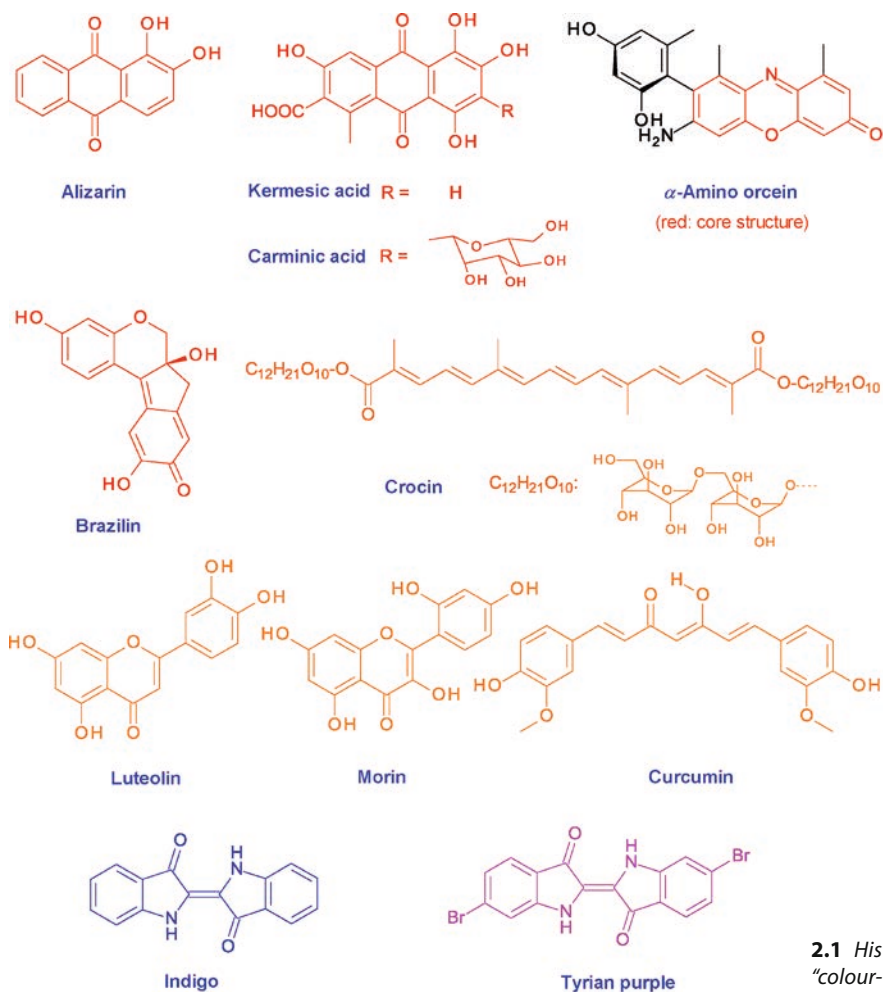


2 | Colourants

For thousands of years Man has made use of dried materials from plant or animal sources. In Chinese as well as European culture, these “drugs” were used – sometimes unaltered and sometimes as extracts – as remedies as well as for technical purposes. For example, kermes served both as a red dyestuff and as a drug for the treatment of heart disease (Fig. 2.1). [1]



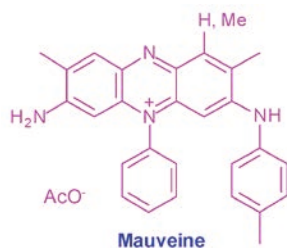
2.1 Historically important “colour-drugs”.

Madder, kermes, carmine, archil and redwood were all used as red dyestuffs. Alizarin (*cf.* Section 2.3) provides the core structure for the dye, which was obtained from the root of madder (*Rubia tinctorum* L.), and also for kermes and carmine, which are both extracted from scale insects (*Kermococcus ilicis* L. and *Dactylopius coccus* L., respectively). These are mordant dyes, which form with transition metal salts, depending on the individual metal, diversely coloured complexes on textiles. Archil is a colour preparation from lichens, which grow on many sea coasts, and are used for direct dyeing of wool and silk. The alcoholic extract of these composite organisms is known as orcein. It contains a series of different colouring dyes based on the phenoxazone chromophore. Brazilin is the colouring component of South American redwoods, and serves as mordant dye for colourising wool, silk and cotton.

