

PIGMENTS OF LACHNANTHES TINCTORIA ELL. (HAEMODORACEAE) I.
ISOLATION AND PHOTOLYSIS OF SOME 9-PHENYLPERINAPHTHENONES.

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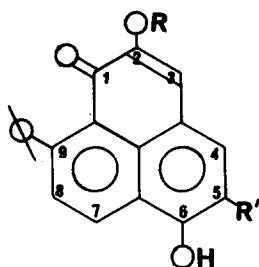
Lachnanthes tinctoria Ell. (Redroot) is the only species of its family to occur in the northern hemisphere. Species of the related Australian genus Haemodorum yield haemocorin (1),^{1a,b,c} the only perinaphthenone pigment found so far in higher plants. Occurrence of this unusual compound in related species, and reports² suggesting the presence of photo-dynamic constituents,* prompted an examination of Lachnanthes.

So far, extracts of the colorful root system have yielded an orange glycoside, lachnanthoside (2), which is a bioside or diglycoside of 3; a red non-glycosidic compound lachnanthofluorone (4), which exhibits bright red fluorescence; and several minor colored constituents. The main pigment of the brownish-red pulp surrounding the seeds is lachnanthocarpone (5). The determination of the structures 2-5 rests largely upon n.m.r. and i.r. spectra; it will be reported elsewhere.³

One characteristic property of the aglycone of 1, and of several other related compounds,⁴ is the occurrence of (M-1)⁺ as the base peak of the mass spectrum; it has plausibly been attributed to the ionic species 6.⁴ We have found the same ready loss of a proton in the mass spectra of 5 and of the aglycone (3) of lachnanthoside.

Since we have observed the occurrence of 4, which has the same naphtho-[8,1,2-jkl]-xanthenone skeleton as 6, and since photochemical reactions often take a path analogous to that of mass-spectrometric transformations,^{5,6} it seemed of interest to examine the photochemistry of 3 and 5, and to attempt a direct correlation of 4 with the non-fluorescing pigments.

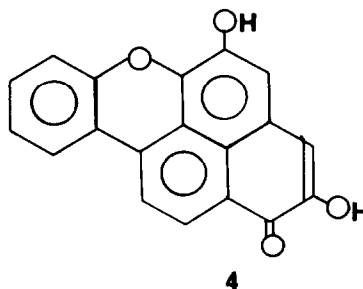
*Confirmed in experiments to be reported elsewhere.



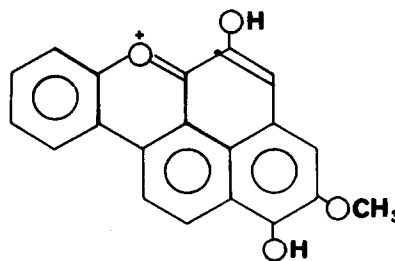
1 R, Cellobiose; R', OCH₃,

3 R, H; R', OH

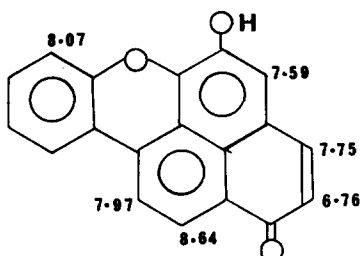
5 R, H; R', H



4



6



7

In general, the photolysis of perinaphthenones under oxidative conditions leads eventually to naphthoic anhydrides;⁷ the generation of some transient, unidentified colored products has been noted.

Irradiation of a solution of 5, either in methanol or benzene (Pyrex glass, high pressure Hg lamp), rapidly yields a purple photoproduct, C₁₉H₁₀O₃ (m.p. 330-2° from methanol-benzene), isolated by chromatography in EtOAc over silica, which can be formulated as 5-hydroxynaphtho-[8,1,2-jkl]xanthenone (7). Prolonged irradiation converts 7 to unidentified yellow compounds. The molecular formula of 7 proves that the elements of hydrogen have been lost from 5, and the u.v. spectrum: λ_{max} 523, 379, 362, 329, 317, 280, 230 m μ (log ϵ 3.6, 3.15, 3.22, 3.29, 3.36, 3.46, 4.1) shows a bathochromic shift of 73 m μ compared to that of 5, implying increased conjugation in the photoproduct. 7 is soluble in polar solvents only, in which it exhibits a very striking bright red fluorescence. It still retains the typical color reactions of a hydroxylated perinaphthenone: a red solution in conc. H₂SO₄, showing red fluorescence; a blue solution in NaOH, unchanged on addition of dithionite; a positive (yellow) FeCl₃ test. It forms a single monomethyl ether (purple crystals, m.p. 217-22°, from CHCl₃-hexane; intense, bright red fluorescence in both polar and nonpolar solvents).

The n.m.r. spectrum of 7 (DMSO) consists of two AB quartets: one δ 6.76, 7.75; $J = 10$ Hz, typical of the C-2 and C-3 protons of an unsubstituted perinaphthenone,⁸ and the other δ 8.64, 7.97; $J = 7.5$ Hz, similar to the C-7 and C-8 resonances of 5.³ The remainder of the spectrum consists of a singlet (1H) δ 7.59, and a broad doublet (1H) δ 8.07, $J \sim 8$ Hz coupled to the other aromatic protons which are found as a multiplet (3H) centered at δ 7.42. These aromatic resonances clearly indicate that the unsubstituted phenyl ring of 5 is no longer present in 7.

These data are consistent with structure 7, and additional support is found in the i.r. spectrum; $\nu(\text{CO})$ 1645 cm^{-1} indicates the absence of a 2-hydroxyl group. In 5 and in 2-hydroxyperinaphthenone, the corresponding vibration occurs at 1625 and 1620 cm^{-1} , in perinaphthenone it is found at 1655 cm^{-1} .

Attempts to study the structure of 7 by chemical degradation proved unrewarding.

Similar irradiation of 3 gave 4, identical in every respect with the compound obtained from Lachnanthes. The photochemical reaction of 3 proceeds much faster than that of 5. This easy interconversion raises the question whether lachnanthofluorone is a true natural product or an artifact formed by photolysis of lachnanthoside aglycone during isolation; we have, however, shown that 7 can be detected even when the root system is extracted and chromatographed rapidly in the dark.

We have been unable to demonstrate the photochemical reaction with synthetic 6-hydroxy-9-phenylperinaphthenone, hence we believe that the 2-hydroxy function is necessary for the reaction, possibly because the tautomeric ortho-quinone structure predisposes the compound to radical-type reactions. Work is in hand to investigate this possibility. Although similar substituted xanthenes have been formed by the photolysis of 1-phenoxy-naphthalenes,⁹ and an analogous ring closure of some diphenylbenzoquinones has been observed,¹⁰ the conversions described appear to be the first examples of the formation of an oxygen bridge by the interaction of a non-quinonoid carbonyl group with a peri-phenyl ring.

Satisfactory spectral data and a determination of molecular formula by high resolution mass measurement have been obtained for all new compounds described.

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