

## Fungus Pigments

IX.\* Some Further Constituents of *Hydnum aurantiacum* Batsch

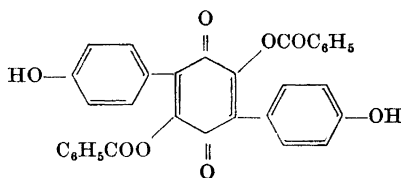
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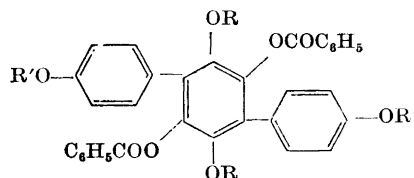
Two further constituents of the fungus *Hydnum aurantiacum* Batsch have been isolated and identified as 1,2,4,5-tetrakis(benzoyloxy)-3,6-bis(*p*-hydroxyphenyl)benzene (dihydroaurantiacin dibenzoate) (II) and thelephoric acid.

The isolation of aurantiacin (I), the pigment of the fungus *Hydnum aurantiacum* Batsch has been described in a previous paper<sup>1</sup>. Another crystalline component has now been isolated from the same extract. This compound is colourless, and was finally shown to have the composition  $C_{46}H_{30}O_{10}$ , although it was at first difficult to get consistent analytical results owing to its great tendency to retain solvent of crystallisation. It was most conveniently recrystallised from dioxan which could be completely removed only by prolonged heating at  $150^{\circ}/0.01$  mm.

When warmed with dilute alkali the compound dissolved and the solution eventually became dark brown. Acidification yielded a mixture of benzoic acid and atromentin. This together with the lack of colour indicated that the compound was a hydrogenated derivative of aurantiacin.



I



- II R =  $COC_6H_5$ ; R' = H  
 III R =  $COC_6H_5$ ; R' =  $COCH_3$   
 IV R = R' =  $COCH_3$   
 V R = R' = H

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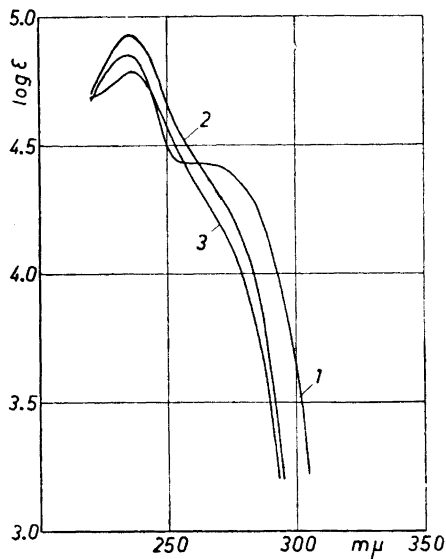


Fig. 1. Absorption spectra of: 1. 1,2,4,5-Tetrakis(benzoyloxy)-3,6-bis(*p*-hydroxyphenyl)benzene (II) (in dioxan), 2. 1,2,4,5-Tetrakis(benzoyloxy)-3,6-bis(*p*-acetoxyphenyl)benzene (III) (in dioxan) and 3. aurantiacin leuco-acetate (IV) (in alcohol).

The composition  $C_{46}H_{30}O_{10}$  corresponds to a dibenzoate of dihydro-aurantiacin. That the compound has free phenolic hydroxyl groups can be seen from the UV and IR spectra. The former (Fig. 1; curve. 1) has a strong inflexion at 270  $m\mu$  and the latter a strong peak at  $3420\text{ cm}^{-1}$ ; both disappear on acetylation. The UV spectrum of the diacetate thus obtained (Fig. 1; curve. 2) is very close to that of aurantiacin leuco-acetate<sup>1</sup> (IV) (Fig. 1; curve 3).

The compound  $C_{46}H_{30}O_{10}$  is very stable, but dihydroaurantiacin (V), prepared from aurantiacin by catalytic hydrogenation shows a great tendency to revert to aurantiacin by aerial oxidation. This indicates that the compound  $C_{46}H_{30}O_{10}$  has no hydroquinone grouping. It should therefore be II (assuming that the two benzoyl groups are symmetrically situated). This view was confirmed by synthesis of III from aurantiacin diacetate by hydrogenation followed by benzoylation. This was identical with the acetate of the compound  $C_{46}H_{30}O_{10}$  referred to above.

The presence of this leucobenzoate of aurantiacin together with aurantiacin recalls the simultaneous occurrence of leucomelone and its leucoacetate in *Polyporus leucomelas* Pers. ex Fries<sup>2</sup>. There are also a number of cases known where a quinone occurs in fungi together with the corresponding hydroquinone, sometimes forming a quinhydrone<sup>3-5</sup>. It is possible that the occurrence of the dihydroderivative either free or acylated, together with the corresponding quinone is more common than is usually appreciated because the dihydroderivatives which are usually colourless are easily overlooked.

