

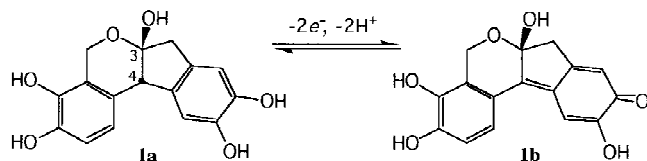
The Progress of Logwood Extract

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ABSTRACT Hematoxylin, $C_{16}H_{14}O_6$, from the extract of logwood, crystallizes as a trihydrate with the water molecules inside helical channels. It was the first organic compound used to deliberately stain a salt crystal and as such played a central role in the general development of the subject of dyeing crystals. We discuss this development and, moreover, show that efforts to stain $(NH_4)H_2PO_4$ crystals with hematoxylin in 1879 provided evidence of enantioselective crystal chemistry recognizable with the unaided eye. What motivated nineteenth century chemists to dye crystals? Why and how was hematoxylin selected as the first colorant, and what were the consequences of this selection? In order to answer these questions, we offer an integrated history of hematoxylin. We trace logwood extract from the height of the Mayan civilization, through the development of the baconian scientific method, during the Atlantic slave trade, and in supramolecular stereochemical associations while dyeing crystals. Along this journey we endeavour to reflect upon the science and conscience of a stereochemist. *Chirality* 10:66-77, 1998. © 1998 Wiley-Liss, Inc.

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This is the tale of a chiral molecule commonly used in dyeing textiles, hematoxylin (**1a**), which is asymmetric and has an absolute (3S, 4R) configuration. It is found in the extract of *Hematoxylin campeachianum*, a tree commonly known as logwood. Linnaeus' botanical name indicates that the heartwood is blood-red—the Germans use the term *Blutholz*, while the French use *bois de sang*—and that the original source of logwood was the shores surrounding the Gulf of Campeche on the southeastern stretch of the Yucatan Peninsula.^a Here, in marshy ground, uncultivated logwood trees grow rapidly with "crooked spinous branches, leaves abruptly pinnate, leaflets inversely heart-shaped, and flowers racemed."¹



First, it must be stated that **1a** is not a dye, it is a colorless compound that is oxidized in air to form hematein (**1b**), the accepted colored species in logwood extract. Unfortunately, the color chemistry derived from **1a** is not only the result of a two-electron oxidation. Hematoxylin also has complex acid/base and coordination chemistries. Bancroft¹ succinctly summed up some of the phenomenologi-

cal color changes to which hematoxylin/hematein (**1**) is subject.

Sulphate of copper added to the decoction of logwood, gives it a purplish blue colour; sulphate of zinc added to a similar decoction, produces a dark purple; nitro-muriate of gold, an orange; muriate of quicksilver, an orange red; muriate of antimony, a beautiful crimson; acetate of lead, a garter blue; arseniate of potash, a deep yellow; muriate of barytes, a reddish purple; nitrate of barytes, a brownish purple; strontia earth, a violet; sulphate of magnesia, a purple; muriate of magnesia, a yellow; sulphate of lime, a purple; and muriate of lime, a violet purple. These effects show that the tingent matter of logwood, is capable of producing, with different mordants or bases, almost all the possible varieties of colour.

Hematoxylin (**1a**) captured our attention while studying the process of dyeing crystals, a major theme in our scientific work since leaving the Princeton laboratory of Professor Kurt Mislow. However, as the centerpiece of a paper in a Mislow Festschrift, **1a** must reflect not only our research, but also the interests and qualities of the honoree. Hematoxylin is such a molecule. This case we make in the following essay that has taken the form of a long and winding thread that crosses oceans, centuries, and themes. We hope that the reader will nevertheless be able to paint it

^aThe name logwood was a 16th century English invention, which was referred to in the Dyer's Fleece as "what Campeachy's disputable shore copius affords to tinge the thirsty web." See ref. 1.

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with logwood extract in a continuous stroke and that (s)he will not be too far, by the last page, from the starting point.

DYEING CRYSTALS WITH LOGWOOD

Virtually every civilization has developed industries for dyeing textile fibers. On the other hand, we rarely countenance dyed crystals; there exist only a handful of examples. Undoubtedly, this distinction has to do with the fact that macroscopic crystals have much smaller area:volume ratios than do textile fibers and are therefore not grossly susceptible to dye adsorption. However, the cumulative area of the crystal subject to dye adsorption as it grows from solution as a function of time is substantial. As long as the adhesion processes do not impede the continued growth of the crystal, the supramolecular chemistries that occur when dyeing crystals should be considered along with those of dyeing cotton and wool.

During the past several years, we have revived the art and science of dyeing crystals emphasizing the use of simple salts as hosts.² We showed how structural studies of some historical dye inclusions were used in the design of new inclusions with prescribed physical properties such as lasing action.³ Stereoselective recognition processes were illustrated.⁴ We probed the internal texture of dyed crystals by using the X-ray topography technique⁵ and studied how ferroelectric host crystals modulate the emission properties of included chromophores.⁶ Organic crystalline hosts⁷ were not excluded from our purview, nor were biological guest molecules carrying covalent dye labels.⁸

Despite these recent contributions, it must be remembered that the scientific study of dyeing salt crystals was initiated by Henri de Senarmont (1808–1862),⁹ a pioneer in the study of thermal conductivity and its relationship to crystal symmetry. In 1854, he turned his attention to the mechanism of the anisotropic absorption of light, pleochroism, in minerals. Senarmont framed the following question: could one make an otherwise transparent crystal pleochroic by including in it some external coloring agent during growth from solution? Senarmont was satisfied by pleochroic crystals of $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ grown from an ammoniacal water solution containing logwood extract¹⁰ that were red or violet in color depending upon their orientation with respect to the plane of linearly polarized light. Senarmont announced “The Production of Artificial Pleochroism in Crystals.”

Strontium nitrate tetrahydrate stained with logwood extract has since been referred to as *Senarmont's salt*, an appropriate name because when others tried to prepare it subsequently, they most often failed. As a privatdozent and before establishing himself as a distinguished petrographer in Heidelberg, Harry Rosenbusch (1836–1914)¹¹ failed to reproduce Senarmont's experiment. No less a scientist than Henri Becquerel (1852–1908),¹² the discoverer of radioactivity in uranyl salts, failed during the course of his doctoral research on pleochroism. Seher-Thoss¹³ also comments on his inability to reproduce Senarmont's salt although he did try to stain other salts with logwood extract and succeeded by producing pleochroic crystals of $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ in which the color was localized in the outer layers of the prismatic faces (more about these later). We

count ourselves among the chemists that have been unable to produce Senarmont's salt in the laboratory. Our $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals grown from solutions containing **1** under a variety of conditions (temperature, pH, supersaturation, secondary additives) were never pleochroic nor even colored.