Chemically related to brazilin are the yellow mordant dyes, luteolin and morin. Both are flavone derivatives; whereas the former is obtained from yellow weed or weld (*Reseda luteola* L.), which grows widely across Europe, the latter comes from dyer's mulberry (*Maclura tinctoria*, syn.: *Morus tinctorius* L.). Alum- and tin-based mordants from luteolin produce a beautiful true yellow on all textile materials. Apart from weld, saffron (*Crocus sativus* L.) used to be the most important yellow colourant. The ancient Greeks and Romans used the dried stigmas from this species of crocus to obtain crocin, which was absorbed onto textiles with an alum mordant. Like saffron, curcuma (also known as turmeric) serves as a colourant for foodstuffs (*e.g.* for mustard and curry), and as a somewhat acrid spice in Oriental and South-east Asian cuisine. Curcuma is obtained from the root nodules of, for instance, *Curcuma longa* L., which is cultivated in plantations in China and the East Indies.

The most important source of blue colourants in Europe was woad (*Isatis tinctoria*), from which indigo could be produced (*cf.* Section 2.1). Chemically related are the purple dyes obtained in ancient times from sea-snails of the genus *Murex* (*cf.* Section 2.2). Depending on the particular species of snail, violet to reddish-purple textile dyes can be obtained. Tyrian purple and indigo are both vat dyes.

Apart from a few inorganic pigments, these represent the important dyestuffs, which determined the colours available for many centuries. In the course of the first Industrial Revolution, with the invention of power looms and steam engines, the textile industry blossomed. There was a growing need for artificial bleaching agents. Initially, dilute sulfuric acid, prepared by the lead chamber process (John Roebuck, *ca.* 1750), was used for this purpose. Since this however caused damage to the fabric, hypochlorite became the preferred bleach (Charles Tennant, 1799). At the same time, there was an increasing need for textile dyes. When in 1856 William Henry Perkin, in an attempt to prepare quinine, found instead the first coal-tar dye, mauveine, no one foresaw that he had thereby laid a crucial cornerstone for an entirely new industry branch. In fact, the most important roots of the chemical industry lie in the production of colourants and the preparation of pharmaceuticals, fragrances and explosives (Tab. 2.1).



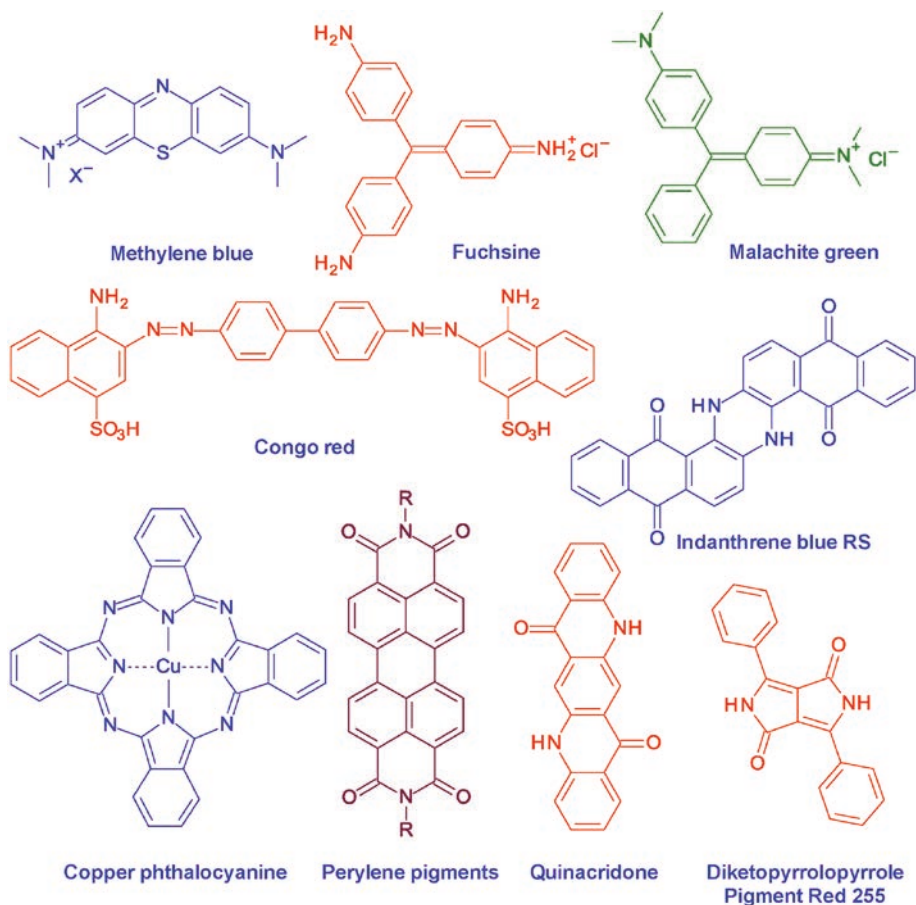
Tab. 2.1 *The original activities of a few major chemical companies*

