

Fascinating Organic Molecules from Nature

1. Some Exotic Red Pigments of Plant Origin

N R Krishnaswamy and C N Sundaresan



(left) N R Krishnaswamy was initiated into the world of natural products by T R Seshadri at University of Delhi. He has taught at Bangalore University, Calicut University and Sri Sathya Sai Institute of Higher Learning. He has the uncanny ability to present the chemistry of natural products logically and with feeling.

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Keywords

Pigments of red sandalwood, Safflower, chica red, Brazil wood, Dragon's blood, Miro wood and Kamala dye.

From the very beginning of civilization, humans have used chemicals from Nature – most of them comparatively small organic molecules now designated as secondary metabolites – for a variety of purposes such as pigments and dyes, arrow and fish poisons and olfactory stimulants.

It is no wonder that many eminent chemists were attracted to these materials to elucidate the underlying chemistry. Willstatter, Baeyer, Richard Kuhn, Karrer, Robinson and others made pioneering studies and isolated several new compounds which were included in the curriculum of earlier days. Another pioneer, A G Perkin, second son of Sir W H Perkin, was, according to his elder brother, W H Perkin, Jr, a dabhand with natural dyes. He and A E Everest wrote a book *The Natural Organic Colouring Matters*, first published in 1918, which was like a *Bible* to natural product chemists of yesteryears. (You can now read it on line!).

As organic chemistry progressed, making leaps and bounds, the newer exciting discoveries gradually pushed the study of several of these compounds out of the curriculum. While one can understand this trend, one also feels sad that students these days are not aware of several interesting facets of natural products chemistry which link organic chemistry with folklore, traditional practices by diverse native communities, indigenous systems of medicine and current ideas of chemical structure and reactivities. It is not possible to fill in these gaps in textbooks which are designed to cater to the needs of students preparing for various university examinations, but articles such as those contemplated here can provide students with knowledge that can be stimulating, interesting as well as enjoyable!

We begin the series with ‘Some exotic red pigments of plant origin’. Several red coloured dyes and pigments of vegetable origin have been known to mankind ever since the dawn of civilization. Their varied uses have been mentioned in ancient literature, including the *Ramayana*, folklores, travelogues and accounts of several explorers. Their chemistry is equally fascinating and has attracted the attention of a number of eminent organic chemists. In this article, we examine a few of these pigments isolated from plant materials found in different parts of the world. They include the pigments of the red sandalwood, the colourants of safflower, the exotic cosmetic chica red, brazilin from the Brazil wood (and the related hematoxylin), the compounds from the Dragon’s blood, the sesquiterpene quinones of the Miro wood and rottlerin, the main red pigment of Kamala dye.

Introduction

From time immemorial, men and women have been interested in improving their appearance by using colours. Primitive people, who wore little or no clothes, painted their faces and other parts of their bodies. As civilization progressed, the art and practice of dyeing clothes used to cover human bodies came into existence. The colouring materials exhibiting vivid colours were obtained from a variety of natural sources including locally available plant parts. The scientific investigations of these pigments began only after European explorers brought back to Europe exotic specimens from different parts of the world. Their stories are, therefore, interwoven with strands of history, travelogue, folklore from ancient civilizations and chemistry. The study of these pigments can provide a student with a wealth of composite knowledge embracing science and humanities. In this article, the chemistry of some of these pigments obtained from plant parts will be briefly discussed. The examples chosen are mainly those which do not figure in the present day organic chemistry textbooks. For reasons not quite clear, the ancients preferred the red colour and its many shades for use as a facial paint and for dyeing clothes. One factor, perhaps, is that red colour, apart from the

Prominent among the European explorers who made significant contributions to the advancement of science was Alexander von Humboldt (1769–1859). Charles Darwin described him as the greatest scientific traveller who ever lived.



Red sandalwood, also known as red sanders, is a durable hardwood. Its Sanskrit name is Rakthachandana. It is offered as the main 'prasadam' in the Sun temple in Adityapuram, near Kottayam, in Kerala.