What is the secret of Senarmont's salt? Pierre Bertin (1818–1884),¹⁴ a successor to Senarmont at the École de Mines, gave the only confirmation that such crystals ever existed. Apparently, Senarmont had left behind a collection of his stained crystals, but none of them showed good absorption brushes¹⁵ when reexamined by Bertin in 1877 even though they were protected by Canada balsam.^b Fortunately, Bertin recalls, a colleague at the École Normale possessed a singular plate from Senarmont showing beautiful brushes. However, the act of transporting this crystal through Paris on a hot day was enough to make it foggy. After many tries, an associate ultimately succeeded in growing Senarmont's salt. These crystals were sectioned and the slices were distributed throughout crystal collections in Europe, but to the best of our knowledge they were not to be heard of again. Nevertheless, Senarmont's success was the inspiration for, and progenitor of, all future researches on dyeing crystals.^{c16}

Why did Senarmont choose as his coloring agent some molecule(s) found in the extract of logwood? Here we are faced with one of the great difficulties of the chemist and one of the idiosyncracies of the science of chemistry: gaining a general understanding of the behaviour of molecules from experiments carried out on specific molecular systems. The choice of a particular molecular system, based on personal intuition, experience, and sometimes convenience, may determine whether a general area of inquiry will flourish or languish. Had Senarmont selected a reliable crystal dye, it is likely early researchers would not have been wedded to Senarmont's salt, the first and most celebrated example of a dyed crystal in the literature. Perhaps, the subject of dyeing crystals would not have suffered the fitful start that impeded its future development. Had Senarmont not started with logwood extract, the practice of dyeing crystals might have progressed along with textile coloring technologies.

FRANCIS BACON'S IDEA OF PROGRESS

Francis Bacon (1561–1626), familiar for his writings that formed the foundation of modern science, was uncomfortable with languishing areas of inquiry. He was a proponent of aggressive, systematic searching and presumed that scientific progress mainly required the tireless accretion of new knowledge. However, Bacon, at the birth of modern science, had an unsophisticated view of its progression, at least when judged from the perspective of a contemporary scientist. Today we delight in the twists, turns, and false

^bThese are Brewster's brushes, dark structures seen when unpolarized light is viewed through highly dichroic crystalline plates cut normal to an optic axis. See ref. 15.

^cA complete history of dyeing crystals is in preparation. References to the work of accomplished practitioners such as Lehmann, Gaubert, Buckley, France, Whetstone, and Neuhaus can be found in ref. 16.

starts that make the development of most sciences dramatic stories worth telling.

Kurt Mislow has illustrated, and is certainly comfortable with sciences that do not progress in a directed fashion. He has shown that the mental constructions that chemists have built to support their virtuoso accomplishments sometimes strain under the accumulated achievements. Serviceable as many of the foundational stereochemical ideas may have been, Professor Mislow has spent much of his scientific energies building sounder structures in their place. For example, had structural organic chemists not first focussed upon carbon compounds with tetrahedral coordination geometries the “infelicitous” linkage of stereochemistry and chirality would never have become enforced.¹⁷ Mislow and Siegel took a mental journey back in time and untied this historical entanglement, separating^d chirality from stereochemistry thereby simplifying the learning and teaching of organic chemistry forever after.

Mislow, like Bacon, was concerned not only with scientific progress but also with how science contributes to human progress. Bacon championed the idea that experimental studies by the new *induction* method will produce a more powerful technical and scientific enterprise which will in turn provide greater control over Nature for “the relief of man’s estate.” He encouraged the founding of places quite like Princeton where students and teachers would come together to carry out this systematic program of experimentation. Bacon conceived of the modern research universities as front-line institutions for the betterment of the human condition.

Until recently, when scientific institutions ceased growing exponentially,¹⁹ Bacon was a benevolent prophet. As we approach the ceiling conditions that must constrain exponential growth in any real system, jaded by those episodes in the history of science that have threatened our continued existence, recent scholars no longer see Baconiana through rose-colored glasses. Faulkner begins *Francis Bacon and the Project of Progress* as follows:

This is the century of totalitarianism, mechanized battle, world wars between countries claiming the cause of the future, and the bomb. . . . Even in the popular press ‘progress’ appears in quotation marks, shorn of the presumption of legitimacy or goodness. . . . The press was once a trumpeter of rational enlightenment; the universities provided the music. Now both are in good part disillusioned.²⁰

This is the sort of sentiment that will find truck with Professor Mislow, who avoided totalitarianism by necessity and the bomb by design. One of us (BK) was Professor Mislow’s graduate student in 1987 when he offered a new course, *Chem 489: Social Responsibilities and Rights of Scientists*. He prepared by reading from the literature on the origins of modern science. The opening lecture challenged the common notion, inherited from Francis Bacon, that scientific progress was necessarily good. It was a scholarly,

eloquent, impassioned, yet balanced presentation from a scientist who does not always believe that Bacon’s program for the advancement of knowledge has led or will lead to a revolution in the conditions of life. Cavalieri has captured Mislow’s sentiments by quoting him in *The Double-Edged Helix*.

. . . I don’t agree that freedom of inquiry should be limited only if actual hazards are perceived. I do not agree that increased human knowledge is of paramount importance. I think these are trademark shibboleths which everybody accepts without questioning. I can think of lots of examples where knowledge is extremely dangerous. And in the search for knowledge, you have to ask what you are going to do with the knowledge once you have acquired it.²¹

SPANISH AND ENGLISH LOGWOOD PIRACY

During the Age of Exploration, knowledge was sought voraciously by Western Europeans. One direct consequence of this search was the destruction of whole civilizations, some having made considerable scientific progress even when judged by contemporary standards.²² The Maya, pre-European occupants of the Yucatan Peninsula, used logwood—called *ek*²³—for dyeing cotton and also for medicinal purposes such as halting diarrhea.^{24,25} Most did not survive the Spanish intrusion.²⁶

Columbus was among the first Europeans to encounter the Maya when he landed just south of the Yucatan Peninsula on his fourth trans-Atlantic voyage in 1502. He also must have encountered logwood. However, the value of the tree was only slowly recognized by Spaniards. Logwood was first used as ballast, and when it finally arrived in Europe, accompanied by near-dead and enslaved *naturales*, instead of the much anticipated cargoes of gold, Spanish sponsors were undoubtedly disappointed.²⁷

Artisans in the Norman ports of Dieppe and Rouen, both textile centers, probably recognized the importance of logwood as a dye source when seafaring French interlopers first began returning from the New World. Once this value was established in Europe, logwood was declared by the Crown of Spain to be contraband cargo and confiscated by the *guarda costas* from any ship not registered in Spain. Spaniards now cut down their own logwood which entered European dyers markets through Seville and Cadiz.

