Bernard T. Golding and
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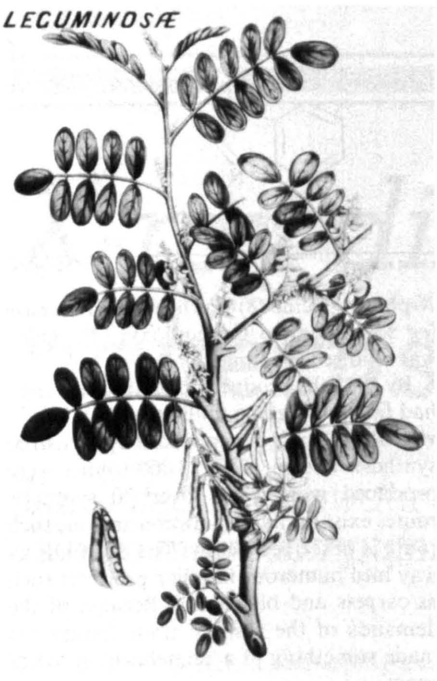
Indigo blue

'Reddit enim, quod sincerum est, flammam excellentis purpurae: et dum fumat, oderum maris'

Pliny

Indigo (*1a*, indigotin, $\Delta^{2,2'}$-biindoline-3,3'-dione) is one of the oldest colouring agents known, having been found in the wrappings of Egyptian mummies. Its natural sources are 'dyer's woad' (*Isatis tinctoria*), a plant indigenous to Europe, and the indigo-plant (*Indigofera sumatrana* and *arrecta*), native to India and Java. Immediately after harvesting, the leaves and stalks of the plant are steeped in water. Fermentation sets in and indican (*2*) is hydrolysed to glucose and indoxyl (*3*). The resulting aqueous solution is decanted and aerated to oxidise indoxyl to indigo.



INDIGOFERA TINCTORIA

In old recipes bamboo sticks were used to beat the aqueous extract and thus speed up the oxidation. The indigo is collected from the bottom of the vat and is filtered, pressed into cube-shaped lumps and dried. Such indigo contains impurities, (*eg* the red structural isomer indirubin, (*4*)). Pure indigo, sometimes called indigotin, is obtained as blue crystals with a metallic shimmer by recrystallisation (*eg* from ethanoic acid) or, as first described by O'Brien in 1789, by sublimation. Pliny's description of the purple flame of indigo as a test of purity is not quite accurate. Indigo does not burn readily; its vapour is violet.

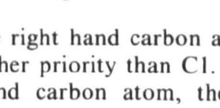
Structure of indigo

The structure of indigo was elucidated in the classical manner. Combustion analyses gave an empirical formula of C_8H_5NO, from which a molecular formula of $C_{16}H_{10}N_2O_2$ was derived by cryoscopic measurements. Alkaline fusion of indigo gave anthranilic acid (2-aminobenzenecarboxylic acid). Oxidation with chromic acid gave two molecules of isatin (*5*) per molecule of indigo. Indole was obtained by the reduction of indigo.

In 1880, with the evidence given in hand, but before the correct structure of indigo had been proposed, von Baeyer synthesised indigo from 2-nitrocinnamic acid. Then, in 1883 in a letter to H. Caro he proposed the structure reproduced in *Fig. 1*, which is taken to be the first correct proposal, although the configuration at the double-bond was not specified. The configuration was settled as (*E*) by a crystal structure analysis which indicated bifurcated hydrogen bonds *ie* each NH group appears to be both intra- and inter-molecularly H-bonded to carbonyl groups. All derivatives of indigo examined by crystal structure analy-

The *E/Z* system

The *E/Z* system of nomenclature for alkenes is an alternative to the traditional *cis/trans* designation. The substituents at each end of the double-bond are ranked according to their atomic number. If the substituents of higher atomic numbers are on the same side of the double-bond (*Z*usammen = German for together) then the configuration is assigned as *Z*. When the substituents of higher atomic numbers are on the opposite sides of the double-bond (*E*ntgegen = German for across) the designation is *E*. For example:



For the right hand carbon atom, Br has higher priority than Cl. For the left hand carbon atom, the atoms connected to the double bond are both carbon, so their substituents must be compared. The methyl group has three substituents of atomic number 1, whereas the hydroxymethyl group has two substituents of atomic number 1 and one of atomic number 8. Thus, the hydroxymethyl takes priority over the methyl. The two substituents of higher rank are on the same side of the double-bond and so the configuration of the above alkene is assigned as *Z*.