The French chemist, P J Pelletier (1788–1842) and his co-worker, J B Caventou are best known for their pioneering studies on alkaloids. The pomegranate alkaloid, pelletierine is named in honour of Pelletier.

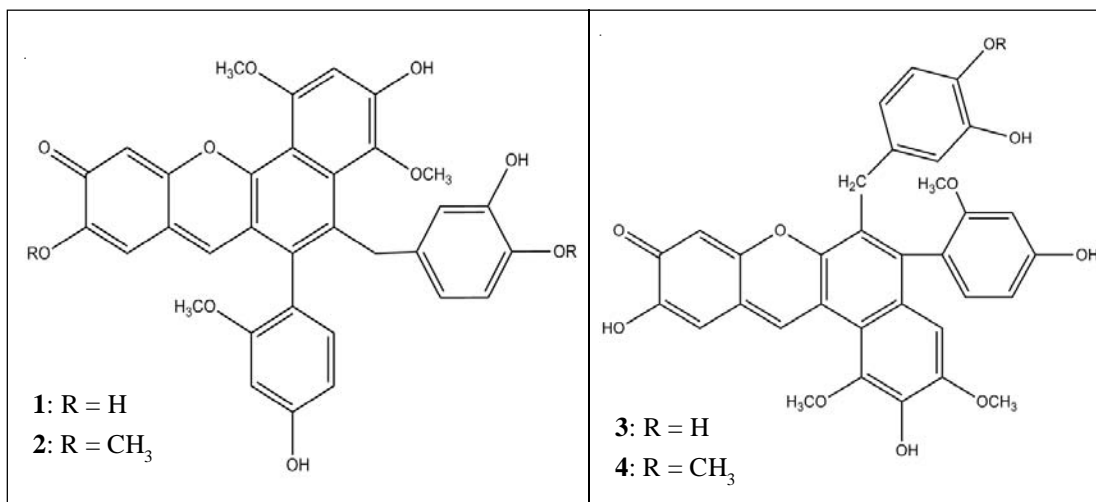
ubiquitous green of foliage, is the most dominant colouration sported by plants. We begin our journey into this world of red-coloured pigments of plants in India.

The Chemistry of Santalin, the Colouring Matter of the Red Sandalwood

Red sandalwood or red sanders is a valuable timber of South India. Its botanical name is *Pterocarpus santalinus* and it belongs to the family Leguminosae. Its deep red-coloured heartwood has been used in India for making figurines and as a paste in cosmetic preparations. In China it was used for making highly prized furniture. It has also been used in the Ayurvedic system of medicine as an antiseptic and wound-healing agent. There are numerous references to it in Valmiki's *Ramayana*. It seems when Hanuman first saw Ravana in the latter's palace (during his search for Sita), he found the demon king liberally smeared with red sandalwood paste on his chest (*Sundara Kanda* canto 10)! It was customary for pilgrims to Tirupati to return with figurines carved out of this wood (along with the mandatory laddus!). You could find these figurines prominently displayed in 'Golu' (or dolls exhibition) during the Navarathri festivals in South India.

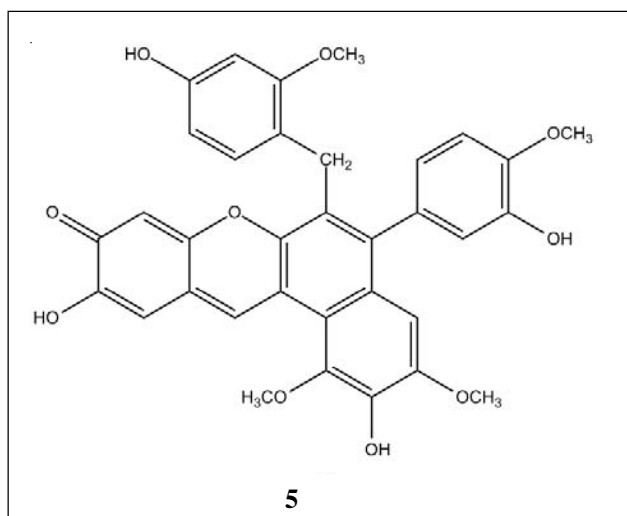
The French chemist, Pelletier, was, perhaps, the first to isolate the pigment of this wood in a crude form in the year 1833. He named it santalin and gave it an empirical formula. However, structural studies could be undertaken only 120 years later after the pigments were separated into pure compounds. Two of these, santalin A and santalin B, could be obtained in the pure state. In a series of publications in the *Journal of the Chemical Society*, Alexander Robertson and co-workers unraveled the major part of the structures of these pigments which they recognized as quinonoid anhydro bases. In 1972–73, three groups of workers, namely Seshadri and his co-workers in Delhi, Whalley of the Robertson school and Nasini and co-workers of Milan simultaneously put forward structure (1) for santalin A and (2) for santalin B based on extensive chemical studies supported by some crucial spectral data and biogenetic considerations.



