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THE CONSTITUTION OF ERYTHROLACCIN

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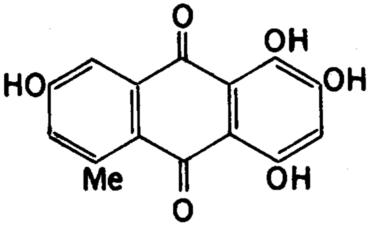
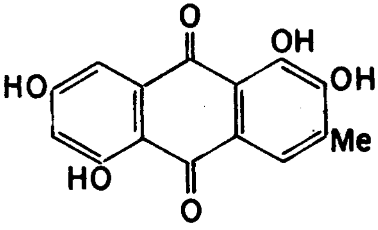
TSCHIRCH and Lüdy[1] isolated from stick-lac a yellow pigment, $C_{15}H_{10}O_6$, which had the " entire behaviour of a tetrahydroxymethylanthraquinone of the tentative structure (I)". It was stated that the positions of the methyl and hydroxyl groups were still to be determined and that the suggested orientation was in view of the relationship to kermesic acid and carminic acid. The only derivative prepared was a tetra-acetate, and no melting point was cited for erythrolaccin or the tetra-acetate.



I



II

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[1] A. Tschirch and F. Lüdy, Helv. Chim. Acta 6, 994 (1923).

By a slight modification of Tschirch and Lüdy's procedure we have isolated erythrolaccin as orange needles, m.p. 314° (dec.). The elementary analysis and molecular weight (Rast) corresponded to $C_{15}H_{10}O_6$. Kuhn-Roth oxidation indicated one C-methyl group. Zinc dust distillation yielded 2-methylanthracene. A tetra-acetate, m.p. 178°, and a tetramethyl ether, m.p. 150°, were obtained, the latter by means of dimethyl sulphate and potassium carbonate in acetone. Erythrolaccin is therefore a tetrahydroxy-2-methylanthraquinone. Two hydroxyl groups are in α- and two in β-positions, because methylation with ethereal diazomethane gave a dimethyl ether, m.p. 224°, which yielded a diacetate, m.p. 199°. Erythrolaccin is an alizarin derivative as shown by the shades obtained on mordanted wool; and it is not a quinizarin derivative since a solution in glacial acetic acid is non-fluorescent. The infra-red spectra of erythrolaccin and its dimethyl ether have strong absorption bands at 1617 and 1614 cm^{-1} respectively (chelated carbonyl), and none around 1672 cm^{-1} (unchelated carbonyl); the two α-hydroxyls in erythrolaccin are therefore in the 1,5 and not in the 1,8-positions. Three hydroxyl groups in erythrolaccin are thus in the 1,2,5-positions. Unlike anthragallol erythrolaccin did not give the Bargellini test, excluding the presence of three hydroxyls in 1,2,3-positions. We have shown earlier that xanthopurpurin undergoes hydroxymethylation readily in the 2-position by treatment with aqueous sodium hydroxide and formaldehyde, and have used the method for the synthesis of lucidin[2] and 1,3,8-trihydroxy-2-hydroxy-

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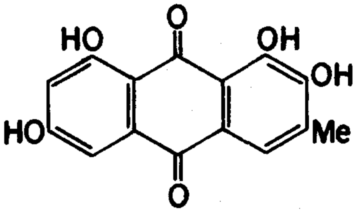
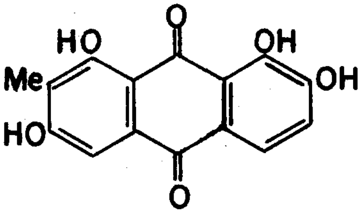
[2] N. R. Ayyangar and K. Venkataraman, J. Sci. Ind. Res. B15, 359 (1956).

methylanthraquinone.[3] We have now found that the reaction is a useful diagnostic test for the presence of two hydroxyl groups in 1,3-positions and the absence of a substituent in the 2-position. Erythrolaccin condensed readily with alkaline formaldehyde to form a hydroxymethyl derivative (dec. >360°), proving simultaneously that the fourth hydroxyl group in erythrolaccin is in the 7-position and the methyl group is in the 3-position. Only one possibility, 1,2,5,7-tetrahydroxy-3-methylanthraquinone (II), therefore remains for the structure of erythrolaccin.



III



IV

Briggs *et al.*[4] isolated from the bark of *Rhamnus alaternus* a pigment, for which the trivial name alaternin may be suggested, and to which they assigned the structure 1,2,6,8-tetrahydroxy-3-methylanthraquinone (III); the chemical and spectral evidence equally supported an alternative (IV) with the methyl group in the 7-position, but (III) was preferred on

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[3] N. R. Ayyangar, B. S. Joshi and K. Venkataraman, *Tetrahedron* **6**, In press (1959).

[4] L. H. Briggs, F. E. Jacombs and G. A. Nicholls, *J. Chem. Soc.* 3069 (1953).

"phytochemical grounds" as a derivative of emodin, the major colouring matter of the plant. Further support for (III) is provided by the fact that alaternin, a small sample of which was sent to us by Professor L. H. Briggs to whom we are greatly indebted, condensed readily with alkaline formaldehyde, although the quantity at our disposal was too small for characterization of the product. The synthesis of (II) and (III) is in progress.

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