

Fascinating Organic Molecules from Nature

2. The Blue of Blue Jeans and Royal Purple

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Indigo and Tyrian purple are two dyes which have captured the imagination of the common man as well as the gentry from the very beginning of human civilization. Their story is like a multi-coloured yarn, with strands from chemistry, history, culture and politics. Their popularity is reflected by the fact that their stories are very well documented not only in scientific journals but also in books and even on the celluloid! Recent studies show that indigo may be utilized even as a semi-conducting material.

Introduction

The colour blue is evocative of sentiments opposite to those associated with the colour red. To students of organic chemistry, blue is synonymous with indigo. One of the much valued and oldest of vegetable dyes, indigo has a long recorded history, going back to the 7th century BC. In the 4th English edition (1949) of the Nobel Laureate Paul Karrer's *Organic Chemistry*, one entire chapter is devoted to the chemistry of indigo and related compounds. Newer and exciting developments in the subject gradually pushed it out of the undergraduate curriculum and it finds no place in the 4th edition (1983) of Morrison and Boyd's *Organic Chemistry*! However, it continues to occupy a prime place in books on organic pigments and dyes and retains its popularity as a blue dye. A feature-length documentary (2011) filmed in India, Bangla Desh, Nigeria, Mexico, El Salvador and the USA, directed by Mary Lance captures on celluloid the myriad nuances of the cultural, political and chemical history of this fascinating dye.

Keywords

Indigo, indican, isatin, indoxyl, thioindigo and Tyrian purple.

The chemistry of indigo was elucidated by Adolf von Baeyer and his co-workers who also effected its first practical synthesis. For



this monumental work, Baeyer was awarded the Nobel Prize in Chemistry in 1905. In the citation, preceding the presentation of the Prize, special mention was made of the fact that following the availability of synthetic indigo, vast tracts of land used for cultivating the indigo plant could be returned for growing food crops. Tyrian purple, also known as Purple of the Ancients, is a dibromo derivative of indigo.

In this article, after a brief account of the history of the compound, the chemistry of indigo and its derivatives is described in considerable detail. In an earlier issue of this journal¹, G Nagendrappa has described the role indigo played in India's struggle for independence in the article 'Chemistry triggered the first civil disobedience movement in India'. This article was reproduced in the special issue of *Resonance* published in 2011, the International Year of Chemistry.

Indigo

Indigo has a very intimate relationship with our country – its very name is derived from India. The indigo plant, *Indigofera tinctoria* belonging to the family *Leguminosae*, is mentioned under the name Nila in Sanskrit manuscripts dating back to the 4th century BC. However, in this article the Indian connection is not elaborated any further as it has been adequately covered in the article mentioned above. From India, indigo travelled to Europe mainly through the agency of Arabian traders and later in much larger quantities by Portuguese, Dutch and particularly English merchant men. However, a blue dye similar to indigo was, perhaps, known to the Pharaohs as well as the Thebans of ancient Egypt. There is speculation that the dye came from India. An inferior variety of indigo was used in Northern Italy, Southern France and parts of England and Germany till imports from India flooded the markets with the superior form. The source of the European indigo was dyer's woad, *Isatis tinctoria*, which belongs to the mustard family. In Japan, indigo derived from *Polygonum tinctorium* (dyer's knotgrass) was the colouring employed in the Sukumo and Aizome traditions of dyeing. There are also historical records

Blue is a popular colour as it is cool and calming.

¹ *Resonance*, Vol.8, No.3, pp.42–48, 2003)

During the 16th century, Germany banned the import of indigo to protect the dye locally produced from woad.



According to The Book of Knowledge, William Wordsworth (1770-1850) 'led poetry back to nature and back to simplicity'. His long poem, 'The Prelude' is autobiographic in nature. Wordsworth's love for nature is beautifully brought out in 'Daffodils'.