English privateers, during the reign of Henry VIII, responded to the Spanish hegemony in the Caribbean by harvesting logwood illegally from territories in the Americas and by sacking Spanish ships bound for Europe. These activities continued throughout the sixteenth century. One notable pirate was the poet, politician, and adventurer, Sir Walter Raleigh, who saw privateering as good business as well as a patriotic duty. Renowned for his hatred of Spain, he captured Spanish ships laden with logwood off the coast of the Azores.²⁸

Raleigh and Francis Bacon were longtime associates. They entered Parliament together in 1581. It was this Par-

^dBut not necessarily unknitting. See ref. 18.

^eAs a hard wood, it was also used to make stakes. See ref. 25.

liment of Elizabeth I that struck out against logwood importation when it issued the following statute:

There hath byn brought from beyonde the Seas a certeyne kinde of Ware or Stuffe called Logwood . . . wherewith dyvers Dyers . . . doe dye dayle . . . As the Colours made with the said Stuffe ys false and deceipteful all such Logwood shalbee . . . forfeited and openlye burnt.²⁹

During the 1580s, despite the fact that English privateers such as Raleigh could profit by stealing logwood either on land or at sea, the official position of the Crown was squarely against logwood importation. The ban was blamed on the fugitive properties of the logwood coloring but, the Queen was most likely responding to pressure to protect growers of woad, a local dye plant.³⁰ An equally important reason for the ban was the desire to limit Spanish revenues through legal logwood importation. Spanish seamen still dominated the logwood trade and Elizabeth's Act could be viewed as a prelude to the English challenge of their naval supremacy; shortly thereafter the English burnt more than Spanish logwood.³¹

Cromwell's Western Design was a plan to capture for England lucrative territories in the New World. In 1655 he sent an army of 9,000 to steal Hispaniola by force. It was rebuffed by the Spaniards. Cromwell's force then sailed on and captured poorly fortified Jamaica as a consolation prize. It was from this island that the English dominated the West Indies.³² Port Royal was used as a trading station for dyewoods from Campeche until 1715 when logwood was first grown on the island itself.³³

Spanish tensions over logwood rights in Mexico and Honduras continued for some time. The English claims to sovereignty over these regions were based on the Treaty of Madrid (1670) which presumably permitted trading from territories already occupied. The Spanish did not recognize this interpretation of the treaty. English settlements were under constant assault by the Spanish Yucatan governors. In 1739, war was declared between Britain and Spain, sparked by Captain Jenkin's emotional account of how the *guarda costas* boarded his ship and cut off his ear, a fragment of which was later displayed in the House of Commons. But, England's principal rival in the eighteenth century was France. The succeeding Seven Years War saw England attempt to induce Spain to join her against France by agreeing to evacuate its logwood settlements. Spain chose to side with France and found itself among the losers. The victorious Britains then gained the explicit permission, as a reparation, to cut logwood within Spanish territories.³⁴

²⁹Elizabeth's dislike of woad supports the idea that this legislation was principally a Parliamentary action. According to Leggett, "It is recorded that Queen Elizabeth so disliked the odor which came from the fermentation of woad that she ordered that, during her progresses through the country, she 'might not be driven out of the towns by the oade infecting the air near them.' The sowing of woad plants was forbidden within five miles of any of the Queen's residences 'whereby any offense may grow from the noysome savour of the same.'" See ref. 30.

THE RESTORATION

Despite the fact that Bacon may best be remembered for his contributions to science, he was not a practicing natural philosopher. As a Parliamentarian he was true to his training as a barrister. Bacon successfully lobbied for and gained the favor of the new king, James I, who acceded to the Throne in 1603, and began to climb through positions of increasing influence. He was quickly knighted, further appointed Solicitor General in 1607, Attorney General in 1613, Privy Councillor in 1616, Lord Keeper of the Seal in 1617, and Lord Chancellor, one of the two or three most powerful posts in the kingdom, in 1618.³⁵ During James' reign Bacon was heavily involved in decisions relating to business and trade.³⁶ In 1619, James, with Bacon as Lord Chancellor, continued the legal assault on logwood by issuing a "Proclamation for prevention and restraint of the abuses and inconsistencies occasioned by dyeing with logwood."³⁷

It is here that Raleigh, the logwood pirate, and Bacon, the anti-logwood legislator, part company.³⁸ Bacon was one of six commissioners who condemned Raleigh to death³⁹ for the latter's violent excesses against the Spanish in Guiana.⁴⁰ Bacon would also soon fall. At the height of his influence he was dismissed from his Chancellorship for accepting bribes. Disgraced, Bacon's health rapidly failed and he died in 1626.

One of Bacon's most significant works, *New Atlantis*, was published the next year, posthumously and incomplete. It features a research institution that he hoped would be a model for future scientific advancement, *Salomon's House*, in which a hierarchy of workers performed and interpreted experiments from Nature.⁴¹

In 1662, James' grandson, Charles II, gave a charter to the Royal Society of London, a scientific institution closely modeled from Salomon's House,⁴² and thereby restored Bacon's reputation.⁴³ This same year Charles also restored the reputation of logwood by repealing the Act of Elizabeth and the Proclamation of James. Charles declared,

the ingenious industry of modern times hath taught the dyers of England the art of fixing colours made of logwood . . . so as that, by experience, they are found as lasting as the colours made with any other sort of dyeing-wood whatever, and on this ground it repeals so much of the Statute of Elizabeth as related to logwood, and gives permission to import it and use it for dyeing.

It is no coincidence that shortly after gaining control of Jamaica and its produce that the Crown began to encourage, rather than discourage, the profitable trade of logwood.

LOGWOOD SLAVES

Much of our first-hand knowledge of the logwood trade comes from British naval officers. By all accounts, logwood

³⁵For a perspective of Bacon as a jurist, see ref. 35.

cutting was a miserable business mainly because the trees grew in inhospitable settings. According to Lieutenant Cook,

... it is a swampy ground that abounds with the logwood ... In travelling thro' the swamps it is very troublesome, the mules being knee deep, in the dry season, in a stiff blueish mud, often times nearly sticking fast, and the boughs of the logwood trees so low, as to oblige you to lay flat on the mules shoulders, whilst the animal is all that time plunging in endeavouring to extricate himself from the mire.⁴⁴

Increased demand for a product that could only be harvested by toiling in malaria and alligator infested waters⁴⁵ meant that logwood cutters were now needed in larger numbers than could be supported by the occasional privateer. Slavery was the mercantilist's solution to such problems.