Extraction of the ether-extracted fungus material with acetone gave a small amount of thelephoric acid. The occurrence of thelephoric acid is by no means surprising, since its presence in a number of *Hydnum* species has been reported before <sup>6,7</sup>.

### EXPERIMENTAL

(The analyses were carried out by Dr. A. Bernhardt, Mülheim, and the IR spectra were taken by Mr. B. C. Fogelberg, AB Centrallaboratorium, Helsingfors.)

*Isolation of 1,2,4,5-tetrakis (benzoyloxy) -3,6-bis (p-hydroxyphenyl) benzene (II).* The mother liquor from which aurantiacin had been filtered off <sup>1</sup> was evaporated under vacuum. The residue was extracted with benzene and then with a small amount of acetone. The grey insoluble powder was repeatedly recrystallised from dioxan giving 1,2,4,5-tetrakis(benzoyloxy)-3,6-(p-hydroxyphenyl)benzene as clusters of colourless needles, m. p. 305–307°. (Found: C 74.47; H 4.07; O 21.83.  $C_{46}H_{30}O_{10}$  requires C 74.38; H 4.07; O 21.55 %.) The benzene and acetone solutions were evaporated to dryness under vacuum and repeated treatment with benzene and acetone gave further amounts of the same compound.

Further amounts of the compound were obtained by purification of aurantiacin by chromatography <sup>1</sup>. It was obtained by evaporation of the fraction just preceding aurantiacin. It was slightly contaminated with aurantiacin which could be removed by crystallisation from dioxan.

*Hydrolysis of 1,2,4,5-tetrakis (benzoyloxy) -3,6-bis (p-hydroxyphenyl) benzene.* The compound (30 mg) on warming with 2 N sodium hydroxide (5 ml) for a few minutes dissolved completely. The dark brown solution was acidified and extracted with ether. The ether was evaporated and the residue extracted with a little benzene. Evaporation of the benzene solution gave benzoic acid (12 mg) identified by mixed m. p. The dark brown benzene-insoluble material was acetylated with acetic anhydride and pyridine giving yellow needles, m. p. 242–244°/290–295°, unchanged by admixture of atromentin tetra-acetate.

*1,2,4,5-Tetrakis (benzoyloxy) -3,6-bis (p-acetoxyphenyl) benzene (III) a.* From 1,2,4,5-tetrakis(benzoyloxy)-3,6-bis(p-hydroxyphenyl)benzene. The compound was suspended in acetic anhydride, a drop of pyridine was added and the mixture was warmed to give a clear solution. On cooling the acetate crystallised out and was recrystallised from dioxan giving glass-like crystals which turned opaque on standing in air, m. p. 317–321°. (Found C 72.66; H 4.29; O 22.89.  $C_{50}H_{34}O_{12}$  requires C 72.63; H 4.15; O 23.22 %.)

b) From aurantiacin. Aurantiacin diacetate <sup>1</sup> (220 mg) was suspended in alcohol and hydrogenated over  $PtO_2$  catalyst. The originally yellow crystals turned slowly colourless, without ever completely dissolving. The consumption of hydrogen was about 10 ml (theor. 8 ml). The crystals and the catalyst were filtered off and the crystals were dissolved in pyridine. Excess of benzoyl chloride was added and the mixture allowed to stand for three days. It was then poured into water giving a colourless precipitate. Ether was added to the suspension and the precipitate was then filtered off and recrystallised from dioxan. The crystals were identical in appearance with those obtained according to b), m. p. 320–324°, mixed m. p. undepressed. The IR spectra of the two preparations were identical

*Dihydroaurantiacin (V).* Aurantiacin (50 mg) was hydrogenated over a prerduced Adams catalyst in dioxan. The uptake of hydrogen was 2.1 ml (theor: 2.1 ml) and the solution turned colourless. It was evaporated under vacuum at room temperature to give slightly yellow crystals of dihydroaurantiacin, m. p. 310–312°. On attempted recrystallisation from dioxan they turned much darker in colour, apparently re-oxidising to aurantiacin. The substance was not analysed.

*Isolation of thelephoric acid.* The ether extracted fungus material was further extracted with acetone in a Soxhlet apparatus giving a violet-red solution in which a small amount of grey precipitate formed during the extraction. This was removed and the solution allowed to stand. A dark blue precipitate gradually formed, which was almost insoluble in all organic solvents except pyridine in which it dissolved with a wine-red colour. Dilution with water gave a blue solution, from which a blue precipitate slowly formed. This had no m. p. but gradually decomposed above 350°. Acetylation with acetic anhydride and pyridine gave an orange-red acetate, which was recrystallised from dimethyl

succinate m. p. 330–335° (decomp.). Reductive acetylation with zinc, acetic anhydride and pyridine gave a colourless leuco-acetate, after recrystallisation from nitrobenzene m. p. 370–380° (decomp.). All these properties agree well with those given for telephoric acid<sup>7-9</sup>.

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