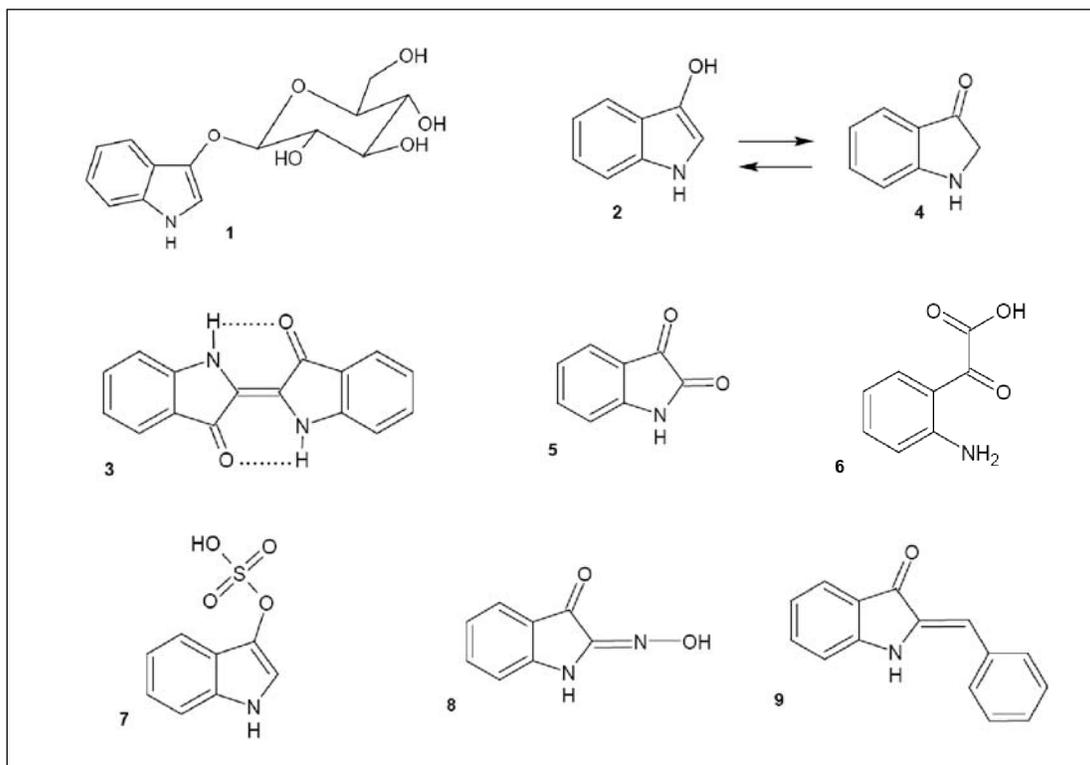
of indigo dyeing extensively practiced in China and Indonesia. In the Sahara region of North Africa as well as parts of West Africa such as Nigeria, for example, indigo has been a much sought after blue dye from ancient times. The Taureg nomads of Sahara use indigo for colouring their robes, turbans, veils as well as their skin. No wonder they are called the blue men! In Latin America, under the Spanish colonial rule, *Indigofera suffruticosa* was widely cultivated in Gautemala and other parts of Central America. The Dutch cultivated the plant in Suriname. Under the British colonial rule, indigo plantations were established in Jamaica and South Carolina. As in India, the labour forces in these plantations were subjected to much oppression and hardship by the plantation owners. In the Spanish plantations and South Carolina, slaves were employed to cultivate the fields and produce the dye which involved a tedious procedure. The waste material left after extracting indigo often proved a serious health hazard. The plight of the workers engaged in the English indigo dyeing industry moved the poet William Wordsworth to write the following lines in his poem 'The Prelude':

*Doubtless, I should have then made common cause
With some who perished, haply perished too,
A poor mistaken and bewildered offering
Unknown to those bare souls of Miller blue.*

Structure of Indigo

The leaves of indigo plant, which bears red flowers, contain a glucoside, indican (1). On acidic or enzymatic hydrolysis this water-soluble compound gives a molecule each of β -D-glucose and indoxyl (2). The latter undergoes ready aerial oxidation to yield the water insoluble indigotin (indigo) (3). In the traditional process of preparing the blue dye from an aqueous extract of the leaves, therefore, the chemical reactions involved are glycosidic hydrolysis followed by oxidation. Indoxyl can also exist in the keto form (4). The systematic name of indigo is 2,2'-bis(2,3-dihydro-3-oxoindolylidene). On oxidative degradation brought about by the use of chromic acid or nitric acid, indigotin breaks