While passing out a charter to the Royal Society, King Charles saw fit to also sanction the Company of Royal Adventurers of England, the successor of an organization formed for selling dyewoods. Transformed and incorporated as the notorious Royal Africa Company⁴⁶ it delivered logwood cutters in the Indies for the price of 17 pounds per head, the value of about six tons of logwood.⁴⁷

Some historians have said that logwood cutting in British Honduras was characterized by a comrade-like, master-slave relationship in which Baymen, as the English logwood cutters were known, and Africans worked side-by-side, quite different from the exploitation that occurred on the sugar islands.⁴⁸ However, Captain William Dampier (1652–1715), having lived among the Baymen for three years, does not paint a picture of kinder, gentler captors. According to Dampier,

(The Baymen) thought it a dry Business to toil at cutting Logwood (and) they often made Sallies out in small Parties among the nearest Indian Towns, where they plundered and brought away the Indian Women to serve them at their Huts; and sent their Husbands to be sold at Jamaica.⁴⁹

LOGWOOD IN THE ROYAL SOCIETY OF LONDON

Dampier first sailed to Yucatan after a brief period mismanaging a Jamaican plantation and he became the most important chronicler of the Baymen. It is wise to trust Dampier because he is remembered for his careful observations. The above passage appeared in his *Voyages and Descriptions* which also introduced the flora and fauna of the West Indies to a British audience. It was hailed by the Royal Society as a great contribution to natural philosophy; a summary quickly appeared in the Society's *Philosophical*

Transactions.⁵⁰ Dampier encouraged the scientific reception of his travel book by dedicating it to the President of the Royal Society, who subsequently introduced Dampier to the leading scientists of the day including Sir Hans Sloane (1660–1753), secretary of the Royal Society and editor of *Philosophical Transactions*. Sloane's best remembered work, his *Natural History of Jamaica*,⁵¹ also treated the logwood trade and was strongly influenced by *Voyages and Descriptions*. Sloane and Dampier were characteristic of that sort of post-Bacon collector of facts who was much appreciated by some in the latter part of the seventeenth century. These travel books were considered as valuable to the scientific enterprise as any laboratory experiments of, say, Robert Boyle.

The chronicler of the natural world was not a type universally appreciated by their contemporaries. William King wrote vicious parodies of Sloane as an author and editor in *The Transactioneer*.⁵² After listening to Sloane's account of a Jamaican fossil fish from the *Philosophical Transactions*, a gentlemen inquires, "Pray what does this contribute to the Advancement of Natural Knowledge?" King replies,

You mistake the Design, it was never intended to advance Natural Knowledge; For who's the wiser for knowing that the Bones of a dead Fish have been dug up, or where? No, the true use of the Story is to amuse the Ignorant; for if they Talk of things that are out of the way ... they *are silenced at an instant*.

As scientists, we are apt to sympathize with Sloane but are moved in the opposite direction when we discover that he is as dispassionate about the human beings he encounters in Jamaica as he is about logwood.⁵¹

The Punishments for Crimes of Slaves, are usually for Rebellions burning them, by nailing them down on the ground with crooked Sticks on every Limb, and then applying the Fire by degrees from the Feet and Hands, burning them gradually up to the Head, whereby their pains are extravagant. For Crimes of a lesser nature Gelding, or chopping off half of the Foot with an Ax.

Curiously, Dampier, the shining example of the Royal Society, Bacon's house of progress, was a strong influence on Jonathan Swift, another savage critic of the science, suspicious of the legs given to the idea of progress during the Enlightenment. Gulliver, while introducing his own *Travels*, claims to have counceled Dampier on publication, but Swift's Lagado Academy, a satirical version of the Royal Society, is populated with buffoon-professors struggling to extract sunlight from cucumbers while begging coins for their labors. Earlier in his travels, Gulliver offers to supply the King of Brobdingnag with gunpowder attempting to seduce him with gory descriptions of the devastation that its possessor can wreak upon his opponents. Swift's sympathies are with the King who was "struck with horror" at Gulliver's proposal.

⁴⁴This account has often been credited to the famous circumnavigator, Captain James Cook; however, Haas has shown that there were two James Cooks in the English navy at this time and that observations of the logwood trade were made by the subordinate. (See "Perspective" by M. Haas, which is appended to the edition of Cook's "Remarks" [New Orleans, LA: Midameres Press, 1935]).

He (the King) was amazed how I (Gulliver) could entertain such inhuman ideas, and in so familiar a manner as to appear wholly unmoved at all the scenes of blood and desolation, which I had painted as the common effects of (gunpowder) . . . he protested, that although few things delighted him so much as new discoveries in art or in nature; yet he would rather lose half his kingdom, than be privy to such a secret.⁵³

Swift, like King, believed that the empirical gathering of facts must be undertaken for moral purposes and that to objectify the search for knowledge is to “unwittingly invite our vices into the intended moral vacuum of the field study and the laboratory.”⁵⁴

LOGWOOD IN PARIS

The French did not become major logwood traders, despite the early Norman interest in dyewoods from the Americas, until they began to exploit the western part of the island of Hispaniola, contemporary Haiti, originally a haven for French pirates from the smaller, northwestern island of Tortuga. During the middle of the seventeenth century, France, like England, was seeking to wrest a lucrative island colony from Spain. While Cromwell's force failed to overpower the Spanish, France succeeded in stealing part of Hispaniola through less dramatic actions. The French West India Company had a number of courtesans brought out from France and sold to buccaneers from Tortuga who frequently made hunting parties on the larger island.⁵⁵ These “famililes” served to establish a foothold. Their successors, while battling the eastern Spanish neighbors, succeeded in quickly covering Haiti with sugar plantations. A vast numbers of Africans—as many as 40,000 per year excluding mortality during the middle passage—considered essential by the colonists for economic development, were brought in chains to work the sugar plantations; Haiti soon become the most lucrative colony in the West Indies.⁵⁶

The logwood tree was introduced into Haiti shortly after it appeared in Jamaica. Its extract was a great success in France at the time of the revolution. In conjunction with tin mordants, it produced a blood-concealing brown-purple color, *prune de Monsieur*, which was very fashionable in Paris.¹ However, logwood exports from Haiti began to soar only after the turbulent years following the French Revolution and the successful slave rebellion led by Toussaint L'Ouverture, when wild logwood trees must have overwhelmed abandoned sugar cane fields. Logwood seed was carried effectively and passed intact by newly introduced, domesticated herbivores.⁵⁷ Only 750 tons of Haitian logwood made their way to France in 1791 and by 1860 this value had reached 52,000,⁵⁸ exceeding pounds of coffee produced.^{59,60}

