Modern Alchemy 103: Indigo and friends

If you're not part of the solution, you're part of the precipitate!

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We're looking at vat dyes, and indigo is the celebrity dye molecule in that category, although there are others as well. Woad and Tyrian purple also fall into the vat dye category. Within each of these are the precursors to the indigotin molecules that we're looking for. They are not water soluble and could be classified as a pigment, but through the magic of chemistry, they are transformed into a water soluble form, used to penetrate the fibre and then transformed again into its insoluble form and precipitates between the fibres. Technically, these are stains and not dyes, but we've been calling them dyes for approximately a bazillion yrs at this point, we're not about to change now. And at least there's chemistry involved! That being said, indigo's famous reputation for coming off on your hands, your spindles, and washing away over time (think fading blue jeans) are entirely due to it being a stain rather than a true dye. We've only just shoved those pigment molecules into the fibres and are hoping like heck they stay put, sometimes they have other ideas. Sometimes that's referred to as 'crocking', and yep. Indigo does that. By the same token, indigotin dyes generally are dyed to darker colours by multiple dips into the dye vat, rather than longer soaks, as you are building up layers of that pigment tangled into your fibre molecules.

Tyrian purple

This comes from a mollusks in the family Muricidae, also often called Murex. They're primarily found in the Mediterranean and in ancient times were ever so slightly less outrageously expensive than now, but not by much. While we are not going to focus on Tyrian purple, know that all of the processes are effectively the same for it as they are for indigo and woad, we just happened to have gotten our precursors from a shellfish rather than a plant.

Woad vs Indigo

Woad (*Isatis tinctoria* L.) grows basically everywhere, with references to it in China, all through Europe, it's all over the place. The plant is part of the mustard family and is considered an invasive species in many places in North America, so beware if you have an urge to grow it in your garden.

Indigo (*Indigofera tinctoria* L.) is known as true indigo, part of the bean family and in our period was grown exclusively in the far East and was an import rather than the locally grown woad. It has a much higher concentration of dye molecule precursor, making it a much larger bang for the buck, so to speak in a single plant. Indigo can also refer to *Persicaria tinctoria* which is better known as Japanese indigo, part of the buckwheat family. Most modern dye gardens seem to have Japanese indigo rather than woad or true indigo, as it holds up better in our temperate rather than tropical climate.

Figure 1 Indigofera tinctoria flowers (Kurt Stüber [1], CC BY-SA 3.0 <http://creativecommons.org/licenses/by-sa/3.0/>, via Wikimedia Commons)

Looking at a tiny selection of period dye manuals from Western Europe and Northern Africa, I found only woad mentioned up to about the 9th century. By the 15th century, there's more mention of indigo and far less about woad, which speaks to the uptick in trade.

There is a great deal of declarations that woad and indigo are oh so very different, one can tell at a glance what was woad dyed and what was indigo dyed. So let's have a look at what's going on in the chemistry.

Let's talk chemistry

First off, both woad and indigo ultimately end up with indigotin. Yes, the very same molecule. They get there from different directions, but they end up with the very same molecule. They absolutely have different concentrations of dye in the plants themselves, and there's an argument about how there could be other additives in each plant that would affect the colour, but at the end of the day, we end up with the same molecule, so they are functionally close enough for me. So, how do we get there?

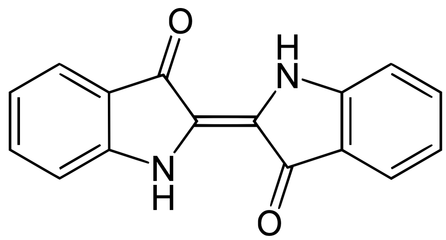

Figure 2 Indigotin (Yikrazuul, Public domain, via Wikimedia Commons)

Woad holds isatan B (indoxyl-5-ketogluconate) as its primary precursor.

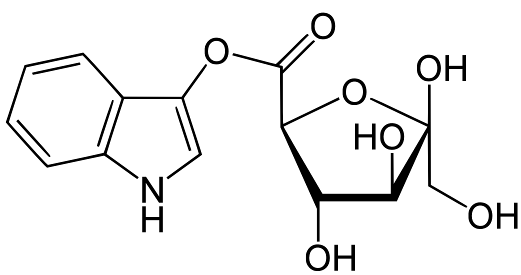

Figure 3 Isatan B (Yikrazuul, Public domain, via Wikimedia Commons)

Indigo holds indican (indoxyl-β-D-glucopyranoside) as its precursor.