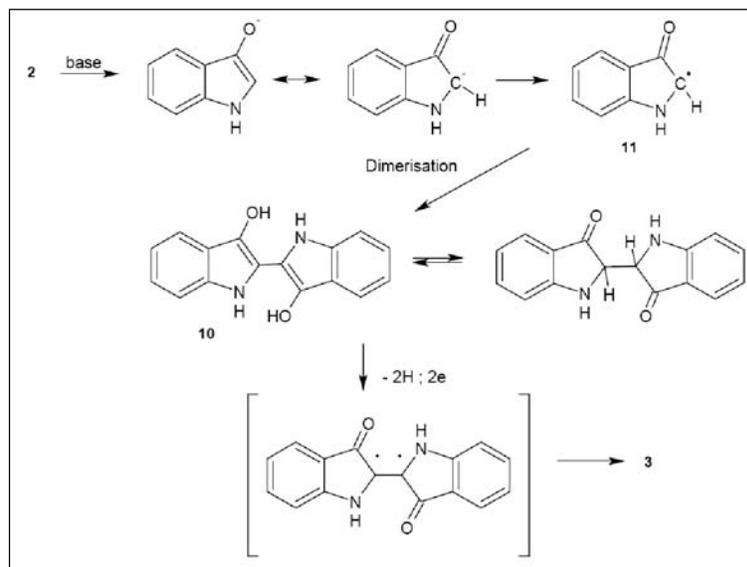
down to isatin (**5**). The structure of isatin was confirmed by its preparation from *o*-aminophenylglyoxylic acid (**6**) by dehydrative cyclisation.

Indoxyl is yellow in colour and exhibits a yellow-green fluorescence. Its resemblance to phenol is shown by its ready solubility in aqueous alkali and the formation of a red colour with alcoholic ferric chloride. As mentioned earlier, indoxyl exhibits tautomerism and can react either as the enol form (**2**) or as the keto form (**4**). Derivatives of (**2**) include indican (**1**) and indoxylsulphuric acid (**7**), whereas (**4**) is responsible for the formation of the isonitroso derivative (**8**) and the benzal derivative (**9**).

Indoxyl undergoes ready aerial oxidation, especially in alkaline solutions. The mechanism of this reaction has been studied using kinetic, stoichiometric and spectrometric (including esr) methods and it is believed that the oxidation proceeds through the

Indoxyl forms yellow coloured crystals which melt at 85°. It is susceptible to easy resinification.

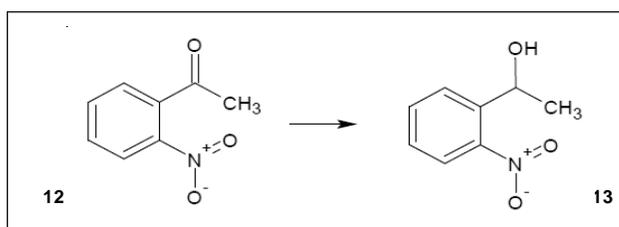
Scheme 1.

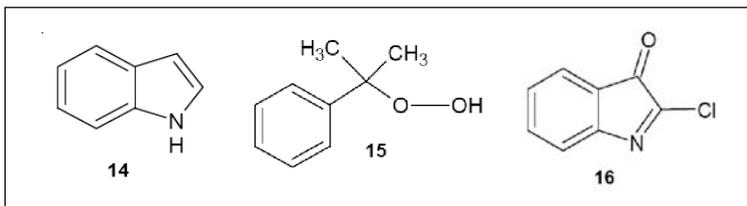


formation of leucoindigo or indigo white (**10**) as an intermediate. Prior to the formation of (**10**), the indoxyl anion loses an electron to give the radical (**11**) which dimerises to yield (**10**). The further oxidation of (**10**) to (**3**) also proceeds through a radical mechanism as shown in *Scheme 1*.