Throughout the 18th and early 19th Centuries, French

chemists were encouraged by the State to study logwood systematically with the goal of increasing the yield of coloring agent from the raw material.⁶¹ The leading French logwood chemists included Charles-François Dufay (1698–1739), Jean Hellot (1685–1766), Pierre Joseph Macquer (1718–1784), Jean Louis Roard, and Claude Louis Berthollet (1748–1822).⁶² Ultimately, Michel Eugène Chevreul (1786–1889)⁶³ isolated **1a** as red crystalline needles (undoubtedly contaminated with small quantities of **1b**). Each of these aforementioned scientists served as a member of the French Academy of Sciences as well as *inspecteur général des teintures* at the state-sponsored Gobelins tapestry works.⁶⁴ Here we see the formation of a century-old tradition in logwood chemistry among the members of the French Academy, an institution founded in direct response to the Royal Society of London but one which functioned in a far more insular fashion.⁶⁵

Henri de Senarmont was also elected to the French Academy. Given his associations within this august community, it is easy to imagine that he would have been familiar with hematoxylin papers read at the Academy and had access to **1a** during his research into artificial pleochroism. From the early encounters with logwood in Yucatan, we can trace a path through the European colonization of the West Indies that plausibly puts logwood extract in Senarmont's hand in 1854. Eight years later, Senarmont died, and his chair in mineralogy at the French Academy was inherited by the most famous mid-nineteenth century crystal chemist, Louis Pasteur (1822–1895).

DYEING ENANTIOMORPHOUS CRYSTALS

Pasteur's demonstration of the link between macroscopic and microscopic chirality in his recognition of the enantiomorphous ammonium sodium tartrate crystals was a dramatic moment in the history of science. He noticed a difference in the presentation of the hemihedral facets that had been previously overlooked by Eilhard Mitscherlich (1794–1863), the discoverer/inventor of the Law of Isomorphism, the important advance in crystal chemistry of the previous generation. The great physicist Jean-Baptiste Biot (1774–1862) had often read Mitscherlich's papers to the French Academy; now, Pasteur was his favorite.

Pasteur's remembrance of his discovery, including Biot's response upon witnessing a levorotatory tartrate solution, “My dear child, I have loved science so much throughout my life that this sets my heart aflutter,” has turned it into a melodramatic moment.⁶⁶ Early accounts recall the interest and encouragement of another senior colleague also at Pasteur's side during this exciting time who is invariably omitted from recent renderings of the discovery: Henri de Senarmont.⁶⁷ Senarmont was quickly invited by Biot to examine Pasteur's mirror image crystals and was included in much of their correspondence. Pasteur to Biot: “Please inform M. Senarmont.” Biot to Pasteur: “I know M. Senarmont will be pleased.” “If M. Pasteur persists in the road he

¹Eventually, the United States became the imperial power in the Caribbean and, under Teddy Roosevelt, sent gunships to Haiti to protect the interests of the New York and Boston Dyewood Company. See ref. 60.

¹McClellan describes the fascinating case of the French Government sponsored efforts to steal the cochineal dye-producing beetle from the Spanish Main and cultivate it on cacti native to San Domingue. See ref. 61.

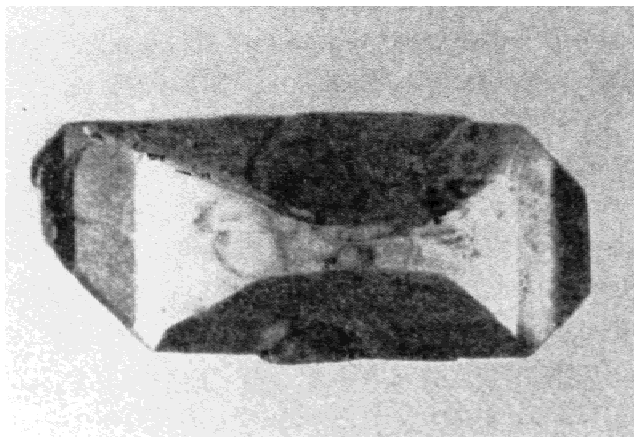
has opened," remarked Senarmont, "it may be predicted of him that what he has found is nothing to what he will find."^{468,69}

The association of Senarmont and Pasteur at the time when the former was beginning his researches on dyeing crystals and the latter was launching the science of molecular chirality, raises the intriguing possibility of a hypothetical collaboration. We can imagine Senarmont and Pasteur having brought the subject of dyeing crystals within the bounds of molecular chirality by selectively coloring and thereby resolving the sodium ammonium tartrate conglomerate with an optically active dye. There is no account of such an experiment. A visual, Pasteur-like resolution of enantiomorphous tartrate crystals via selective adsorption, was not reported until 1994 when Hanein, Geiger, and Ad-dadi deposited cultured epithelial cells differentially on dextro- and levorotatory crystals of calcium tartrate tetrahydrate.^{170,71}

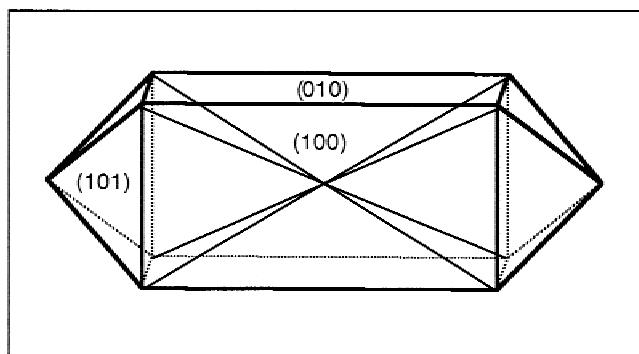
Can we accomplish the hypothetical Pasteur-Senarmont resolution of a conglomerate by color? Can we dye tartrate crystals? Have crystals been dyed enantioselectively and can **1** be used for this purpose? We can answer these questions affirmatively only by studying the literature, but with an extra century of experience.

Shortly after the discovery of the phenomenon of ferroelectricity in sodium potassium tartrate (Rochelle salt), an isomorph of Pasteur's sodium ammonium tartrate,⁷² Milligan⁷³ reported that crystals of Rochelle salt can selectively adsorb and overgrow dyes on particular surfaces. Dyed tartrate crystals were never again studied until we recently prepared some, invented others with colored {010} growth sectors, and recorded their linear dichroism and fluorescence lifetimes.^{6a} However, none of the dyes we used were optically active.

