Tetrahedron Letters No.33, pp. 3161-3163, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE CONVERSION OF TRI-O-METHYLSOLORINIC ACID INTO TETRA-O-METHYLAVERYTHRIN

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(Received 1 May 1967)

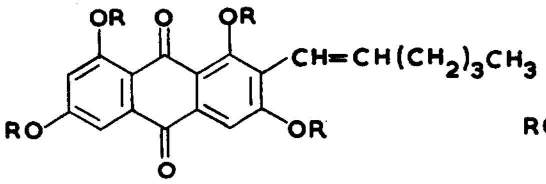
The mould *Aspergillus Versicolor* (Vuillemin) Tiraboschi produces a number of metabolites including averythin[1] (I), averantin[2] (II), and averufin[3] (III). These pigments possess biogenetic similarities to each other, and to the lichen product solorinic acid (IV), which have been previously noted.[4]

In an earlier communication[4] we described a revision of the structure of averufin. Our attention has now been directed towards the synthesis of this natural product. For this purpose we required certain novel anthraquinones as intermediates, and consequently we have examined various model reactions on more readily available systems.

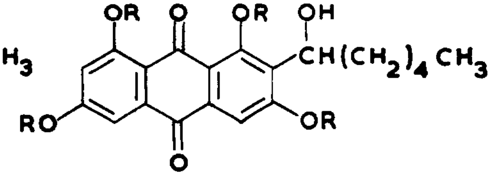
We now describe the conversion of synthetic tri-*O*-methylsolorinic acid (V), prepared by the method of Thomson *et al*[5]., into tetra-*O*-methylaverythrin (VI). Reductive acetylation of (V) using zinc dust in pyridine/acetic anhydride afforded the *leuco*-acetate[6] (VII) as lemon-yellow plates, m.p. 98-100°, in 63% yield after chromatography and crystallisation from cyclohexane; $\nu_{max.}$(KBr) included 1708 (ketone) and 1762 (acetate) cm.$^{-1}$; $\lambda_{max.}$(EtOH) 273,376, and 395 mμ (ε 79,500,4600, and 5200 respectively), and $\lambda_{infl.}$ 249,360 and 415 mμ(ε 30,000,3600, and 3500 respectively). The n.m.r. spectrum ($CDCl_3$) showed a singlet τ 3.09 (1H) 4-proton, a doublet τ 3.29 (1H, J=2.5 c.p.s.) 5-proton, a doublet τ 3.41 (1H, J=2.5 c.p.s.) 7-proton, three singlets a τ 5.95, 5.99 and 6.01 (3,6 and 3H respectively) OMe protons, a triplet centred at τ 7.12 (2H) 2'-protons, two singlets at τ 7.38 and τ 7.50 (each 3H) acetoxy protons, and a humped region *ca* 8.5 - 9.2 (9H) side chain protons.

Treatment of (VII) with LAH in THF under nitrogen achieved smooth reduction of the keto-group and the quinonoid system was regenerated on exposure to air to give (±) - tetra-*O*-methylaverantin (VIII) in 67% yield. Compound (VIII) formed yellow prisms from cyclohexane, m.p. 83-88°; $\nu_{max.}$ (CCl_4) *inter al*., 3570 (OH) and 1678 (quinone C=O), but no C=O at 1708 cm^{-1}; $\lambda_{max.}$ (EtOH) 224, 283, and 335 mμ(ε 36,500, 25,400, and 5900 respectively), and $\lambda_{infl.}$ 400mμ(ε 3000).

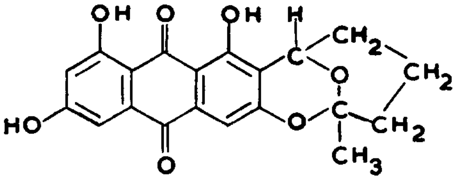
Brief treatment of (VIII) with *p*-toluene sulphonic acid in benzene at 70° afforded, after



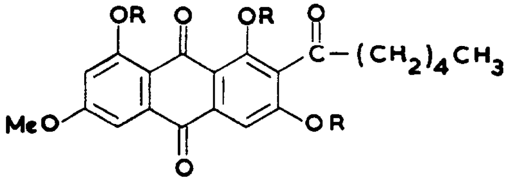
I, R=H
VI, R=Me



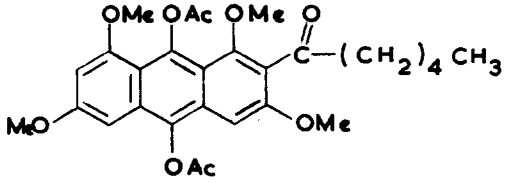
II, R=H
VIII, R=Me



III



IV, R=H
V, R=Me



VII

preparative TLC on silicic acid and crystallisation from ether/chloroform tetra-*O*-methylaverythrin (VI) as yellow needles in 30% yield, m.p. 174-175° (lit[1]., 176-177°), undepressed on admixture with authentic material.

The i.r. and mass spectra were superimposable with those of authentic material. Further work is in progress.

References

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6. All new compounds gave satisfactory microanalyses.