formation; for example, choosing the shorter of two detours.

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SOIL SCIENCE

Nature and Distribution in Irish Soils of a New Soil Pigment

THE isolation of a green pigment (green humic acid) probably related to perylenequinone from widely distributed soils, chiefly podzols, has been described¹. A pigment of the hydroxyanthraquinone type has now been found in a large number of Irish soils. Although hydroxyanthraquinones occur widely in plant roots and fungi² we have been unable to find any previous account of their isolation from soil.

The pigment may be readily obtained from dried soil (a) by Soxhlet extraction with chloroform or (b), more specifically, by extraction into the upper (acetone) layer of a 1 : 1 mixture of acetone and 2 normal aqueous sodium hydroxide. Pigment was isolated from *B_h* horizon of the screen (Co. Wexford) podzol (which also contains green humic acid) by method (b); it was precipitated by acidification and purified by extraction into chloroform from which it crystallized spontaneously. A sample of 13 kg of soil gave 170 mg of crystalline (by X-ray diffraction pattern) pigment, melting point $>360^{\circ}\text{C}$. It was soluble in alkaline acetone, concentrated sulphuric acid (purple solutions) and chloroform (yellow solution) but was insoluble in water, aqueous sodium hydroxide, dilute sulphuric acid, acetone, ethanol and other common solvents.

The pigment appeared homogeneous when eluted from columns of magnesium carbonate, silica gel or 'Sephadex LH-20'. Its colour in aqueous alkali and concentrated sulphuric acid suggested that it was a quinone; its ultra-violet and visible absorption spectra (Fig. 1) suggested that it was a hydroxyanthraquinone³. Reduction with

Fig. 1. Spectra in chloroform of soil pigment (—) and of 1,8-dihydroxyanthraquinone (---), the latter being almost identical with that of 1,8-dihydroxy-3-methylanthraquinone.

Fig. 2. Location of soils containing pigment. Approximately one in eight or twenty-four in all of the soils from the south-south-east showed pigment compared with one in more than 450 from the rest of the country. ■, Indicates screen.

zinc dust gave material with an ultra-violet spectrum similar to that shown by anthracene. Prolonged treatment in a sealed tube with hot aqueous alkaline dithionite gave, in addition to unchanged starting material, a small amount of pigment with an ultra-violet and visible spectrum identical with that of 1,8-dihydroxy-3-methylanthraquinone. The relationship of the soil pigment to 1,8-dihydroxyanthraquinone was further indicated by the similarity of the infra-red spectra in liquid paraffin of the two pigments especially in the characteristic 1,600–1,700 cm^{-1} region⁴, both having absorption bands at 1,672 and 1,624 cm^{-1} . The unknown pigment is not 1,8-dihydroxy-3-methylanthraquinone nor does it seem to be any polyhydroxyanthraquinone reported in the literature⁵.

Many soil samples (678) from all parts of the Republic of Ireland have been examined for pigment. These were available from a previous survey⁶ and had been randomly selected with two sites/10 km^2 of the national grid. The top 4 in. of soils under permanent pasture only were taken, bog, forest and mountain areas being excluded. Soils giving a positive test were taken from the locations shown in Fig. 2. With one exception they were all in the south and south-east of the country (Fig. 2). In view of the known root growth stimulating properties of some hydroxyanthraquinones⁶ it may be significant that the principal tillage areas are in this region.

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