Ferroelectricity was discovered in the KH_2PO_4 (KDP) family of crystals in 1935.⁷⁴ $(\text{NH}_4)\text{H}_2\text{PO}_4$ (ADP) is an isomorph.⁷⁵ In 1946, Blattner, Mathias, and Merz⁷⁶ were systematically studying the effects of impurities in ferroelectric crystals. Making reference to Seherr-Thoss's colored ADP crystals described previously, they deposited colored crystals of KDP and ADP from solutions containing several percent **1**. They determined that the organic colorant affected a 2°C reduction of the Curie temperature in the resulting mixed KDP/**1** crystals.⁷⁶ Because they were primarily interested in how impurities modulate the ferroelectricity, they provided no discussion of the optical nor morphological characteristics of their crystals but they did present an unlabeled photograph of one of their specimens (Fig. 1). The crystal pictured seemed odd to us because it appeared that only two of the four symmetry related prismatic growth sectors in the tetragonal crystals were colored. We initially interpreted this as an idiosyncrasy of the growth of the particular crystal photographed but we could not support this interpretation after having successfully col-



(a)



(b)

Fig. 1. a: Photograph of KDP or ADP crystal grown from solution containing **1** (see ref. 76). **b:** Idealized representation of KDP or ADP crystal for comparison.

ored KDP crystals where only two opposing growth sectors were red.

Hematein (**1b**), with an absolute S configuration,⁷⁷ does indeed stain only one pair of the four prismatic sectors: the {010}, but not the {100} sectors. The *a* and *b* faces of KDP are related by diagonal glide planes in space group $\bar{A}2d$ and are thus enantiomorphous (Fig. 2). Therefore, **1b** must recognize the KDP faces *enantiospecifically*. Seherr-Thoss also must have observed this selectivity in staining the prismatic faces of the isomorph ADP in 1879. *He could have partitioned the prismatic faces of ADP crystals into enantiomorphs merely by judging the color of their associated growth sectors.* This is remarkable given the difficulty of demonstrating the selective adsorption of racemates by chiral mineral crystals. Bonner⁷⁸ has reviewed the literature on the recognition of enantiomers by minerals and the relation of enantioselective supramolecular adsorption to the origin of bimolecular handedness. He showed that this was an enterprise fraught with difficult analyses and conflicting interpretations of controvertible data. Surprisingly, as far back as 1879, Seherr-Thoss did indeed produce a resolution by color of enantiomorphous crystal surfaces. However, it would have been too remarkable for him to recognize his observations as such. KDP is optically inactive in solution and its idealized crystals have D_{4h} point

⁴Senarmont was an advocate for Pasteur to fill a vacancy in the French Academy in 1857. See ref. 68.

⁷This was one experiment in a tradition at the Weizmann Institute of making stereochemistry manifest in the appearance of crystals. See ref. 71.

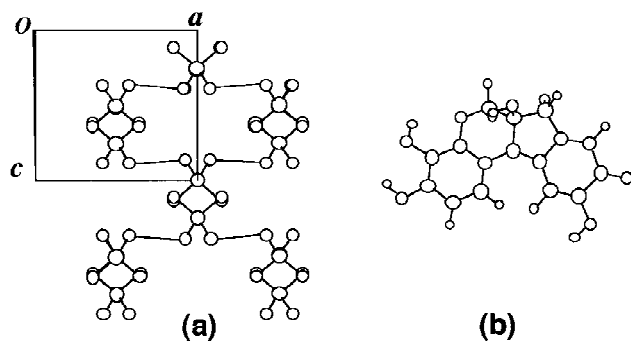


Fig. 2. Relative dimensions of the KDP phosphate lattice and **1b**. **a:** Absolute stereochemistry of the (010) face of KDP. K^+ ions have been omitted for clarity. Long connections represent H bonds. **b:** Absolute (S) configuration of **1b** with geometry optimization based on the AM1 Hamiltonian.

symmetry. Seherr-Thoss could not have known that the tetragonal axis was improper (S_4); the crystal structure of KDP was not determined until 1930.⁷⁹ Only in hindsight can we assign the proper stereochemical interpretation to his experiment.

HEMATOXYLIN AND ITS DERIVATIVES IN^m CRYSTALLINE STATES

The isolation of **1a** as crystalline needles by Chevreul was an important step in the development of logwood chemistry which ultimately led to efforts by several research groups to determine the constitution of hematoxylin at the beginning of this century.⁸⁰ But, the structure of Chevreul's crystals has not been reported. Accurate structure determinations of **1a** and **1b** would be a first step toward understanding their enantioselective associations with KDP crystals. Here, then, we report the structure of Chevreul's crystals⁶³ which were obtained as long (1 cm), red, tetragonal needles when commercial hematoxylin (Aldrich) is recrystallized by evaporation of water solutions at room temperature. Repeated crystallizations from a 1% aqueous $NaHSO_3$ solution containing a small amount of urea will ultimately yield colorless needles, the initial red color presumably due to the presence of small quantities of **1b**. A needle fragment was mounted in epoxy on a glass fiber. Crystal data: $C_{16}H_{14}O_6 \cdot 3H_2O$, $M = 302.283 \text{ g mol}^{-1}$, crystal dimensions $0.45 \times 0.25 \times 0.10 \text{ mm}$, tetragonal,⁸¹ space group $P4_1$ (No. 76), $a = 13.898(3) \text{ \AA}$, $c = 8.651(2) \text{ \AA}$, $V = 1666.6(2) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.205 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 0.871 \text{ cm}^{-1}$, $\lambda = 0.7107 \text{ nm}$, $Z = 4$, 1403 reflections collected, 1240 observed ($I < 3.0\sigma(I)$) with $5.0^\circ < 2\theta < 47.5^\circ$. Intensity data were recorded at 296 K with an Enraf-Nonius Kappa Axis CAD4 diffractometer ($\omega - 2\theta$ scans) and corrected for Lorentz and polarization effects. Heavy atoms were refined anisotropically (Fig. 3) and hydrogen atoms were placed in

idealized positions and refined with a riding model ($d(\text{C-H } sp^3) = 1.01 \text{ \AA}$, ($d(\text{C-H } sp^2) = 0.96 \text{ \AA}$) using the programs contained in CRYSTALS.⁸² $R = 0.068$, $R_w = 0.072$ with max./min. residual electron densities of $0.30/-0.29 \text{ e}^- \cdot \text{ \AA}^{-3}$. Atomic positional parameters can be found in Table 1. Refinement in the enantiomorphous space group $P4_3$ gave $R = 0.077$ and $R_w = 0.098$; on this basis and by comparing those reflections most sensitive to anomalous dispersion, we were able to conclude that the absolute configuration is indeed (3S, 4R) consistent with that determined by classical degradation studies⁷⁷ and by NMR spectroscopy.⁸³