Company	Founded in (year)	Initial area of activity
Geigy	1758	Colourants
Ciba	1859	Colourants (fuchsine)
Bayer	1863	Colourants (ultramarine)
Hoechst	1863	Colourants
BASF	1865	Colourants
Sandoz	1886	Colourants
Merck	1827	Pharmaceuticals (morphine)
Eli Lilly	1876	Pharmaceuticals
Boehringer Ingelheim	1885	Pharmaceuticals
BMS	1887	Pharmaceuticals
Hoffmann La Roche	1896	Pharmaceuticals
Haarmann & Reimer	1874	Flavourings (vanillin)
Dragoco	1919	Aroma chemicals
Dupont	1802	Explosives
Nobel Industries	1894	Explosives

Towards the end of the 19th century, many of the newly established firms developed aniline- and triphenylmethane dyestuffs. In 1859, Ciba began the production of fuchsine, which enabled the dyeing of silk. In 1877, BASF was granted the first German patent for a coal tar dye entitled “Preparation of Blue Dyestuffs from Dimethylaniline” (*viz.* Methylene Blue) (Fig. 2.2).

In the same year, Otto Fischer synthesised Malachite Green. A year later, Adolf von Baeyer elucidated the structure of indigo. Several firms manufactured alizarin, but the first industrial-scale synthesis of indigo followed only in 1897. Around the same time, several firms developed and produced the first azo dyes, after Paul Böttiger had improved the preparation of Congo Red from benzidine in 1884. René Bohn synthesised the first anthraquinone dye, Indanthrene Blue RS in 1901 – a vat dye, like indigo, but much more light- and water-fast. In 1927, Henri de Diesbach and Edmond von der Weid prepared the first copper-phthalocyanine pigment, a material which was marketed a few years later by several firms. After the Second World War, phthalocyanines developed into an important class of colourant in their own right. The first perylene pigments became technically accessible in 1950: their most important application is currently in premium automotive finish. In 1952, the first reactive dyes with vinyl sulfone groups came on to the market. Quinacridone pigments for high-quality colour printing, automotive enamels and powder coating for plastics followed in 1958. In the 1960s, dyes for the colouring of synthetic fibres grew in importance. One of the more recently introduced organic pigment classes are the diketopyrrolopyrroles (DPP). These red pigments were developed by Ciba in the 1980s and 1990s. They are used

**2.2** *Patent document for the preparation of Methylene Blue.*



2.3 Selected synthetic colourants of the last hundred years.

predominantly in high performance plastics and automotive paints, and are known for their outstanding brightness and weather stability.

Modern developments in the dyestuff and pigment sector are luster pigments, IR-reflectors for house façades and windows, light-harvesting systems for solar collectors and light-emitting diodes in the electronic industry (Fig. 2.3).

The following sections of this chapter deal with indigo, Tyrian purple and alizarin. By example of these three important colourants, we can familiarise with the historic processes which had a lasting impact on shaping the chemical industry. Alizarin was the first natural dyestuff to be prepared synthetically on a large scale, and along with indigo it can be considered as a trigger for the development of modern industrial production processes for a number of basic inorganic chemicals, such as chlorine, ammonia and sulfuric acid. Dyeing with Tyrian purple had already in the ancient world an industrial dimension. However, the demand for mauveine stimulated the advancement of industrial chemistry to a different level. The market was conquered by this

synthetic product, before Tyrian purple from synthetic origin could even claim a position. Thus, there was never an industrial manufacturing process developed for Tyrian purple.

Summary in Bullet Points

- Man has used natural colourants for thousands of years.
- With the synthesis of the first coal tar dyestuff, mauveine, W. H. Perkin laid an important cornerstone for modern chemical industry.
- More recent developments in colour chemistry focus on luster pigments, IR-reflectors, light harvesting systems and light-emitting diodes.

