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PHLEBIARUBRONE, A BASIDIOMYCETE PIGMENT RELATED TO POLYPORIC ACID [1]

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The Basidiomycete Phlebia strigosozonata produces in artificial culture a bright red pigment which remains mostly in the mycelium. The pigment, which we have obtained crystalline and named "Phlebiarubrone", has been shown to be the p-terphenyl derivative, 3,6-diphenyl-4,5-methylene dioxy-1,2-benzoquinone (I).

Phlebiarubrone can be extracted from the mycelium with acetone from which it crystallises along with a colorless compound. The latter is removed by washing with methanol in which phlebiarubrone is very sparingly soluble. Recrystallisation from acetic acid gives red needles, mp 248-250°. These analyse satisfactorily for $C_{19}H_{12}O_4$ and have λ_{max} 268, 332 and 465 mμ (ϵ29,900, 4,400 and 3,500 resp., in ethanol); ν_{max} 1653, 1640 cm^{-1} (quinone).

The red color, together with the absence of hydroxyl groups (as indicated by infrared) is in agreement with an ortho-quinone structure. On treatment with acetic anhydride and zinc dust in pyridine, a leuco -acetate [2] (mp. 227-9°, ν_{max} 1770, cm^{-1}), $C_{23}H_{18}O_6$, is obtained. Phlebiarubrone can be regenerated from the leuco-acetate: refluxing with dilute sulphuric acid in acetic acid gives a brown crystalline product, presumably the hydroquinone (ν_{max} 3500, 3400 cm^{-1}; nujol) with no

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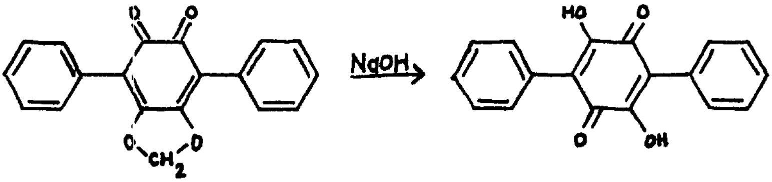
[1] This work was supported by a grant (E-226) from the National Institute of Allergy and Infectious Diseases, National Institutes of Health.

[2] With sodium acetate and acetic anhydride another colorless diacetate mp 115-117° is obtained, the structure of which has not been elucidated.

carbonyl absorption in the infrared. This product is oxidised to phlebiarubrone by bubbling oxygen through its pyridine solution.

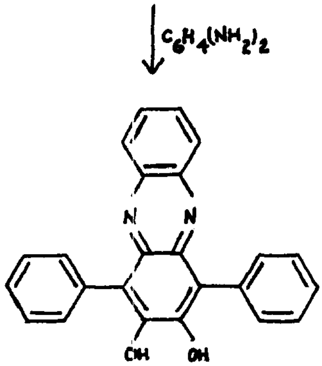
Phlebiarubrone undergoes an interesting reaction with alkali which essentially establishes its structure: The pigment is insoluble in alkali but if it is dissolved in acetic acid, and this solution added to excess dilute alkali, a purple solution results. Acidification gives a brown quinone, $C_{18}H_{12}O_4$, identified as polyporic acid (II) by comparison with a synthetic sample.[3]



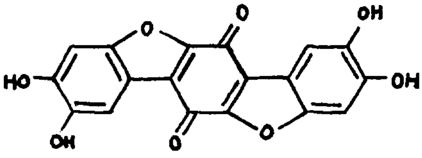
I

II

+ HCHO



III



IV

The ready conversion to polyporic acid indicates that the four oxygen atoms of phlebiarubrone are on the central ring. If two of these

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[3] Frank, R. L., Clark, G. R. and Coker, J. N. J. Am. Chem. Soc. 72, 1824 (1950).

form the ortho-quinone, the other two must be involved in ether linkages. The nuclear magnetic resonance spectrum[4] (in deuterated dimethyl sulfoxide) reveals the nature of these. It shows aromatic resonances centered at about 7.45 ppm due to ten protons; there is a sharp resonance at 6.25 ppm which can be assigned to the protons of a methylene dioxy ether. The leuco-acetate of phlebiarubrone (in $CDCl_3$) similarly shows resonances at 7.45 ppm (ten aromatic protons) and a singlet at 5.97 ppm ($-O-CH_2-O-$) as well as one at 2.03 ppm (diacetate). Confirmation of the methylene dioxy structure came from the reaction with alkali which gives formaldehyde (isolated as its dimedone derivative) in quantitative amount.

The ortho-quinone structure is demonstrated by formation of an o-phenylene diamine derivative (III). Analysis of this dark red crystalline compound, m.p. ca 305° (partial), indicated a formula $C_{24}H_{16}O_2N_2$. The infrared spectrum shows hydroxyl absorption ($\nu_{max.}$ 3260 cm^{-1}), and treatment with acetic anhydride and pyridine gives a yellow diacetate (ν_{max} 1786, 1207 cm^{-1}). Thus, cleavage of the methylene dioxy ether linkages occurs also in the formation of the phenazine.

It is interesting that a related quinone, thelephoric acid (IV)[5], has been obtained from the sporophores of Phlebia strigosozonata.[6]

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[4] N.M.R. spectra were determined by Dr. D. P. Hollis and Mr. A.E. Pier of Varian Associates, whom we wish to thank for helpful discussion in connection with interpretation of the results.

[5] Gripenberg, J. Tetrahedron **10**, 135 (1960).

[6] Maki, S. Nippon Ringaku Kaishi **40**, 195 (1958) C.A. **52**, 18638^a