Synthesis of Indigo

After elucidating the structure of indigo, Baeyer turned his attention to the synthesis of the compound. However, the first synthesis of the blue dye was effected by Engler and Emmerling who prepared the compound by the distillation of *o*-nitroacetophenone (**12**) with zinc dust and soda-lime. The yield of the final product was, however, extremely low. The first step in this synthesis is the formation of hydroxylamine derivative (**13**) which presumably undergoes dehydration to give indoxyl. Later, Nencki observed

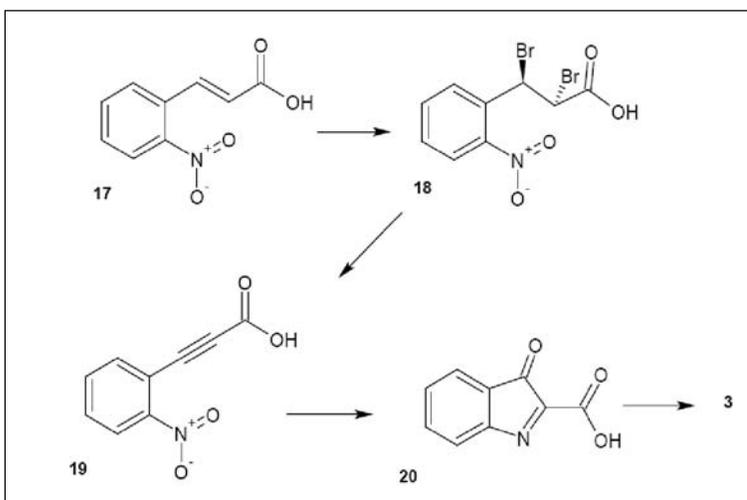




that on oxidation, indole (**14**) gives indigo along with other products but this did not prove to be a practical procedure for the synthesis of pure indigo. However, in 1994, a Japanese group developed a viable one-pot method² in which indole was oxidised with cumyl peroxide (**15**) in the presence of a molybdenum complex; the yield of indigo was 81%.

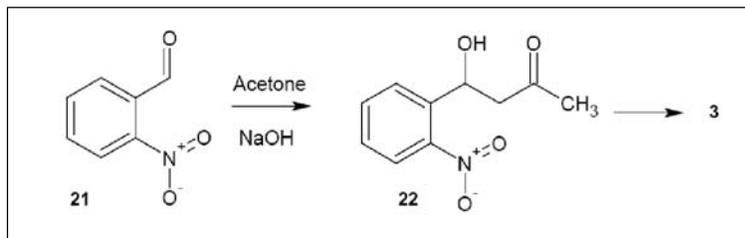
In his first synthesis of indigo, Baeyer used isatin (**5**) as the starting material. On reaction with phosphorus pentachloride it yielded isatin chloride (**16**) which on reduction gave indoxyl. Later, Baeyer developed a better method in which *o*-nitrocinnamic acid (**17**) was first converted into its dibromo derivative (**18**) which lost two molecules of HBr, on treatment with potassium hydroxide to yield *o*-nitrophenylpropionic acid (**19**). This compound, when boiled with alkali and reducing agents gave indigo, presumably via the intermediate, isatogenic acid (**20**) as shown in *Scheme 2*.

² One-pot synthesis is a procedure in which successive reactions are carried out in the same reactor vessel. As a consequence time-consuming work-up steps are eliminated thereby improving the overall yield of the final product.



Scheme 2.

Scheme 3.



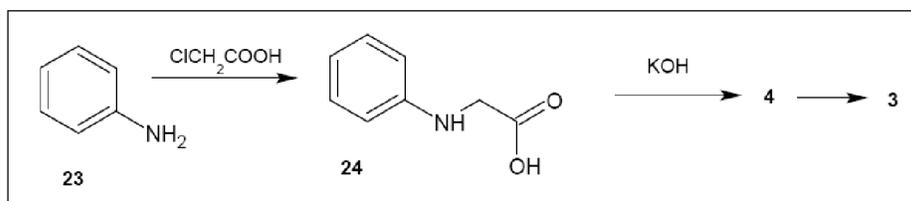
³ The Claisen–Schmidt reaction is a cross aldol condensation involving a ketone and an aldehyde. A typical example is the base-catalysed reaction between two molecules of benzaldehyde and one molecule of acetone resulting in the formation of dibenzylideneacetone.

