in base, turned to blue-green with ammonia, and gave a blue solution with NaOH, which was unaffected by the addition of $Na_2S_2O_4$. The PMR spectrum revealed the presence of a single OMe group (δ 3.93); all other resonances were attributable to aromatic protons. The IR spectrum (ν CO 1801, 1717, and 1630 cm^{-1}) suggested the presence of a β,γ-unsaturated γ-lactone (5), a ketone group, and of a hydrogen-bonded carbonyl similar to that of 1 (3). The pigment formed a diacetate and a single dimethyl ether with CH_2N_2 in ether. The IRs of these derivatives (ν 1630 changed to 1645

cm^{-1}) confirm the assignment for the hydrogen-bonded carbonyl (3). The isolation of a single dimethyl ether demonstrates the absence of the tautomerism (1-keto-6-hydroxy $\rightleftarrows$ 1-hydroxy-6-keto) so often noted among the haemodoraceous pigments (3). The color of both derivatives changes from yellow to deep purple when exposed to ammonia on TLC plates.

Methylation (CH_2N_2) of the unknown compound in wet MeOH gave two isomeric, orange, crystalline products, $C_{43}H_{32}O_8$ (addition of the elements of CH_3OH and $3CH_2$), whose IR spectra (ν CO 1730, 1720, and 1645 cm^{-1}) suggest that an ester grouping has replaced the γ-lactone of the parent molecule. The less polar isomer (22%) exhibited an orange fluorescence under UV light (6), and had in its NMR spectrum an OMe resonance characteristic of a methyl ether shielded by a *peri*-phenyl ring (3). A single crystal (0.2x0.1x0.05mm) of the second, more polar isomer (mp 174-176° from EtOAc) was subjected to X-ray analysis.

Crystal data. $C_{43}H_{32}O_8$; M=676.72; Orthorhombic, Pbca; $\underline{a}$=19.874(5), $\underline{b}$=29.835(8), $\underline{c}$=11.569(2) Å; Z=8; $D_{\underline{calc.}}$=1.310, $D_{\underline{obs.}}$(flotation-H_2O,KI)=1.304 gcm^{-3}. Intensity data (3604 reflections, $2\underline{\theta}$ <115°;741 <$3\underline{\sigma}[I_{\underline{o}}]$) were collected with CuKα radiation (λ=1.5418 Å) on a PICKER FACS-I diffractometer. Data reduction included corrections for Lorentz, polarization and absorption. The structure was solved by MULTAN (7) which afforded a map including all 51 of the heavier atoms. Full-matrix least-squares refinement, first isotropically and then anisotropically (in two sections) converged at R=0.087 minimizing $\Sigma \underline{w}(|F_{\underline{o}}|-|F_{\underline{c}}|)^2$. A thermal ellipsoid plot of the molecule showing the numbering system, structure and conformation is shown. A more definitive paper on this crystal structure will be published elsewhere.

Structure *3* for the derivative leads to structure *4* for the compound isolated from *L. tinctoria*, for which we propose the name lachnanthospirone. The positioning of the OMe group at C-4' rather than at C-5' is based upon the observed shifts in the NMR resonance of the proton at C-6' on derivatization of *4* (upfield 0.14 ppm in the ether and 0.47 ppm in the acetate), and upon biosynthetic considerations. The dimeric pigment is reasonably formed by the oxidative coupling of one molecule of *1* with an oxidation product derived from *2*; the exact nature of the oxidation product is not known, but the presumed involvement of 2 suffices to fix the position of the methyl group. The tautomeric form of 3 (1-OMe, 6-keto) would be formed to a minor extent (3). The color changes observed when the diacetate and dimethyl ether of 4 were exposed to ammonia clearly reflect the ready opening of the γ-lactone and the generation of a stable phenoxide ion at C-6.

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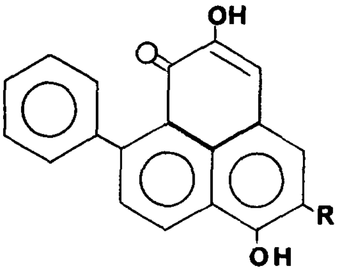
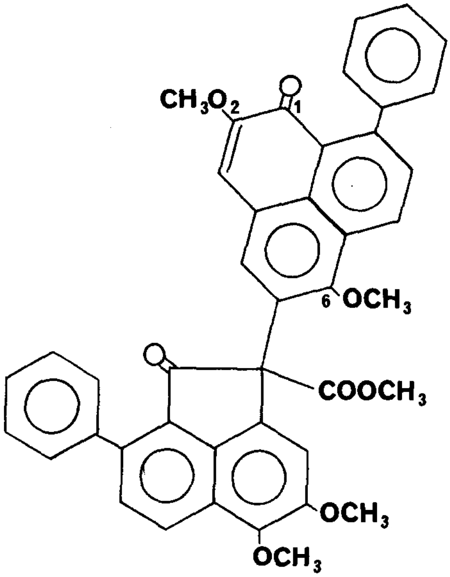


1 R=H

2 R=OCH_3



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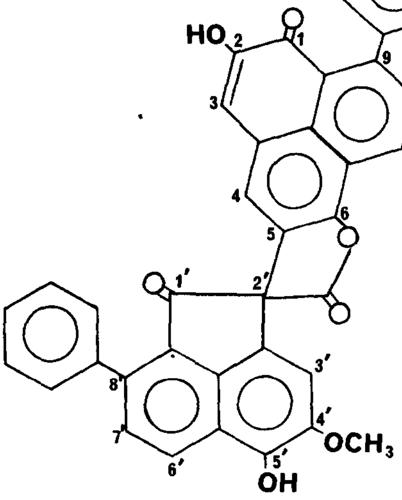

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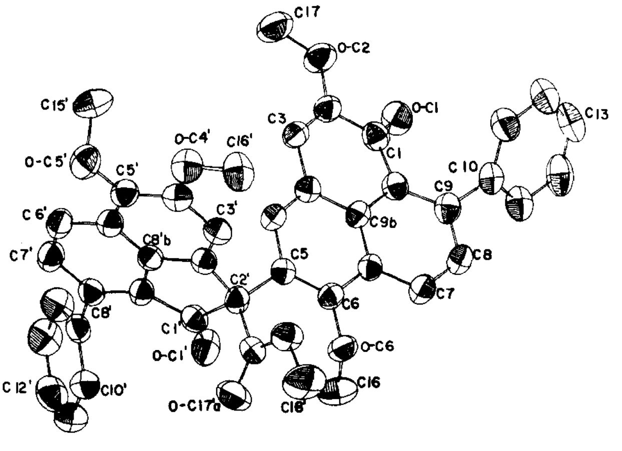

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