2.1 Indigo

2.1.1 Introduction

Among the earliest preserved evidences of our culture are cave paintings of the Cro-Magnon Man (European Early Modern Humans, EEMH, *Homo sapiens sapiens*), which were produced 10 000 to 30 000 years ago in places like the caves at Lascaux, located in France's Dordogne region. The pictures display a broad colour palette with subtle shading – what they are lacking is blue (and green, which could have been produced by mixing with yellow ochre). Yet, blue tones are not uncommon in Nature, where they are however frequently caused by interference phenomena, not only in media like water and air, but also in the feathers of birds and wings of butterflies and beetles. The colour of the rose chafer (*Cetonia aurata*) for example, changes from bronze to green depending on the observation angle (Fig. 2.4).



2.4 Cave painting from Lascaux and a rose chafer.

Apart from ultramarine (see marginal note on next page) [2], indigo was one of the few colourants to close this “blue gap” in the colour palette. In ancient times, it was reckoned as valuable on account of its beauty and lightfastness, which lent itself to wider applications, not only for the colouring of precious textiles but also for artwork.



2.5 During the years 1858–1861, relics of the Roman Iron Age were found in the peat of Thorsberg Moor near Süderbrarup, Schleswig-Holstein, Germany, where a Germanic tribe, the Angles, deposited votive offerings for approximately four centuries. Among them was the so-called Thorsberg cape (probably dating to 3rd/4th century AD). Its blue colour resulted from dyeing with woad.

It is also known from grave-finds that Egyptians liked to colour their linen with indigo. From the early Iron Age, the Teutons used woad to produce blue textiles, as in the magnificent (reconstructed) cape from Thorsberg (Fig. 2.5). The ancient Greeks and Romans already knew the indigo which came from India, as we have learned from the writings of Dioscurides and Vitruvius. However, it was used mainly as an artist's pigment; for the dyeing of textiles they used also woad. Pliny the Elder (23 or 24 AD – August 25, 79 AD, while attempting the rescue of a friend and his family by ship from the eruption of Mount Vesuvius) describes in his *Naturalis Historia* the high value of indigo. He also mentions that dishonest dealers tried to eke out the expensive product by colouring chalk with woad.

In *De Bello Gallico*, Julius Caesar (100–44 BC) describes another interesting use of indigo by the British Celts. Indigo serves as a component of make-up for war-paint. (see marginal note) [3]

In the High Gothic period, there developed a diverse colour symbolism. By virtue of the price of clear deep blue shades, artists confined themselves to use blue only to depict the saints. In this way, blue emerged as the symbolic colour for the Virgin Mary (Fig. 2.6).

The word “indigo” is derived from the river Indus, where traces of the Indian Harappan civilisation were found: this was the first such culture to use indigo for colouring. [4] In the whole of the Mediterranean region there were no indigenous blue plant colourants. Marco Polo (1254–1324) was the first to describe the production of indigo from the indigo plant in India. In 1498, indigo from India was imported for the first time on a larger scale. [5] Thus, from the Old Indic word “nilaa” meaning “dark blue” came the Portuguese term “anil” for indigo (and thereby “aniline”, the name of a decomposition product from indigo, obtained by Carl Julius Fritzsche in 1841 by oxidation of indigo in molten potash [6]).

Apart from the tropical and subtropical indigo plant, *Indigofera tinctoria* (Fig. 2.7), the dyer's knotweed (*Polygonum tinctorium*, syn.: *Persicaria tinctoria*) was cultivated in southern China and Japan, and woad (*Isatis tinctoria*) in northern Europe. In the 13th century the cultivation extended to the whole of central Europe, e.g. to England (Somerset and Lincolnshire), France (Normandy, Somme, and Languedoc), Germany (the Jülich area and Thuringia) and Italy (Piemont and Tuscany): in corresponding areas of France and Germany (e.g. in Thuringia) it generated considerable wealth. Nowadays, these plants can still be found growing wild along the river Rhine. [7, 8]

In the 18th century, the spread of woad cultivation contracted, since British-Indian companies had established large *Indigofera* plantations, particularly in Eastern India. The yield of the colourant from *Indigofera* was around 30 times higher. From 100 kg of leaves one could obtain 2 kg of indigo. [9] So in 1897,

i The name ‘ultramarine’ for the semi-precious stone, Lapis lazuli (“Blue Stone of Heaven”), which occurs in Nature as a deep-blue coloured mineral (lazurite), relates to the overseas origin of this material, which was brought over the sea to Italy: *ultra* (Latin) = on the other side, *mare* (Latin) = sea. The best Lapis lazuli comes from Afghanistan. It had already been imported into ancient Egypt, where e.g. the death mask of Tutankhamun is richly decorated with this matter.

i Omnes vero se Britanni vitro inficiunt, quod caeruleum efficit colorem, atque hoc horridiores sunt in pugna aspectu. All the Britains, indeed, dye themselves with woad, which occasions a bluish colour, and thereby have a more horrible appearance in fight.