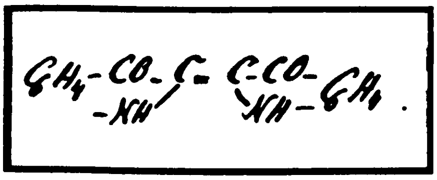


Fig. 1. von Baeyer's structure of indigo (Reproduced with kind permission from Ciba Geigy's *The story of the chemical industry in Basle,* 1959.)

sis also show the (*E*)-configuration. The (*Z*)-form of indigo is probably destabilised by repulsion of carbonyl dipoles and has never been isolated.

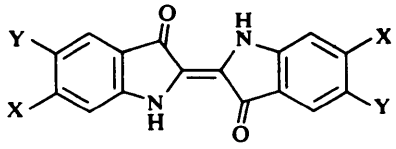
The reason for the unusual deep colour of indigo has been discussed by theoreticians in terms of the contribution of several resonance structures (*Scheme 1*) to the chromophore. Replacing the NH groups of indigo by other heteroatoms causes sharp colour changes *eg* the thia analogue of indigo is red.

Tyrian purple

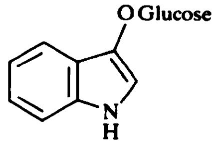
Another dye with the indigoid skeleton is Tyrian purple (*1b*, 6,6′-dibromo-$\Delta^{2,2'}$-biindoline-3,3′-dione), once the most sought after of all dyes although it is no longer in demand. Tyrian purple acquired popularity as early as 1600 BC, because of its properties of brilliance and non-fading. Later, the Roman Emperor Augustus Caesar decreed that only he and his household might wear the 'Purple'.

The source of the dye is the purpura shellfish, or *Murex brandaris*, found in shallow waters of the Mediterranean. Each mollusc contains a few drops of a colourless glandular mucous which on exposure to light changes gradually from yellow-green to reddish-purple. In ancient recipes the shellfish were crushed and salted, left for three days and then boiled for 10 days to extract the dye. Over 12000 molluscs were required to obtain 1.5 g of dye, and this was the main reason for the decline of usage of Tyrian purple.

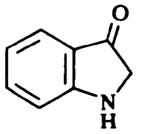
Studies of the biosynthesis of Tyrian purple have shown that it arises from an indolic precursor (*6*). This undergoes enzymic hydrolysis of the sulphate to an indole derivative, which is oxidatively dimerised to compound (*7*). Model studies have shown that (*7*) is readily converted into Tyrian purple and dimethyl disulphide either by heating or by photolysis.



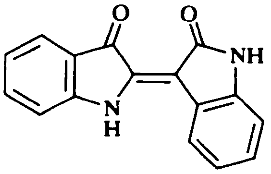
(*1a*) X = Y = H
(*1b*) X = Br Y = H
(*1c*) X = H Y = SO_3^-



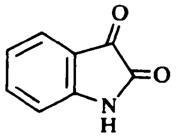
(*2*)



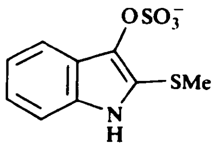
(*3*)



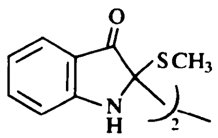
(*4*)



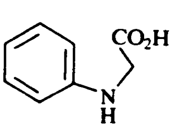
(*5*)



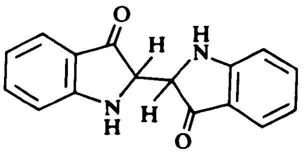
(*6*)



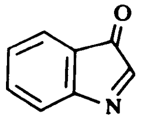
(*7*)



(*8*)



(*9*)



(*10*)

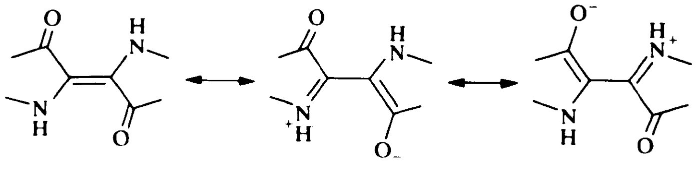
Synthetic indigo

In 1897 the West Indies exported 19 million pounds of indigo produced in the manner described. However, the German chemical industry was vigorously pursuing the development of a commercially viable synthesis of indigo, and in 1897 the first synthetic indigo was marketed. In the 'Heumann I synthesis' discovered by Karl Heumann working at BASF Ludwigshafen, *N*-phenylglycine (*8*) was heated with a base (*eg* sodamide) to give indoxyl (*3*), which was oxidised to indigo.

By 1913 the production of natural indigo had fallen to *ca* one million pounds. Now, virtually all indigo is produced by industrial synthesis and in 1978, 13000 tonnes were produced worldwide. Over 30 synthetic routes exist for its preparation and one such route is described below. The dye finds its way into numerous familiar products such as carpets and blue jeans. Because of the demands of the fashion trade indigo has made something of a 'comeback' in recent years.

