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Short Communications

Fungus Pigments

XVI*. The Pigments of *Peniophora sanguinea* Bres.

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Peniophora sanguinea Bres. (*Corticium sanguineum* Fr.) is a fungus which attacks branches and pieces of wood lying on the ground. The infected wood is coloured dark red by the mycelium of the fungus. Thin layer chromatography (TLC) of a crude acetone extract of the infected wood reveals the presence of several pigments. By a combination of column chromatography and crystallisation four of these pigments have been obtained in a pure crystalline state. They are provisionally termed pigments A, B, C, and D in order of decreasing mobility in TLC.

Pigment B, which appears to be the main component of the mixture and for which the name xylerythrin is proposed, has m.p. 252–254° and corresponds to the formula $C_{26}H_{16}O_6$, confirmed by a mass-spectrometric molecular weight determination. It gave a dimethyl ether, m.p. 213–215°, and a diacetate, m.p. 228–230°, showing the presence of two hydroxyl groups in the molecule. The I.R.-spectra of xylerythrin and its derivatives all show strong absorption in the region 1755–1780 cm^{-1}, indicative of a lactone group. The presence of a lactone could also be demonstrated chemically by alkaline hydrolysis of xylerythrin dimethyl ether. The red coloured alkaline solution regenerated xylerythrin dimethyl ether upon acidification.

Xylerythrin itself is decomposed very readily in alkaline solution giving benzoic acid and a yellow acid of composition $C_{19}H_{14}O_6$. The formation of benzoic acid shows the presence in xylerythrin of at least one monosubstituted benzene ring, which is also supported by I.R.-bands at 688 and 751 cm^{-1}.

A band at 1625 cm^{-1} in xylerythrin, shifted to 1635 cm^{-1} in the methyl ether and to 1645 cm^{-1} in the acetate can be attributed to a chelated conjugated carbonyl group, thus accounting for the fifth oxygen atom in xylerythrin.

Xylerythrin can, in spite of its colour, evidently not be a quinone. The U.V.-spectrum (in dioxan) with maxima at 255 mμ (log ε 4.37), 360 mμ (log ε 3.94), and 450 mμ (log ε 4.18) gives little information as to the nature of the chromophoric system. Reductive acetylation gave a colourless leuco-acetate, which has no maximum above 205 mμ, but inflexions at 210, 250, and 285 mμ. This indicates the absence of any condensed aromatic system in xylerythrin.

The NMR-spectra of the acetate and methyl ether of xylerythrin show the absence of any aliphatic protons, except those of the acetyl and methoxyl groups, respectively.

An X-ray crystal structure determination of the bisbromoacetate of xylerythrin by Abrahamsson and Innes (accompanying paper [1]) has shown that this has the structure I. Xylerythrin is accordingly II, as there is no reason to expect that a rearrangement has occurred during the preparation of the derivative.

This structure accounts well for the chemical and physical properties of xylerythrin. Only the formation of benzoic acid under very mild alkaline conditions is somewhat unexpected.

Xylerythrin is thus a quinone methide, a number of which earlier have been found in fungi, such as citrinin,[2] purpurogenone,[3] fuscin,[4] and pulvilloric acid.[5] It is obvious

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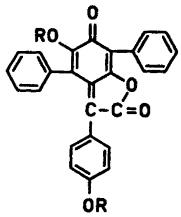

I: R = $COCH_2Br$
II: R = H

that xylerythrin is also closely related to polyporic acid (2,5-diphenyl-3,6-dihydroxy-1,4-benzoquinone) another fungus pigment.[6] Its structure can, at least formally, be constructed from one molecule of polyporic acid and one molecule of *p*-hydroxyphenylacetic acid.

Of the other pigments of the fungus, pigment A has the composition $C_{27}H_{18}O_5$ with one methoxyl group. Methylation gave a monomethyl ether, identical with xylerythrin dimethyl ether. Pigment A is thus one of the two possible monomethyl ethers of xylerythrin.

Pigment C has the composition $C_{26}H_{16}O_6$ and its spectral properties suggest that it is a hydroxy derivative of xylerythrin. Pigment D has not yet been completely characterised, but its optical properties are similar to those of the other pigments, suggesting a close relationship to them.

It is hoped to publish a full account of the isolation of the pigments, the chemical reactions of xylerythrin and the determination of the complete structure of the other pigments at a later occasion.

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A Study of the Ninhydrin-Positive Components Derived from Cystine during the Cyanide-Nitroprusside Test

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The cyanide-nitroprusside test, or Brand's test,[1] has frequently been used for the detection of an increased amount of cystine in the urine. The test depends upon the fact that cystine (CSSC) is reduced by sodium cyanide (NaCN) to its sulphydryl derivative, cysteine (CSH), and the latter reacts with sodium nitroprusside (NaNP) to give a magenta red colour in slightly alkaline medium. In practice the procedure has the disadvantage of involving a poison, NaCN, and in laboratories without adequate ventilation systems it is potentially hazardous to carry out large series of Brand's tests, as in screening examinations for the detection of cystinuria.[2-5]

In order to minimize the hazard, sodium hydridoborate was tested instead of NaCN as a reducing agent for CSSC. Sodium hydridoborate is known to have a low toxicity and its water solutions are capable of reducing CSSC into two moles of CSH. The reduction of CSSC by NaCN, however, has been reported to produce only one mole of CSH per mole of CSSC, the other half of the CSSC molecule being converted *via* α-amino-β-rhodanpropionic acid into a cyclic compound, 2-aminothiazoline-4-carboxylic acid or its tautomer, 4-carboxythiazolidon-2-imide,[6,7] which do not take part in the colour reaction with NaNP. It was found that the reduction of CSSC took place rapidly when sodium hydridoborate was used and the nitroprusside reaction yielded about the same colour intensity by visual comparison, as when NaCN was used as reducing agent. However, the colour produced when sodium hydridoborate was used faded very quickly. This is in agreement with the finding that fading of the colour developed by the nitroprusside reaction can be inhibited by addition of cyanide.[8,9] In order to obtain some qualitative and quantitative data regarding the ninhydrin-positive components produced during the reaction be-