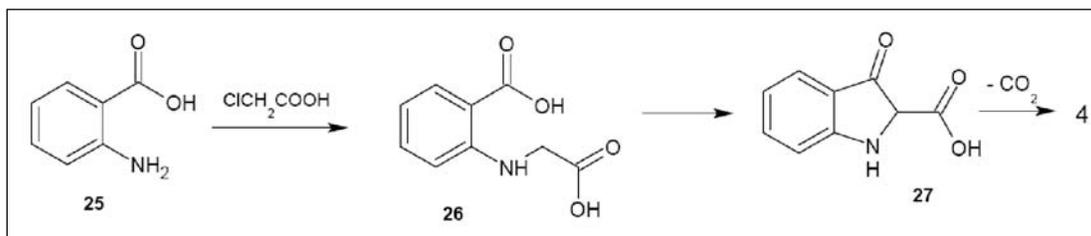
Subsequently, Baeyer and Drewsen devised a better method in which o-nitrobenzaldehyde (**21**) was condensed with acetone in the presence of alkali (Claisen–Schmidt reaction³) and the resulting product (**22**) heated with alkali to obtain indigo in good yield (*Scheme 3*).

However, for large scale preparation of indigo, the above methods were not suitable as the cost of production was too high. Heumann developed two methods in the first of which aniline (**23**) served as the starting material. It was converted into indoxyl via phenylglycine (**24**) (*Scheme 4*). The overall yield of indigo was still low as the alkaline fusion step required a high temperature which brought about partial decomposition of indoxyl. Further, the water formed in the reaction hydrolysed a part of the phenylglycine. The temperature of this key step could be brought down by using sodamide in place of alkali; at the same time, sodamide reacted with the water formed liberating ammonia and sodium hydroxide.

In his second synthesis, Heumann used anthranilic acid (**25**) as the starting material. Condensation of (**25**) with chloroacetic acid gave phenylglycine-o-carboxylic acid (**26**), which on fusion with alkali yielded indoxylic acid (**27**) in very good yield. Decarboxylation of (**27**) gave indoxyl (*Scheme 5*). Anthranilic acid itself was obtained from the coal-tar product, naphthalene. This process

Scheme 4.





was later improved at the laboratories of the Bavarian chemical company, BASF (Badische Anilin und Sodafabrik), as a result of an accidental discovery involving a broken thermometer (used as a stirrer!)¹.

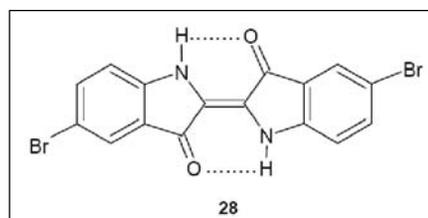
Scheme 5.

Tyrian Purple

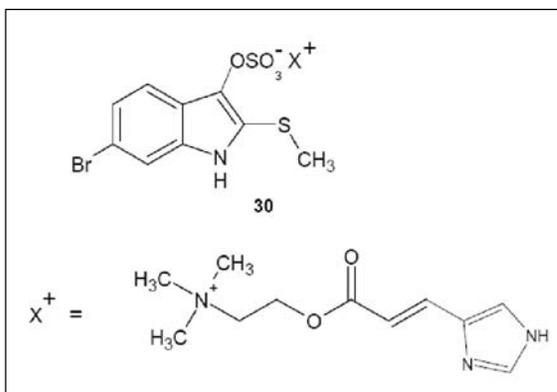
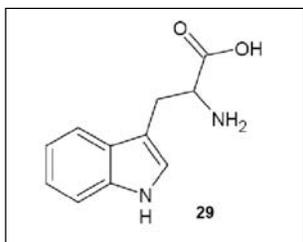
This pigment, variously known as Tyrian purple, Royal purple, Imperial purple, shellfish purple and purple of the ancients, is one of the oldest known organic compounds. It is obtained from the secretions of some species of marine mollusks found off the shores of the Atlantic ocean and the Mediterranean Sea. Earliest records of this precious dye go back to the 13th century BC. It was produced in the city of Tyre, located in the present-day state of Lebanon, by the Phoenicians, though there are evidences that the dye was also known to the Minoans who inhabited the Greek island of Crete in the 17th century BC. The German chemist, Paul Friedlander (1857–1923) reported in 1909 the isolation of the pure pigment from *Murex brandaris*⁴; from 12,000 snails he could get 1.4 g of the pure compound! Friedlander also established the structure of tyrian purple as 6,6'-dibromoindigo (28) by elemental analysis and direct comparison with a synthetic sample which was already available.