The molecules of **1a** form helical channels that encapsulate three water molecules per unit cell (Fig. 4). The channels are assembled from hydrogen bonds within and between helices, which are buttressed by chains of three water molecules that crisscross individual channels. Specifically, O(4) in some molecule of **1a**, is joined by water molecules containing O(7), O(8), and O(9), to O(2) associated with another molecule **1a** related by a 4_1 operation. O(2) can then also make a direct H bond to an O(4) atom in a molecule related by consecutive 4_1 operations to the original molecule. Diagonal channels are "stitched" together by H-bonds between O(2) and O(5) atoms. The ring geometry of the molecule is ordinary and compares favorably with that previously determined for a tetramethylated derivative.⁸⁴

We measured the absorption spectrum of KDP crystals grown in the presence of solutions of **1** by evaporation in air at room temperature. The crystals, colored red in two of the four prismatic growth sectors, absorb visible light at 450 nm(br) and 560 nm which compares favorably to the

TABLE 1. Atomic positional parameters ($\times 10^4 \text{ \AA}$) for $C_{16}H_{14}O_6 \cdot 3H_2O$

| Atom | x/a | y/b | z/c |
|-------|-------------|------------|------------|
| C(1) | 0.1386 (8) | 0.5757 (8) | 0.019 (2) |
| C(2) | 0.0653 (9) | 0.6377 (8) | 0.061 (2) |
| C(3) | -0.0157 (8) | 0.6044 (9) | 0.130 (2) |
| C(4) | -0.0247 (8) | 0.505 (1) | 0.161 (2) |
| C(5) | 0.0486 (9) | 0.4411 (8) | 0.118 (2) |
| C(6) | 0.1297 (9) | 0.4779 (9) | 0.052 (2) |
| C(7) | 0.1854 (9) | 0.3228 (9) | -0.016 (2) |
| C(8) | 0.1314 (9) | 0.2774 (9) | 0.120 (2) |
| C(9) | 0.0385 (8) | 0.3328 (8) | 0.147 (2) |
| C(10) | 0.0993 (9) | 0.1752 (9) | 0.081 (2) |
| C(11) | 0.0041 (8) | 0.1915 (8) | 0.001 (2) |
| C(12) | -0.0310 (9) | 0.2809 (9) | 0.046 (2) |
| C(13) | -0.0464 (9) | 0.1313 (9) | -0.101 (2) |
| C(14) | -0.135 (1) | 0.162 (1) | -0.152 (2) |
| C(15) | -0.1716 (9) | 0.251 (1) | -0.115 (2) |
| C(16) | -0.1190 (9) | 0.3117 (9) | -0.016 (2) |
| O(1) | 0.0764 (6) | 0.7332 (6) | 0.025 (2) |
| O(2) | 0.2206 (6) | 0.6118 (6) | -0.045 (2) |
| O(3) | 0.2088 (5) | 0.4231 (6) | 0.006 (1) |
| O(4) | 0.1891 (6) | 0.2827 (6) | 0.255 (1) |
| O(5) | -0.1840 (6) | 0.1048 (6) | -0.254 (1) |
| O(6) | -0.2574 (7) | 0.2784 (8) | -0.173 (2) |
| O(7) | 0.552 (6) | 0.664 (4) | 0.33 (1) |
| O(8) | 0.478 (2) | 0.730 (3) | 0.105 (4) |
| O(9) | 0.525 (3) | 0.604 (3) | -0.33 (1) |

^mCrystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (1223) 336-0333; e-mail: teched@chemcrs.cam.ac.uk).
ⁿThere are several reports in the literature of monoclinic crystals of **1a**. We have never observed them. See ref. 81.

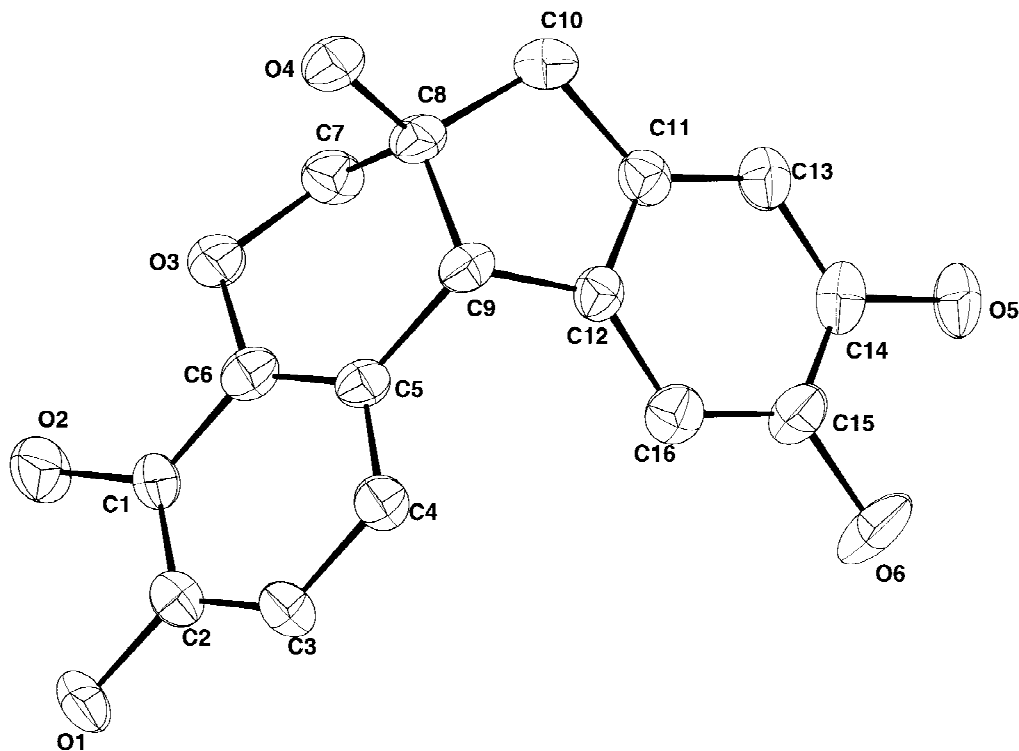


Fig. 3. ORTEP representation (50% probability ellipsoids) of the nonhydrogen atoms, excluding water molecules of crystallization, in the crystal structure of **1a**.