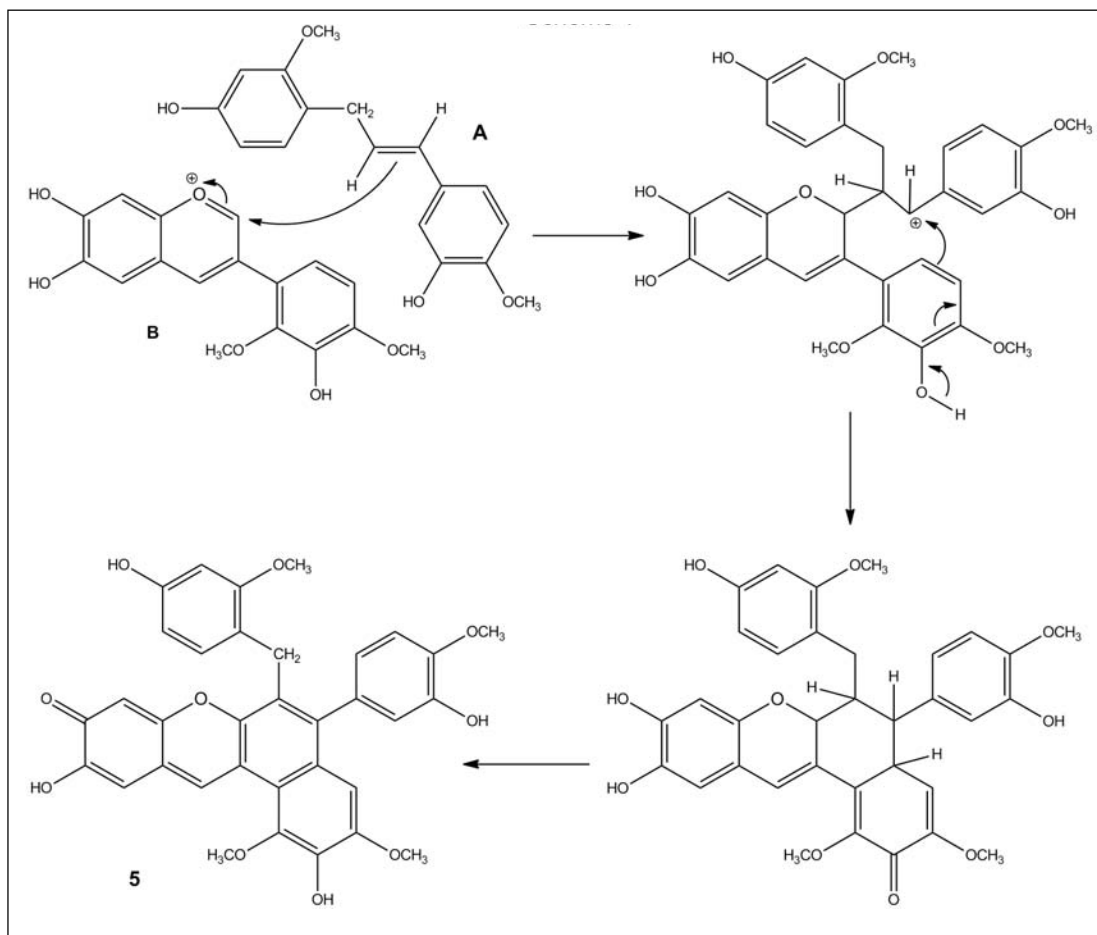


However, with the use of advanced nmr spectral methods such as COSY (both homo and hetero), NOESY and HMBC these structures were later revised to **(3)** and **(4)**. Another pigment, santarubin, is an isomer of santalin B and has the structure **(5)**.