6,000 tonnes of natural indigo were produced. In the year 1853, at the time of the Californian gold-rush, an immigrant from Bavaria to the USA, by the name of Levi Strauss, set up a wholesale business of haberdashery in San Francisco. Along with a tailor, Jacob Davis, he produced canvas pants for the gold-diggers, which were reinforced at their stress points with copper rivets (Fig. 2.8). In 1873, Levi Strauss obtained a patent for these. He got the material for the blue, white and brown sailcloth trousers from the Amoskeag mill in New Hampshire. In particular, the indigo-coloured denim enjoyed great popularity and morphed over the years into “blue jeans”.

Even before the outbreak of the First World War, synthetic indigo had almost completely superseded the natural product. In India alone, the area of the plantations had diminished from 700,000 ha in 1897 to 121,000 ha in 1914. On account of the naval blockade during the First World War, natural indigo became scarce in the short term; and its final end came after the war, when dye manufacturers in Switzerland, the USA, Japan and England set up their own indigo production.



2.6 The “Madonna in the Rose Bower” by Stephan Lochner (ca. 1410–1451), the most important late Gothic painter of the Cologne School (Wallraf-Richartz Museum, Cologne).



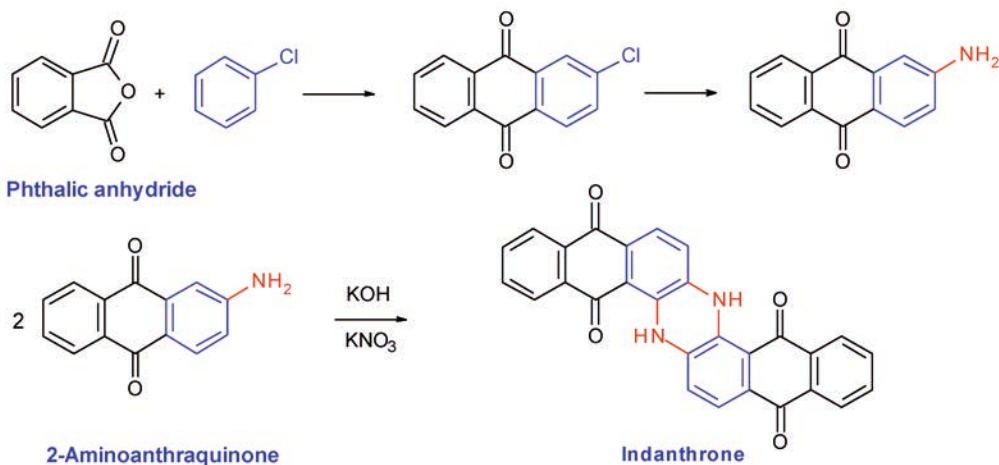
2.7 *Indigofera tinctoria*: Coloured copperplate print by Nicolaus Friedrich Eisenberger, taken from the herbal of Elisabeth Blackwell, Nuremberg, 1765 and a photograph of the flowering plant. Woad (*Isatis tinctoria*) can be seen on the image to the right.



2.8 Levi Strauss (left), the “father” of indigo-coloured “blue jeans”, which scored their first success at the time of the Californian gold-rush.

Nevertheless, with the arrival of synthetic indigo in the 20th century, more beautiful and water-fast cotton dyes than ever before could be produced, e.g. Indanthrene Blue. Arising out of the chemistry of alizarin, work began on anthraquinone dyestuffs. In 1901, René Bohn at BASF made a remarkable dis-

covery: melting 2-aminoanthraquinone with potassium hydroxide and potassium nitrate gave a blue dye, which, on account of its origin and its colour, Bohn called “Indanthrone”.

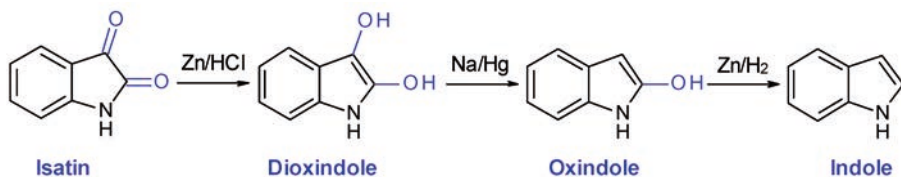


Only in the 1960s, indigo experienced an unexpected comeback. It was James Dean's blue jeans and leather jacket which became initially a symbol of protest, and then the uniform for a whole generation. Indigo, the king of colourants, and once reserved for the establishment, became the colour of the non-establishment and the label for a particular life style.

