Tetrahedron Letters No.1, pp. 33-35, 1965. Pergamon Press Ltd.
Printed in Great Britain.

ERYTHROLACCIN

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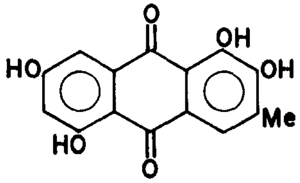
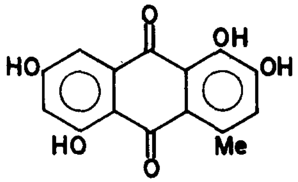
(Received 16 November 1964)

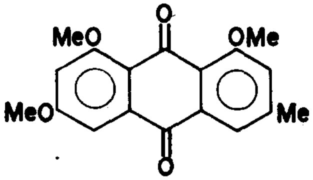
Structure I was assigned to erythrolaccin, the yellow pigment of stick-lac, on the basis of colour reactions, UV and IR spectra, and the isolation of 2-methylanthracene by zinc dust distillation.[1] In our work on other lac pigments[2] we happened to determine the NMR spectra of erythrolaccin and its tetramethyl ether, from which it is clear that the methyl group has to be shifted to the adjacent α-position as in II.



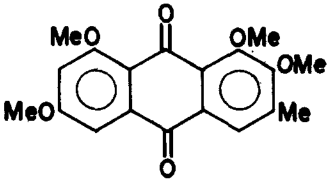
(I)



(II)



(III)



(IV)

The NMR spectrum of erythrolaccin in DMSO shows 3 protons in the aromatic region: a singlet at 3.17 and two doublets

(J=2.5 cps) at 3.08 and 3.58 (chemical shifts on the τ scale). The doublets can obviously be assigned to the resorcinol nucleus, but the singlet absorption at 3.17 is too high for an α-proton in anthraquinone. The spectrum of the tetramethyl ether in $CDCl_3$ shows a single proton absorption at 3.30, characteristic of an anthraquinone proton which is flanked by two methoxyl groups; the doublet character (J=2.5 cps) in conjunction with a doublet at 2.76 with the same coupling constant indicates that the substituents in one ring are two methoxyl groups in 1,3-positions. A third aromatic proton appears as a singlet at 3.03, which is too high for an α-proton in anthraquinone, but is in the right position for a β-proton flanked by a methyl and a methoxyl group. In the spectrum of emodin trimethyl ether (III) the corresponding β-proton appears at 2.95.

For a close comparison with erythrolaccin tetramethyl ether we determined the NMR spectrum of alaternin tetramethyl ether (IV), which was synthesized by Lovie and Thomson[3] and by us in an attempt to synthesize the tetramethyl ether of I. The spectrum of IV in $CDCl_3$ exhibits two doublets (J=2.5 cps) at 3.28 and 2.61 and a singlet at 2.12 in complete agreement with the aromatic proton substitution in IV.

The methyl signals in the NMR spectra of erythrolaccin tetramethyl ether, III and IV confirm structure II for erythrolaccin. In erythrolaccin itself (solvent pyridine) the methyl signal is at 7.28; in erythrolaccin tetramethyl ether it occurs at 7.25. The β-methyl groups in III and IV appear at 7.58 and 7.63; in 1,3-dimethylanthraquinone[4] the α-methyl is at 7.22 and the β at 7.55.

Polyhydroxyanthraquinones occurring in plants carry a methyl group or other carbon side-chain in a β-position, but the insect pigments, kermesic acid and carminic acid, are α-methylanthraquinone derivatives.

The isolation of 2-methylanthracene from the zinc dust distillation of erythrolaccin must be ascribed to methyl migration to form a thermodynamically stabler product. It has been observed that the zinc dust distillation of 1,8-dihydroxy-3-hydroxymethyl-4-methylnaphthalene yields 1,3-dimethylnaphthalene.[5] The behaviour of various polyhydroxyanthraquinones containing a methyl group in the 1-position towards zinc dust distillation is being studied.

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