The biosynthesis of santalins and santarubin apparently involves an oxidative coupling of an isoflavene derivative with a benzylstyrene. Biogenetic schemes have been suggested such as the one shown in *Scheme 1* for the formation of santarubin. The alternative possible involvement of the double bond of the styrene component would lead to santalins. However, considering



Correlation spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY) and heteronuclear multiple bond correlation (HMBC) are techniques used in two-dimensional NMR spectroscopy.



Scheme 1.

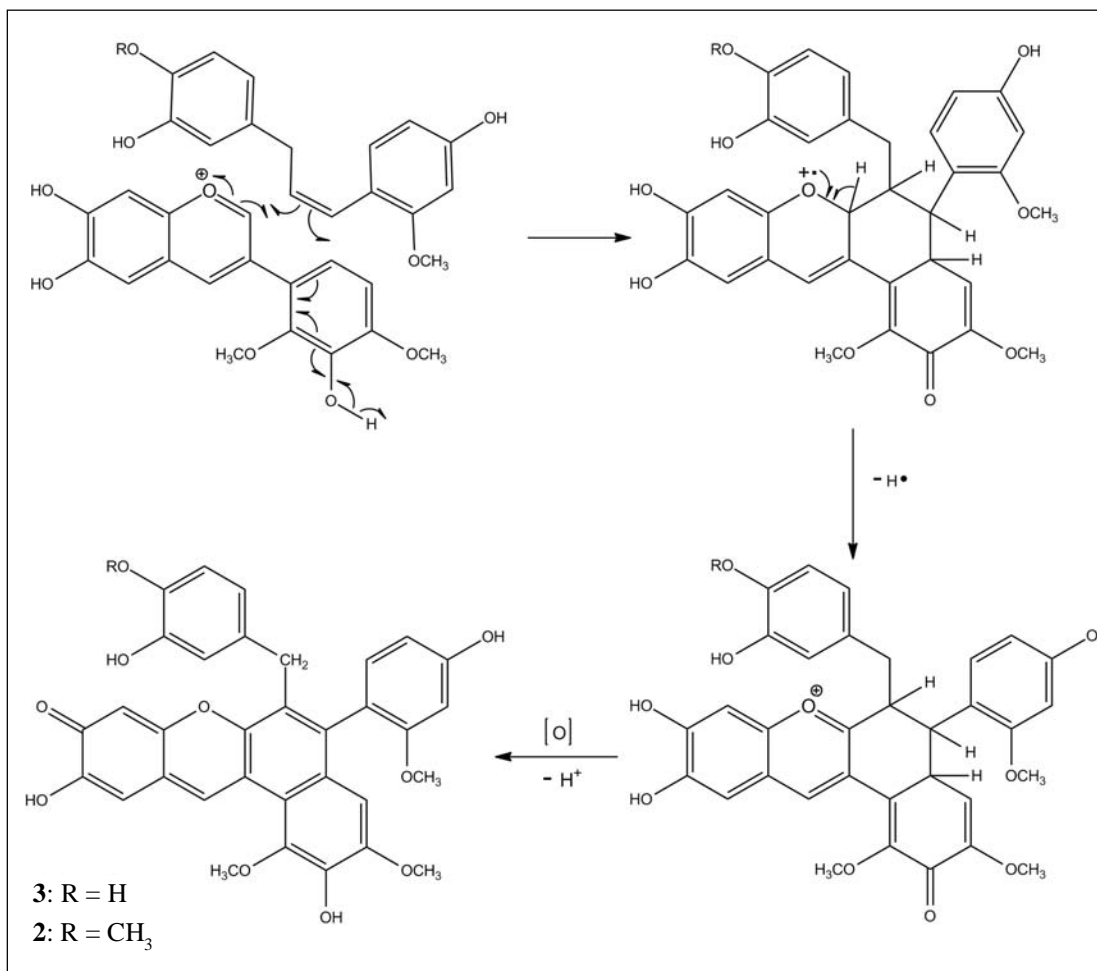
that biochemical oxidations involve one electron transfers rather than an ionic mechanism an alternative biogenetic scheme is suggested in this article as shown in *Scheme 2*.