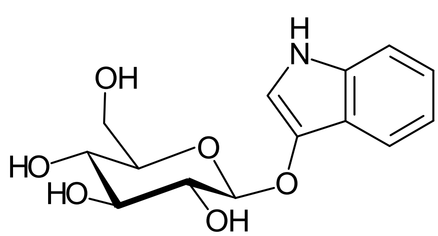

Figure 4 Indican (By NadirSH - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=77206000)

Both of them form indoxyl (and glucose) thanks to the enzymes in their very own leaves, a bit of fermentation and warm temperatures.

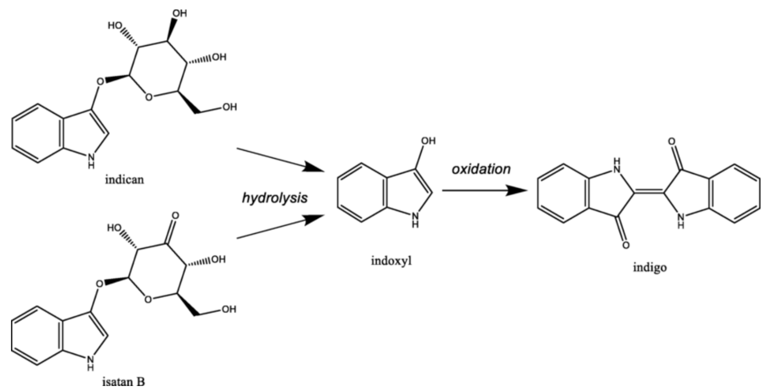

Figure 5 Structural formulas of indigo, indoxyl, and some of its plant precursors, indican and isatan B (Source: https://www.researchgate.net/figure/Structural-formulas-of-indigo-indoxyl-and-some-of-its-plant-precursors-indican-and_fig1_337927469/)

This murky water full of indoxyl is generally poured off the leaves and dirt, often a couple of times before it is then converted into indigotin, by introducing oxygen. Generally a good frothy mixing works well, beating the mixture with sticks is also common enough, or pouring from one vessel to another. At that point, the insoluble indigotin is left to settle out. Some traditions include adding an alkaline at this point, but it is not strictly necessary. It is at this stage that you have your blue cakes of powder (or sludge, depending on how dry you make it), and you can store that, ship that, do whatever you want with it, but are no longer dependent on rapidly rotting leaves to work with. There are some traditions that dry the leaves and work with those later, but certainly for ease of transport, generally the extracted form is the easier one.

But wait! Indigotin is the insoluble version? How is that helpful?

We need to get the istan B or the indican into indoxyl and then into an indigotin pigment first before we can start futzing about with it. We can then solubilize it, shove it in our fibre and then precipitate it back out again. Simple, right?

This is the stage that most people who buy indigo get it at, the blue powder (natural or synthetic) and a giant list of directions on how to coax it along. I'm not going to lie to you here, indigo vats have a temperament and personality and take some babying. They are magic when they are working, and the most frustrating black box when they are not. Have faith, it's all just chemistry.

So here we are with our fibre, and our chunk of indigotin and we need to make an indigo vat out of it. We've already covered that indigotin is insoluble and won't play nice with our fibres, but it can be converted into another form that soluble, and that form is leuco-indigotin, also sometimes known as white indigo. This process is known as reduction, and why you can buy synthetic indigo as pre-reduced, where they have started this process for you. Indigotin happily shifts back and forth between its oxidized and reduced forms. This reaction needs to be alkaline (basic.. high pH) and with some means of getting those oxygen molecules to get back in the game, which is by using some sort of reducing agent. Historically, that was done with stale urine.

