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ON THE FORMATION OF INDIGOTINS

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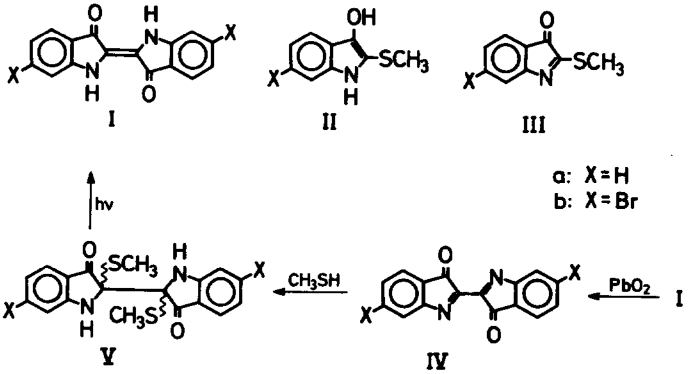
Although the structure of indigotin (Ia) and Tyrian purple (Ib) has been known for a long time, the exact details in the formation of the latter from a variety of molluscs are not yet elucidated.

Baker *et al.*[1-3] have suggested that the immediate precursor for Tyrian purple (Ib) is a "quinhydrone" (tyriverdin) consisting of tyrindoxyl (IIb) and dehydrotyrindoxyl (IIIb), *i.e.*, a charge transfer complex with the elemental composition $(C_{18}H_{14}Br_2N_2O_2S_2,\frac{1}{2}H_2O)$[1,2] or $(C_{36}H_{28}Br_4N_4O_4S_4,H_2O)$.[2] This was based on elemental analysis, mass spectrometry and ^1H magnetic resonance spectrometry.

The long-standing interest in quinhydrones of this laboratory[4] as well as our own interest in the formation of indigotins have led us to examine this problem using the formation of indigotin as model.

Indigotin (Ia) was oxidized with lead dioxide to give dehydroindigotin (IVa)[5], which upon treatment with methanethiol gave the rather unstable addition product Va.



The structure of the green compound Va was assigned on the basis of elemental analysis,[6] ^1H m.r. spectroscopy (270 MHz, $CDCl_3$; CH_3S: δ1.91, s, 6H; aromatic H: δ7.79, m, 2H; δ7.65, m, 2H; δ7.09, m, 2H;

besides signals corresponding to -NH and H_2O) cf. ref. 3 and mass spectrometry. Using the direct inlet system and 50 eV at 200°C, no M^+ peak could be observed with certainty, whereas strong peaks were found corresponding to the M^+ of IIa and IIIa. However, field ionization/field desorption mass spectrometry permitted the observation of the M^+ corresponding to Va.

Compounds V are indeed precursors of I both thermally and upon irradiation. Thus heating of Va led to the formation of indigotin and irradiation with 400 ±20 nm light transformed Va to Ia in an apparently quantitative reaction with high quantum efficiency (Fig.1), generating dimethyldisulphide in the process.

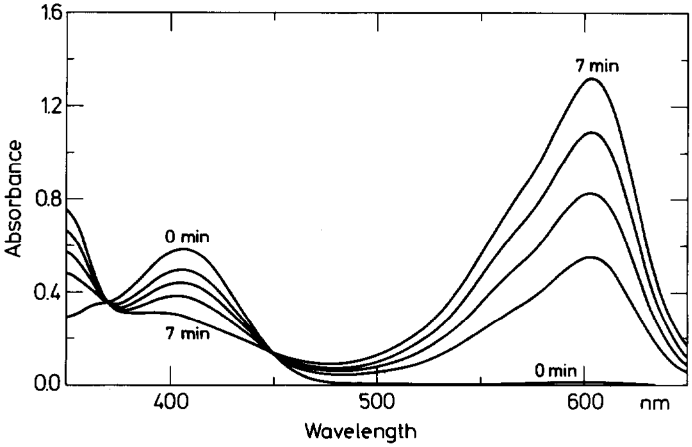


Fig. 1. Light-induced transformation of Va to indigotin. 400 ±20 nm light, conc. 2 mg Va in 50 ml $CHCl_3$.

On the basis of this we propose that the immediate precursor of Tyrian purple (Ib) has the structure Vb. This is being further investigated using synthetic material, as well as material isolated from molluscs.

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