⁴ *Murex brandaris*, commonly known as the spiny dye-murex, is a predatory marine gastropod. In their natural environment, the snails use this mucus secretion from the hypobranchial gland situated near the head for their predatory operations as well as a defensive chemical.

After the Phoenicians had perfected the process of extracting the dye, it became an article of luxury. From the eastern Mediterranean it was transported to Europe by the silk route. The nobility in the Roman Empire used the dye to colour their ceremonial robes as the dye was found to be fast and non-fading. The colour of the dye on the fabric depended on the quantity used; smaller



X-ray crystallography shows that in the solid state each molecule of Tyrian purple is linked to four others through hydrogen bonding. Van der Waals interactions between the bromine atoms are responsible for a tighter packing of the parallel rings as compared to indigo. As a consequence, the solid pigment looks purple in colour.



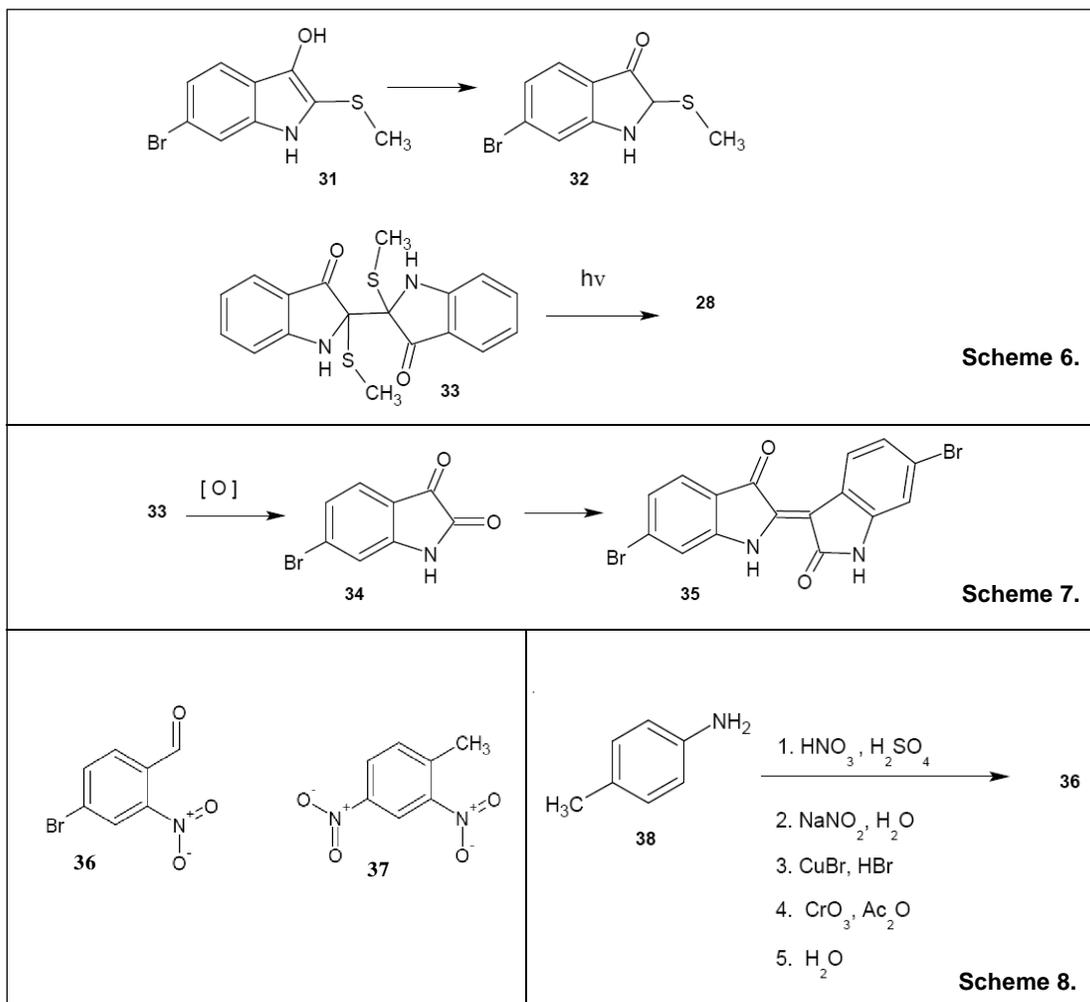
amounts gave a blue colour whereas on increasing the concentration the colour changed to a deep purple. Indeed, in solution, the colour of Tyrian purple is blue but as mentioned above, as a dye, in the solid state, it is purple. Spectral data lend support to this observation. The visible spectrum of the pigment in tetrachloroethane has an absorption maximum at 590 nm, whereas wool-dyed reflectance spectrum shows the maximum at 520 nm.