Red sandalwood pigments continue to be used as a food colouring and for imparting a burgundy colour to alcoholic beverages. The mixture is also used to dye silk, wool and leather. More important is its use as a dye sensitizer in solar cells.

Carthamin and Related Compounds

In our quest for exotic pigments we now look at another material found in the same region as the red sandalwood. This plant, *Carthamus tinctorius*, commonly known as safflower or bastard

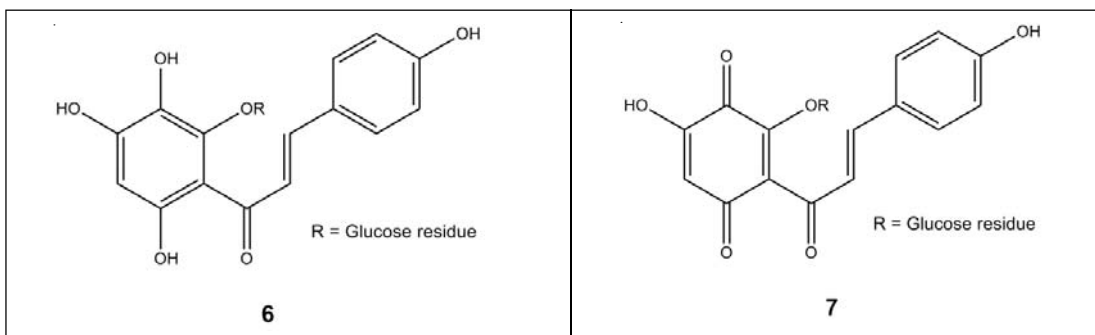




saffron is present cultivated extensively in Andhra Pradesh and also in the neighbouring states of Maharashtra and Karnataka mainly for its seed oil which is used as a cooking medium. However, in ancient times, it was grown for its flowers which yield a rich red coloured pigment known as carthamin. The plant is also grown in China and that variety has a deeper red colour than the Indian one. Kametaka and A G Perkin were the first to isolate a red crystalline compound in the year 1910 and they named it carthamin. Later, two compounds were isolated, one yellow and the other red. Kuroda was, perhaps, the first to recognize these compounds as chalcone derivatives. Further studies by Seshadri and Thakur in 1960 confirmed that the red coloured

Scheme 2.

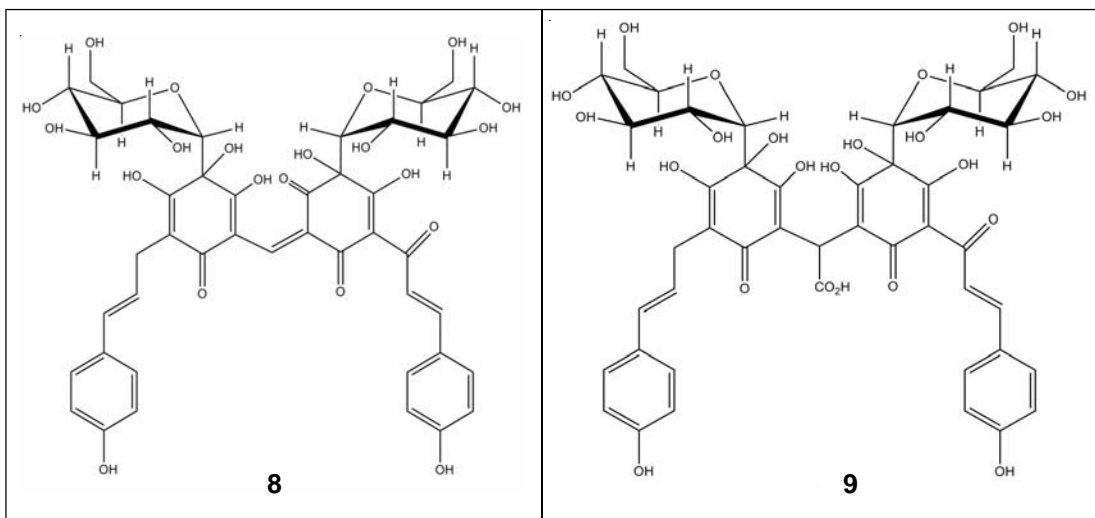
In Spain and the regions bordering the eastern shore of the Mediterranean Sea (the Levant), safflower plants are used in the preparation of the cosmetic rouge.