Scheme 1. Resonance structures contributing to the chromophore of indigo.

Scheme 1



Dyeing with indigo

Wool

For dyeing wool, the insoluble indigo is sulphonated using concentrated sulphuric acid and is converted into the water-soluble disulphonic acid, indigocarmine (*1c*). A small amount of indigo is added to concentrated H_2SO_4 (1-2 cm^3) and the mixture is warmed gently. The resulting solution is cooled and cautiously poured into water to give a deep blue solution. A small skein of wool or piece of woollen cloth is moistened, immersed in the blue solution for a short time, removed and rinsed with water. The colour is both detergent- and light-fast.

Cotton

For dyeing cotton an indigo-vat is prepared. In this process the insoluble indigo is reduced to colourless indigo white (*9*), a water-soluble leuco-compound. The reduction is usually effected by iron (II) sulphate or by dithionite – the resulting solution is called an indigo-vat. When a piece of cotton is immersed in the solution, indigo white is absorbed. On removal from the liquid the leuco-compound is converted into blue indigo by aerial oxidation and remains firmly attached to the fibre.

Experimental

A. Preparation of sodium 1-(2-nitrophenyl)-2-nitro ethanolate

Prepare a solution of sodium methoxide in methanol by dissolving either sodium (0.90 g, 39.2 mmol) or sodium methoxide (2.12 g, 39.2 mmol) in dry methanol (15 cm^3). Add this solution dropwise to a magnetically stirred solution, cooled to 0–5 °C, of 2-nitrobenzenecarboxaldehyde (5.0 g, 33.1 mmol) and nitromethane (2.3 g, 37.7 mmol) in methanol (25 cm^3). Towards the end of addition the crystallisation of yellow sodium 1-(2-nitrophenyl)-2-nitroethanolate begins. Leave the stoppered reaction flask in a refrigerator overnight.

B. Preparation of Indigo*

After the crystallisation in Part A is complete,† methanol is removed under reduced pressure (*eg* at 45 °C using a rotary evaporator). The residue is taken up in water (100 cm^3) and treated with 2 M aqueous sodium hydroxide (30 cm^3) to give a yellow-orange solution, which is cooled to *ca* 6 °C in an ice-bath. With good stirring add sodium dithionite (16.8 g, 96.5 mmol) in small portions so that the temperature of the solution does not rise above 15 °C (the addition should take less than 10 minutes). The solution rapidly becomes dark-coloured and indigo separates as a blue-black solid. After adding the dithionite bubble a stream of air through the mixture for *ca* 20 min. Filter the indigo off and wash it with water until alkali-free (test with pH paper) and then with ethanol and ethoxyethane. Then dry the indigo at 120°C for 3 hours to obtain a dark blue, crystalline powder.

λ_{max} (in $(CH_3)_2$ SO) 619 (4.2) and 287 (4.4) nm

NB The mp of indigo is too high (390-393 °C, dec) to determine with a conventional apparatus.

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*The mechanism of the process described is a challenging problem. It is believed that 3*H*-indol-3-one (*10*) is the likely but elusive intermediate in this and related syntheses of indigo.

†If desired, the crystals can be filtered off, washed with methanol followed by ethoxyethane, and dried. The dry salt can be stored unchanged for several months at -20 °C.

M.F.M. Coleman

X-ray diffraction powder patterns on the Apple II

Simulated xrd powder patterns are interpreted using a microcomputer

At Wellington Polytechnic several programs have been developed for the teaching of structural chemistry to New Zealand Certificate students. Such programs include concepts of space lattices, close packing of spheres, and unit cells of metallic and ionic crystals.[1] The two most recently developed programs are concerned with the interpretation of x-ray powder diffraction patterns, obtained with automatic powder diffractometers, using file cards such as those supplied by the American Society for the Testing of Materials (ASTM). These two programs fulfil several needs –

1. As the Polytechnic has no x-ray equipment, the student can obtain a copy of a realistic diffraction pattern.

2. Use of Bragg's law for calculation of interplanar spacings with insistence that the calculations are correct which also implies that the diffraction angles are correctly measured.

3. The searching of file cards to identify the crystalline substances.

4. Hands-on experience of microcomputers tackling 'real' problems.

The programs are written in Applesoft Basic and are suitable for use with Apple II instruments having 64 K RAM. The simulated powder patterns are programmed into the high resolution graphics pages of the memory which have four lines of text at the bottom for titles and instructions. A wide chart, dot-matrix printer (*eg* Logitec FT 5000) gives a print-out of the pattern with sufficient resolution to enable accurate