Synthesis of Tyrian Purple

The biosynthesis of Tyrian purple has been investigated in depth. Two sites in the hypobranchial glands of the mollusk, *Dicathais orbita*, have been identified as the active sites where prochromogens of the Tyrian purple are synthesised from tryptophan (29) through the agency of the enzyme bromoperoxidase. The primary product is tyrindoxyl sulphate (30) which on enzymatic hydrolysis by aryl sulphatase (purpurase) gives tyrindoxyl (31). The latter then undergoes oxidation to yield the red-coloured tyrindoleninone (32). Coupling of (31) with (32) gives the green-coloured tyriverdin (33) which on photolysis loses two molecules of dimethyl sulphide to give Tyrian purple (Scheme 6).

In another bisynthetic pathway, tyriverdin undergoes oxidation to yield 6-bromoisatin (34) and then 6,6'-dibromoindirubin (35) (Scheme 7). Thus, the native Tyrian purple pigment is primarily a mixture of (28) and (35).

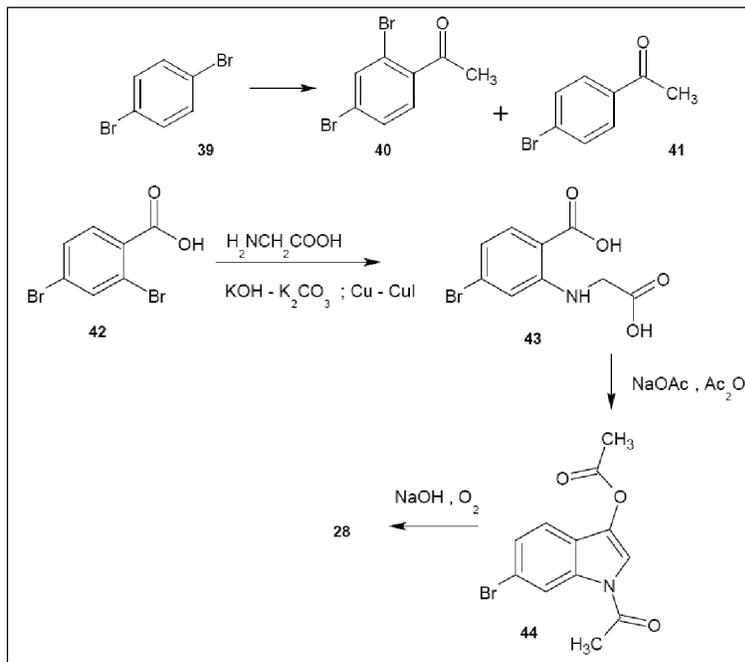
Unlike indigo, Tyrian purple is no longer used as a dye on a large scale. Therefore, its synthesis is more of academic interest. Several methods have been developed for this purpose. Sachs and Kempf were the first to synthesise it from 4-bromo-2-nitrobenzaldehyde (36) following the method used by Baeyer and Drewsen for the synthesis of indigo. They prepared (36) from 2,4-dinitrotoluene (37) using a lengthy procedure. Subsequently, several groups of



workers developed shorter routes to (36). These methods have been critically evaluated in a recent review by Wolk and Frimer [4]. In one of these, p-toluidine (38) is used as the starting material (*Scheme 8*)