One of us (NRK) recalls that when Professor Seshadri requested Professor W Bradley for a sample of carthamin, it was taken out of the personal collections of Professor Perkin in the colour laboratories of Leeds University as a special gesture.

pigment is a quinonoid compound derived from the yellow material to which they assigned the structure 2', 3', 4', 6', 4-tetrahydrochalcone -2'-O-glucoside (**6**); the quinone should, therefore, be (**7**).

However, later studies by Japanese workers (Obara *et al.*, 1979, 1981; Takahashi *et al.*, 1982, 1984) showed that the structure of carthamin is much more complex though it is, indeed, a quinochalcone. The correct structure is (**8**). It is enzymatically derived from a yellow precursor, precarthamin which has the structure (**9**). Newly bloomed flowers of the plant are, indeed, yellow in colour and they gradually change to red due to the transformation of (**9**) into (**8**). The enzyme *precarthamin decarboxylase* responsible for this oxidative decarboxylation has been isolated.



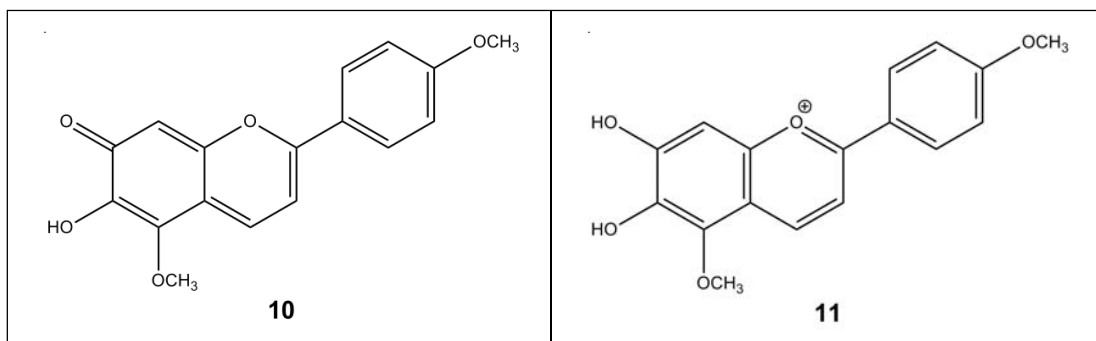
Carajurin

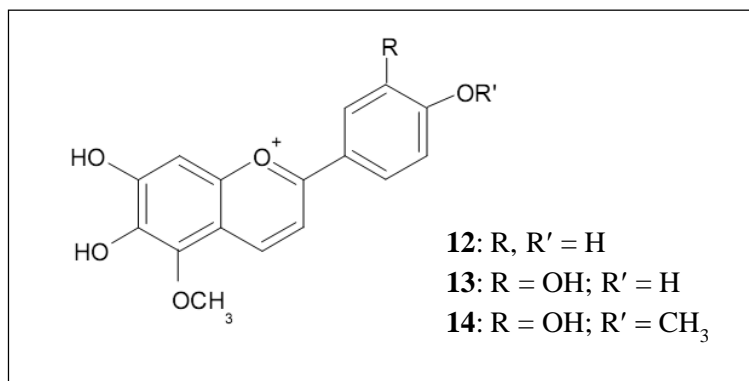
We shall now move to the other side of the globe. *Carajura*, also known as chica red, is a rare pigment prepared by the Indians of the Rio Meta and Orinoco river basins in the South American tropics. Von Humboldt recorded its use as a facial pigment by the natives of Brazil, Bolivia and Guiana during his travels through these regions. He observed that the process of extracting the colouring material from the leaves of the liana, *Arabidaea chica* (*Bignonia chica*), was tedious and the yield small, thus accounting for the high cost of the pigment: "It is so valuable that it is said of a poorer native that he can paint only half of his face!"