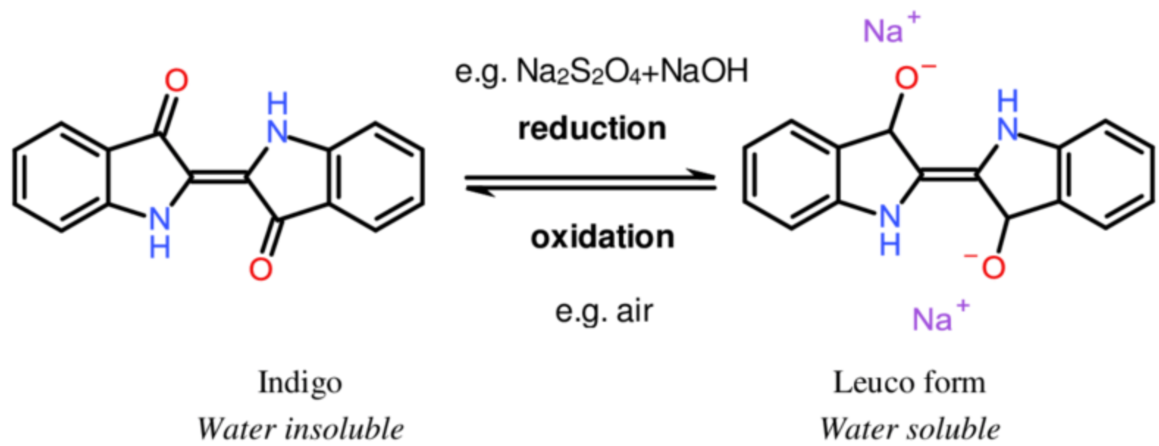

Figure 6 Indigotin vs Leuco-indigotin (Source: https://www.researchgate.net/figure/The-intensely-colored-and-hydrophobic-indigo-dye-can-be-reduced-to-water-soluble-leuco_fig11_236199553)

Urine Vats

Contrary to popular wisdom, human urine is not sterile. Even healthy people, without any urinary tract infections, have some level of bacteria in their urine, and that bacteria helps to break down the urea ($(CO(NH_2)_2$) into ammonia (NH_3) as the urine sits and gets stale. The process can start in as little as 30 minutes, and samples more than a couple hours old (at room temperature) are

$$\underset{\text{urea}}{NH_2CONH_2} + \underset{\text{water}}{H_2O} + \text{heat} \rightarrow \underset{\text{ammonia}}{2\,NH_3} + \underset{\text{carbon dioxide}}{CO_2} \qquad [1]$$

Figure 7 Simplified reaction of urea into ammonia.

no longer considered valid for urinalysis. ("Urine Changes When Urine Left at Room Temperature and Without Preservatives," 2020) Both urea and ammonia are basic solutions, and the urine becomes more alkaline the longer it sits and stales. The stale urine is mixed with the indigotin and when kept warm should change from the blue of indigotin to the yellow-green colour of leuco-indigotin. Fibre gets dipped, careful to introduce as little oxygen as possible back into the vat, and then the oxygen in the air converts the leuco-indigotin back to indigotin and blue. Often urine vats were combined with an extra dose of fermentables to help coax the process along, often wheat bran, madder, effectively just giving the bacteria more food to work on things.

Modern Vats

There are many options for both reducing agents as well as akaline solutions in modern indigo vats. While I have found no evidence of that being used in period, fructose vats are a modern vat that is often turned to when people are looking for a less toxic chemical soup than most of the vats used today. Fructose is a fruit sugar, and also a reducing agent. So that can be used to reduce your indigotin, along with something to bump the pH up high, and get your happy leuco-indigotin that way. The other most common reducing agents today are iron(II) sulphate, sodium hydrosulfite or thiourea dioxide (thiox). The alkaline compound is often calcium hydroxide (slaked lime) or sodium carbonate (washing soda, or soda ash).

Synthetic Indigo

A brief foray into modern history here, as we have a quick conversation about synthetic indigo and pre-reduced indigo. If you are out shopping for indigo, rather than growing dye plants, you have probably run into indigo being sold under a million names and most of them happily include ‘natural’, ‘organic’ and then in the next breath tell you that it’s pre-reduced for ease of use! Pre-reduced means that they have started the next process for you, it’s about 60% leuco-indigotin (stay tuned, that’s coming in the next section), and is synthetic indigo. This is not necessarily a bad thing! Indigo was one of the last dyestuffs to have joined the commercial chemical manufacturing, not until the late 1890s. (Hofenk de Graaff et al., 2004) It will be pure indigotin, where natural indigo has other impurities that will affect the colour, for better or worse.

References

Buccigross, J., M. (2006). *The science of teaching with natural dyes*. BookSurge.

Chemistry of Indigo | Wild Colours natural dyes. (n.d.). Retrieved May 16, 2021, from http://www.wildcolours.co.uk/html/indigo_chemistry.html

Epp, D. N. (1995). *The chemistry of vat dyes*. Terrific Science Pr.

Gerber, F. H. (1977). *Indigo and the Antiquity of Dyeing*.

Hofenk de Graaff, J. H., Roelofs, W. G. T., & Bommel, M. R. van. (2004). *The colourful past: Origins, chemistry and identification of natural dyestuffs*. Archetype Publ.

Indigo. (n.d.). Natural Dyes. Retrieved May 16, 2021, from https://naturaldyes.ca/indigo

Klos, D. (2004). *The dyer's companion*. Interweave Press.

Urine changes When Urine Left at Room Temperature and Without Preservatives. (2020, January 25). *Labpedia.Net*. https://www.labpedia.net/urine-changes-when-urine-left-at-room-temperature-and-without-preservatives/