Wolk and Frimer have developed a short laboratory method starting with 1,4-dibromobenzene (39) (*Scheme 9*). After a Friedel–Crafts acetylation, the product mixture (40 and 41) is oxidised to obtain 2,4-dibromobenzoic acid (42) as the main product. This is then subjected to a Ullmann reaction when (43) is obtained. The latter is converted to Tyrian purple via the intermediate (44).

Scheme 9.

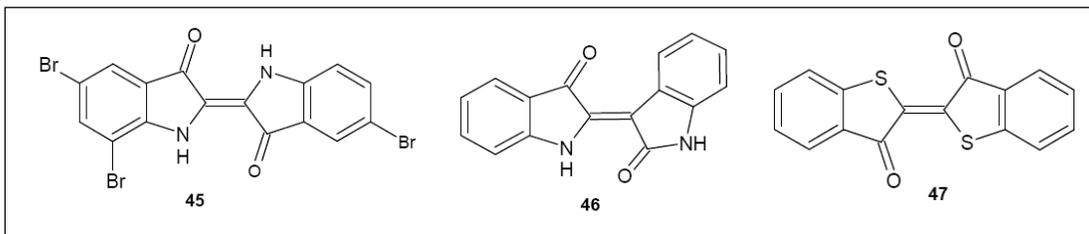


Indigo Derivatives

Bromination of indigo in nitrobenzene solution brings about substitution at the 5,5', the 7,7' and finally the 4,4' positions. Interestingly, the 6,6' dibromo derivative (Tyrian purple) cannot be prepared by direct bromination of indigo. Ciba blue B is 5,7,5'-tribromoindigo (**45**). Indigo red (**46**) is an isomer of indigo and is a minor component of the natural material. Thioindigo (**47**) is a pure red vat dye (*Box 1*). Its fastness to light and oxidation is greater than that of indigo.

Box 1. A Brief Note on Vat Dyeing

Indigo's lasting popularity as a dye is due to a combination of factors such as the excellent quality of the colour it produces on a variety of fabrics, fastness to light, and resistance to washing and chemicals. However, it cannot be applied directly onto a fabric due to its insolubility in water. The 'vat-dyeing' technique was developed to overcome this problem. In this process, the dye is reduced in an alkaline medium (sodium dithionite is a convenient reagent for this purpose) to the yellow-coloured leuco indigo which is soluble in aqueous alkali. The material to be dyed is then dipped in a solution of the reduced product and then exposed to air which brings about the oxidation of the leuco compound to the blue dye on the material itself. Of course, the most popular indigo-dyed fabric is denim. Levi Strauss, a German emigrant, introduced blue jeans to the US in the late 1800s. Since then, it has grown in popularity and is now used all over the world.



Conclusions

The story of indigo has not yet ended. As mentioned earlier, its potential as a semiconductor (*Box 2*) is yet to be fully explored. In the meantime, it remains a very popular dye and will remain so as long as the blue-jeans culture continues. In recent years efforts are under way to make the vat-dyeing process greener. The focus has been on replacing the sodium dithionite used as a reducing agent by environmentally friendly methods such as catalytic hydrogenation and electrolytic reduction. The problem is to make these techniques commercially viable.

It is gratifying to note, therefore, that indigo remains ever blue!

Suggested Reading

- [1] P Karrer, *Organic Chemistry*, 4th English Edition, Elsevier, Amsterdam, pp.567–576, 1950.
- [2] J Balfour-Paul, *Indigo: Egyptian mummies to blue jeans*, British Museum Press, London, 2011.
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Box 2. Indigo and Tyrian Purple as Semiconductors

Recent studies have shown that these two dyes act as semi-conducting materials in the solid state, as due to H-bonding and p-stacking they are capable of forming highly-ordered, crystalline thin films. As a consequence, they can be used in the preparation of high performance organic field-effect transistors.

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