From a specimen of the crude pigment, Chapman, Perkin (AG) and Robinson isolated pure carajurin to which they assigned the structure **(10)**. Subsequent studies have shown that it is better represented by the 3-desoxyanthocyanidin structure **(11)** rather than the anhydro base **(10)**. Chemometric studies have shown that at pH 1 carajurin is present entirely as the flavylium cation **(11)**. Increasing the pH does bring about some change but not to the extent observed with the more common 3-hydroxy anthocyanidins. While proton nmr spectral data are in agreement with structure **(11)**, mass spectral data indicate that it is in equilibrium with the anhydro base form **(10)**.

A recent phytochemical examination of the chica leaves revealed the presence of three more related compounds, namely, desmethyl-carajurin **(12)**, 5-methoxy-6,7,3', 4'-tetrahydroxyflavylium **(13)** and its 4'-O-methyl ether **(14)** as minor components.

For the isolation of carajurin, Chapman, Perkin and Robinson used a material obtained from Messrs Wright, Layman and Umney, wholesale druggists. It was in the form of red coloured fragments packed in woven baskets.



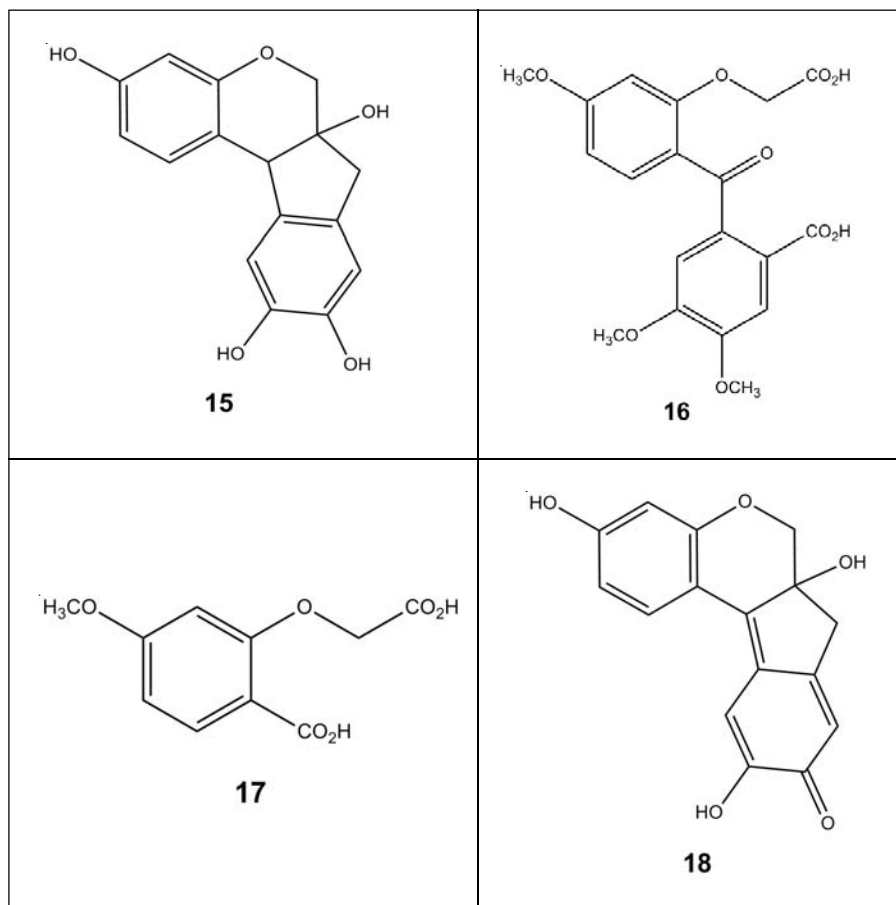


Brazilin and Hematoxylin

Portugese explorers found trees of *Caesalpinia* species growing profusely on the Atlantic coast of South America. They called the tree Braza because of the deep red colour of its wood and the land on which it grew came to be known as Brazil. The true Brazil wood is *C. braziliensis*. The related sappan wood, *C. sappans*, is common to the warmer regions of Asia. *C. crista* yields the best pigment and this tree is seen in Jamaica as well as in Brazil. When freshly cut, the heartwood appears a light yellow but soon turns deep red on exposure to air. Long before the discovery of America, sappan wood dye was used in India.

