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# FUNGUS PIGMENTS XXIII⁺

## HYDNUFERRUGIN: A NOVEL TYPE OF A 2,5-DIPHENYLBENZOQUINONE-DERIVED PIGMENT

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Extraction of sporophores of Hydnellum ferrugineum (Fr.)Karsten and H.zonatum (Batsch)Karsten has yielded a brown-violet pigment for which the name hydnuferrugin is proposed. The composition of hydnuferrugin corresponds to the formula $C_{18}H_{10}O_9$, which can be formally derived from that of thelephoric acid ($C_{18}H_8O_8$)(V) by addition of one molecule of water. The connection with thelephoric acid is also supported by the botanical origin of hydnuferrugin, since thelephoric acid is a common constituent of Hydnellum species.[1,2]

Hydnuferrugin is optically inactive and gives a triacetyl and a tribenzoyl derivative. With methanol and a little hydrochloric acid it reacts to give, slowly even at room temperature, a monomethyl derivative, which on acetylation gives a diacetate.

There are thus three hydroxyl groups in hydnuferrugin, one being of a different nature from the other two. Reductive acetylation gives a pentaacetoxydihydro derivative, indicating that hydnuferrugin is a quinone, a fact which is also supported by an IR absorption at 1655 $cm^{-1}$.

The UV spectrum of hydnuferrugin is very similar to that of 8-hydroxy-2,7-dimethoxydibenzofuran-1,4-dione (Fig.1), and the spectrum of the leucoacetate is similar to that of dibenzofuran (Fig.2). In the NMR spectrum of the acetate and the leucoacetate the signals of two uncoupled aromatic protons are observed. All this information leads to the partial structure I for hydnuferrugin.

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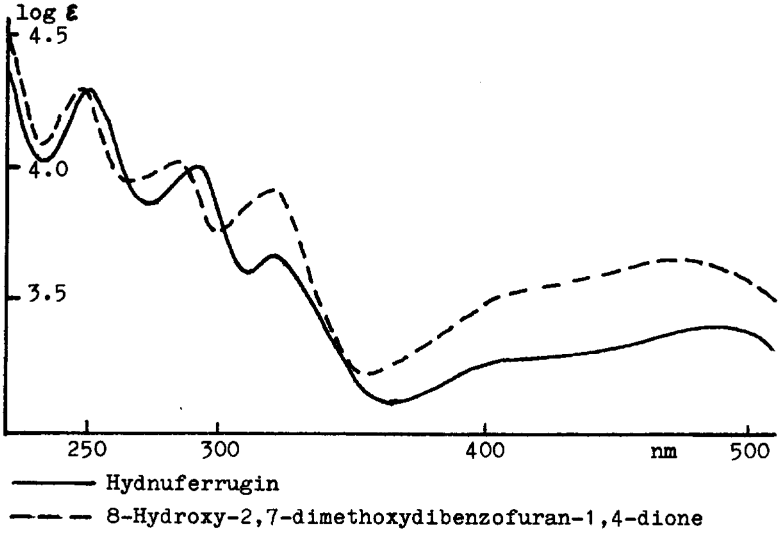


Fig.1

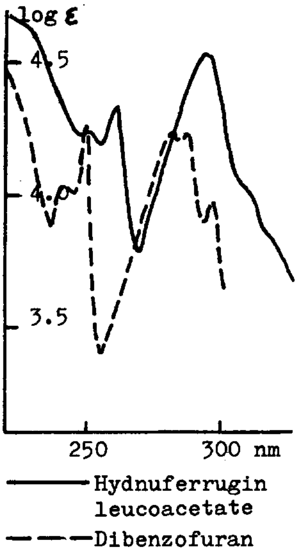
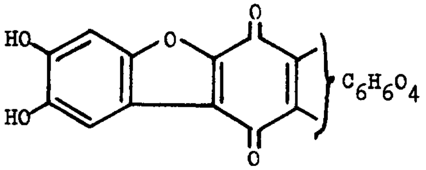
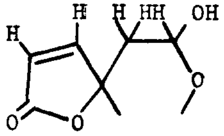


