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USTILAGO MELANIN, A NATURALLY OCCURRING CATECHOL MELANIN*

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Very few dark pigments, found in plant kingdom, have been investigated so far. We have now examined the brown amorphous product contained in the spores of Ustilago maydis DC. (corn smut, corn ergot), a well-known corn parasite.

Fungus spores (40 g), mechanically isolated from tumours of corn plants, were continuously extracted first with hot light petroleum (60-80°C) and then with hot ethanol. The material thus obtained, after drying at 60°C, was suspended in conc HCl (300 ml) and left at room temp for 14 days; it was then centrifuged, washed with water and successively with ethanol.

The pigment, further purified by continuous extraction with ethanol and tetrahydrofuran, was kept in boiling 6N HCl for 200 hr, centrifuged and washed with 1 % HCl, water and eventually aceton. A brown, amorphous powder (3.12 g), insoluble in any solvent, was obtained. For analysis the material was dried over phosphoric oxide in vacuo, at 80°C for 24 hr (Found: C, 61.81; H, 3.89). It contained traces of nitrogen, probably due to the presence of unremoved impurities, but was deemed sufficiently pure for subsequent work.

When heated in a stream of nitrogen, the pigment yielded catechol, identified by chromatography and electrophoresis. Moreover, catechol, protocatechuic acid and salicylic acid were obtained by alkali fusion of Usti-

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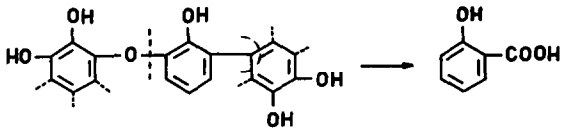
lago melanin.

Since these results suggested that the pigment under investigation could be related to catechol melanin, we subjected a biosynthetically prepared catechol melanin (1) to heating and to alkali fusion in the same experimental conditions used for Ustilago melanin; even in this case, the above said degradation products were obtained.

The identification of catechol in the ethanolic extract of fungus spores further strengthen the position of catechol as the precursor in the biogenesis of the naturally occurring pigment.

The formation of salicylic acid from Ustilago and catechol melanins by alkali fusion can be explained by assuming the presence in the polymers of ether linkages; the isolation of diphenylenedioxide-5,6-quinone among the enzymic oxidation products of catechol (2) proves that carbon-oxygen coupling occurs during melanogenesis.

Such linked units can originate salicylic acid by degradation, for example according to the following scheme:



Should this hypothesis be correct, even the in vivo polymerization proceedes, at least partially, by free radical intermediates.

Full details of this investigation will be published elsewhere.

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