2.1.2 Structure Determination

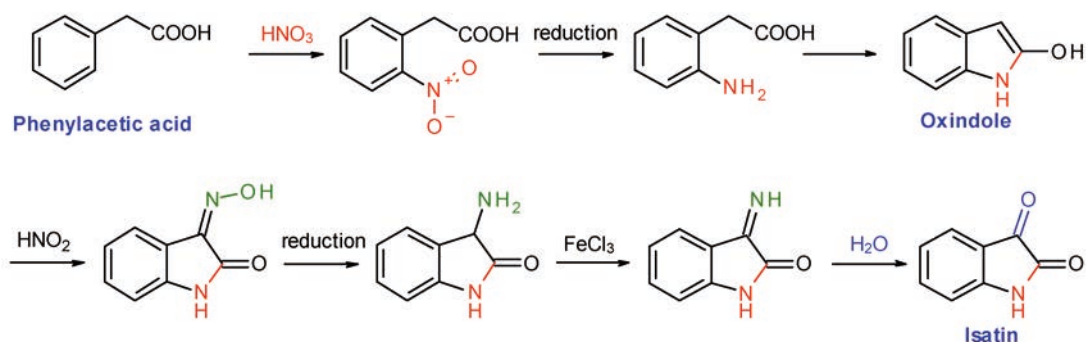
More than half a century passes from initial research the pharmacist Otto Paul Unverdorben (1806–1873) had conducted in 1826 to elucidate the structure, when Adolf von Baeyer was able to dispose of the final uncertainties regarding indigo's chemical constitution in 1883.

By attempted distillation of indigo with lime, Unverdorben obtained aniline. Under milder conditions, anthranilic acid was produced. The most important degradation reaction of indigo is oxidation with nitric acid, as performed in 1841 by Otto Linné Erdmann (1804–1869) and Auguste Laurent (1807–1853), which resulted in isatin. This was, more or less, the state of knowledge when Adolf von Baeyer began in Strasbourg his work on indigo in 1865. One of the critical questions was, at which position in the five-

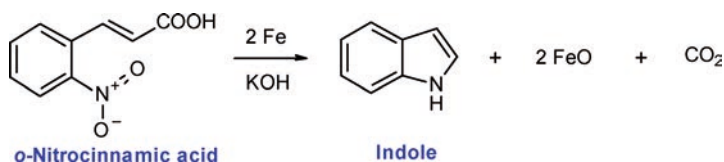


membered ring of indigo is the oxygen atom attached? For this purpose Baeyer reduced isatin stepwise to indole. Zinc/hydrochloric acid reduction rendered first dioxindole, which he reduced further with sodium amalgam to oxindole; finally, he obtained indole by distilling oxindole with zinc dust in a stream of hydrogen.

Baeyer confirmed his results by the total synthesis of oxindole, isatin and indole. Nitration of phenylacetic acid, isolation of the *o*-nitro isomer, and reduction of the latter followed by ring closure gave oxindole. Reaction with “nitrous acid” (*i.e.* potassium nitrate and sulfuric acid) gave isatin oxime, from which by reduction, dehydrogenation with iron(III) chloride and final hydrolysis, isatin itself was obtained.

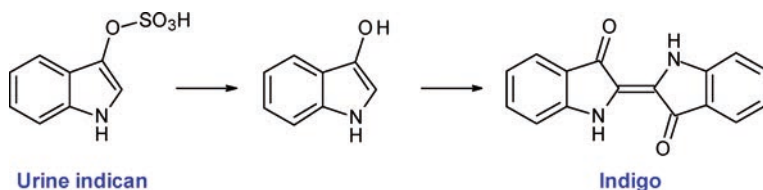


Baeyer synthesised indole by reduction of *o*-nitrocinnamic acid with iron and potassium hydroxide (Baeyer-Emmerling indole synthesis).



All this work was novel, but did not answer the question concerning the structure of indigo. As we shall see, with oxindole, Bayer had chosen the wrong substitution pattern.

As it often happens, a decisive piece of information came from an entirely different quarter. In 1879, Baumann and Tiemann had isolated urinary indican. This is the potassium salt of indoxyl sulfate, which arises in the urine under



i Baeyer had tried out zinc dust distillation for the first time as a synthetic route to indole. In connection with the structure determination of many natural products, this later proved a valuable method for the transformation of phenols into hydrocarbons.

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