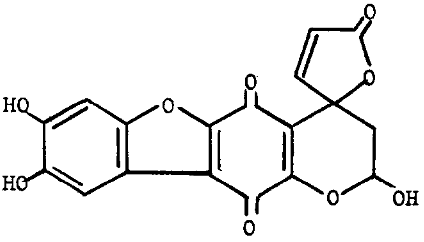
Fig.2



I



II

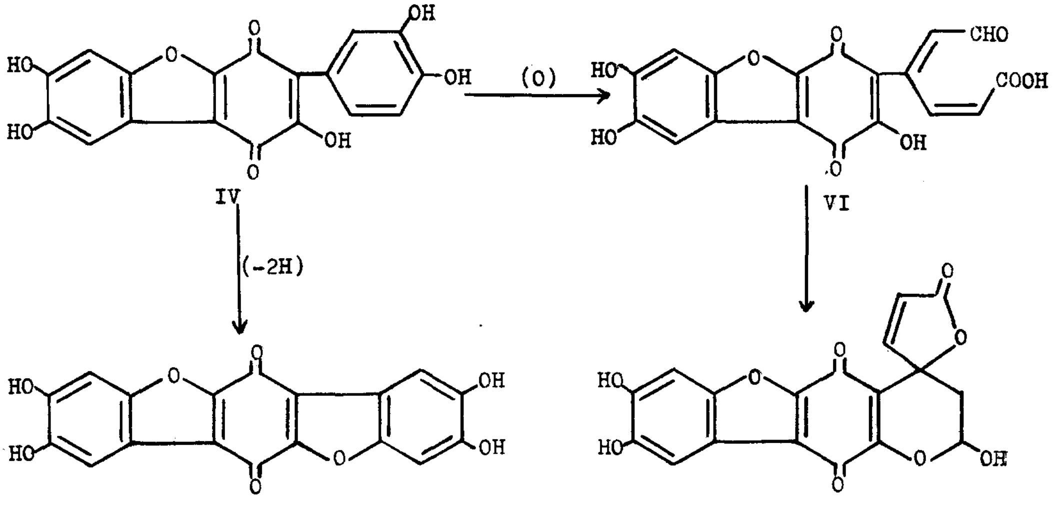


III

A strong complex absorption at 1740-1750 $cm^{-1}$ in the IR spectrum of hydnuferrugin indicates that the remaining part of the molecule contains a carbonyl group, most probably that of a lactone. That this is an $\alpha,\beta$-unsaturated $\gamma$-lactone, wholly substituted at the $\gamma$-position, is revealed by the NMR spectrum of the leucoacetate, which shows a two-proton AB-system ($\delta$ 6.21 and 7.76; J = 5.5 Hz). These values are in good agreement with those found for similar systems.[3-7] Furthermore, the NMR spectrum of the leucoacetate shows a three-proton AMX-system with $\delta_A$= 2.21 $\delta_M$ = 2.94; $\delta_X$ = 6.65; $J_{AM}$ = 14 Hz; $J_{AX}$ = $J_{MX}$= 3 Hz. The signal of the A-proton is partly hidden behind those of the acetate groups, but double resonance experiments have confirmed the values given for A. The chemical shift and the coupling constants of the X-proton agree well with values reported for the proton found in the 2-position of 2-acetoxydihydrobenzopyrans[8-12] and a 2-hydroxydihydrobenzopyran structure also explains the ease with which hydnuferrugin reacts with methanol and acid.

Insertion of the lactone group into the 2-hydroxydihydrobenzopyran system leads to the partial structure II for the $C_6H_6O_4$-group. The two moieties I and II can be combined in two ways, but the structure III is much to be preferred from a biogenetic point of view, and is therefore proposed for hydnuferrugin.

It is easy to visualize IV as a precursor from which thelephoric acid (V) is formed by dehydrogenation, and from which hydnuferrugin (III) is formed by oxidative rupture of the aromatic ring <u>via</u> VI.



V
Thelephoric acid

III
Hydnuferrugin

The hemiacetal hydrogen is evidently equatorial as is usual in 2-hydroxydihydrobenzopyrans,[10,13] but nothing is known about the stereochemistry of the γ-carbon of the lactone.

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