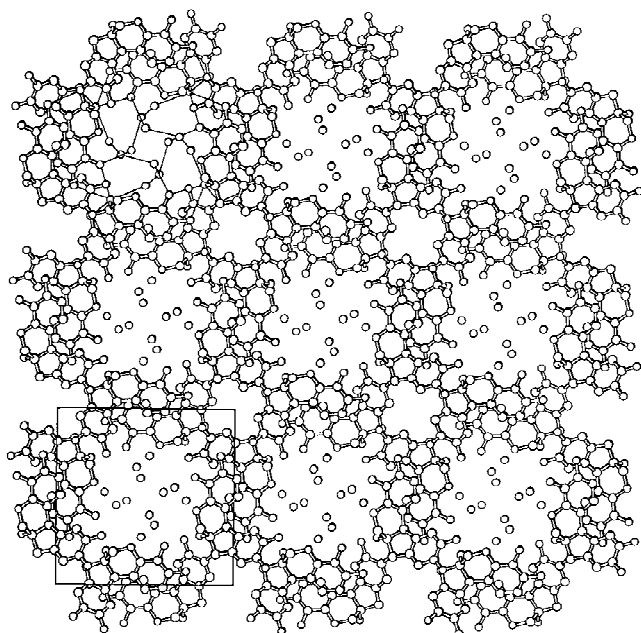


Fig. 4. Nine unit cells of the crystal structure of **1a** · 3H₂O viewed along the *c* axis. Hydrogen atoms have been omitted for clarity. Hydrogen bond connections between oxygen atoms are indicated as thin lines only in the upper left-hand channel. The square section of the unit cell is drawn upon the lower left-hand channel.

absorption spectrum of **1b** in distilled water showing maxima at 445 nm and 558 nm.⁸⁵ On this basis, we conclude that the colored species in KDP crystals is **1b**.

The inclusions of **1b** in KDP are strongly dichroic; absorption is pronounced for light polarized along *a* or *b* but absent for light polarized along *c*. INDO/S calculations⁸⁶ indicate that the electric dipole moment for the most intense visible transition runs along the vector connecting the ispo-phenyl carbons thus suggesting that molecules of **1b** are oriented such that this vector is parallel to [110].

CONCLUSION

No portrait of Europeans in the Caribbean would be complete without mention of the Dutch⁸⁷ who stockpiled logwood on St. Eustacius and slaves on Curaçao.⁸⁸ Similarly, no study of dyeing crystals would be complete without mention of Jan Retgers (1856–1896),^{89,90} former Java State Geologist and retiree in The Hague, who was the first scientist to attempt to produce a family of dyed crystals by systematically adding colored compounds to saturated salt solutions. Retgers was motivated to understand the limitations of Mitscherlich's Law of Isomorphism and seized upon Senarmont's salt as a hybrid material that could not be reconciled with this Principle. It had been presumed that substitution in a mixed crystal was only possible if the foreign molecules replace very similar collections of atoms; needless to say **1b** and Sr(NO₃)₂ have different constitutions. From some 962 experiments (assuming he crossed all 26 dyes with each of 37 salts listed in his paper) Retgers

TABLE 2. Dyeing crystals with hematoxylin

| Scientist (year) | Host crystal | | | Ref. |
|---------------------------|---|--|---------------------------------|------|
| | Sr(NO ₃) ₂ · 4H ₂ O | NH ₄ H ₂ PO ₄ | KH ₂ PO ₄ | |
| Senarmont (1854) | √ | | | 10 |
| Rosenbusch (1873) | X | | | 11 |
| Bertin (1877) | √ | | | 14 |
| Seherr-Thoss (1879) | X | √ | | 13 |
| Becquerel (1888) | X | | | 12 |
| Retgers (1893) | | X | X | 90 |
| Blattner et al. (1946) | | √ | √ | 76 |
| Kahr et al. (1996) | X | X | √ | 66 |

√ indicates a colored, pleochroic crystal; X indicates no crystal coloration.

obtained four mixed crystals that he deemed worthy of further study: K₂SO₄/Bismarck Brown, KNO₃/Nigrosin, NH₄NO₃/Indulin, and BaCl₂ · H₂O/Water Blue. But, he also could not prepare Senarmont's salt. And, unlike Seherr-Thoss and despite the subsequent experiments of Blattner et al. and the present authors, Retgers failed to stain any crystal with logwood (*Kampecheholzextract*), including (NH₄)H₂PO₄ and its isomorph, KH₂PO₄.

At this juncture it is useful to summarize the results of all of the attempts to dye crystals with **1** as we do in Table 2. We find two successes, out of seven reported attempts, to stain Sr(NO₃)₂ · 4H₂O, and four successes, out of seven reported attempts, to stain KDP or ADP. What accounts for this unscientific irreproducibility?⁹¹ One reason might be the result of the mercurial acid/base, oxidation/reduction, and coordination chemistries of **1** previously mentioned, which must render it highly susceptible to experimental conditions, an unfortunate situation when dealing already with the highly kinetically controlled processes of crystal growth from solution. A second reason might be that *Hematoxylon campechianum* has frequently been confused with other red woods, especially Brazilwood and others from the *Caesalpinia* family (see, for example, ref. 92).

POSTSCRIPT

Germany, shut out of the colonization of the West Indies, could not profit from the logwood trade. Instead she supplanted it. The development of the synthetic dyestuffs industry in Germany signaled the end of the heady days of logwood in commerce and politics. In 1923, the year Kurt Mislow was born, the French, now dependent on Germany's synthetic dyes, occupied BASF dyeworks that had fallen behind in their reparation payments.⁹³ Logwood extract experienced a renaissance as a dye source in the United States during the second world war when German trade was again interrupted and substitutes for aniline dyes

were needed. Today logwood is still used in histology, in specialty silk dyeing applications, and ink formulations, but it is unlikely to attract the attention of pirates. Logwood chips may be best known to readers of this article who, like myself, found a bottle of them included in the chemistry kits that were popular with American children in the 1960s.^P

ACKNOWLEDGMENT

We thank Kurt Mislow who taught us at least two things that we hope are supported by this essay: "Out of the crooked timber of humanity, no straight thing was ever made" ["Aus so krummen Holze, als woraus der Mensch gemacht ist, kann nichts ganz Gerades gezimmert werden"].⁹⁴ and out of logwood, no achiral thing was ever made. The sources for this study were obtained at the Libraries of Columbia University, New York University, Princeton University, Purdue University, the University of Washington and Yale University, as well as the New York City Public Library. We thank J. Daniel Bryan for his contributions to the crystal structure determination of hematoxylin and attempts to resolve racemates by cocrystallization. We also thank Guy Crundwell for his struggle to prepare Senarmont's salt, Dr. Sei-Hum Jang for helpful discussions, and the National Science Foundation for financial support.

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⁹¹Similar variability can be seen in the histological use of **1a**. See ref. 91.

^PWe recently found such an old Gilbert chemistry set in a shop in Lafayette, Indiana, and persuaded the owner to sell to us just the bottle of logwood, arguing that it would never be missed.

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