Brazilin is extracted from powdered heartwood of the Brazil tree by boiling with water or better still with a hot solution of alum. Apart from being used as a dye it is also used in the preparation of red inks.

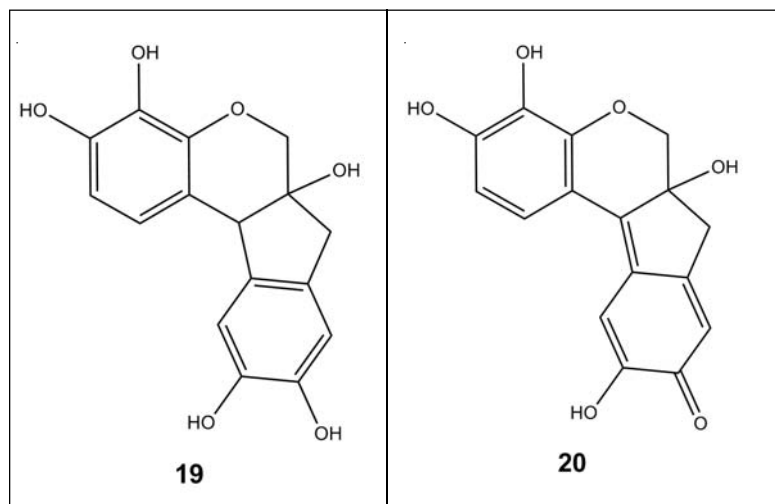
The colouring matter from the wood became a craze in Europe and it was used to dye velvet. The French chemist, Chevreul isolated the pigment which was named brazilin. Following the leads from earlier studies, Robinson and his co-workers investigated the structure of brazilin in great detail and arrived at the structure (15). One technique that was used in preliminary studies was dry distillation, a method rarely used these days, which gave resorcinol as a product. Oxidative degradations employing potassium permanganate yielded 2,4-dihydroxybenzoic acid (β -resorcylic acid) confirming the presence of a resorcinol unit in brazilin. For further studies, the tri-O-methyl ether of brazilin was used. On controlled permanganate oxidation it yielded brazilinic acid (16), which retained all the carbon atoms of brazilin (15). This keto dibasic acid was assigned the structure (16), on the



basis of the following observations. Further oxidation of brazilinic acid gave, among other compounds, 3,4-dimethoxyphthalic acid (m-hemipinic acid), and the dicarboxylic acid (**17**). Mild oxidation (for example aerial oxidation) of brazilin gives the more deeply coloured brazilein (**18**).

Hematoxylin (**19**), which is closely related in structure to brazilin (it has one more hydroxyl group) is obtained from the wood *Haematoxylum campechianum*. With metal ions such as Fe^{3+} and Al^{3+} , it forms deeply coloured complexes which are used in histological studies to stain cell nuclei. Like brazilin, hematoxylin can also be oxidized under mild conditions to obtain hematein (**20**).





The natives of the Amazon rainforests use dragon's blood for the treatment of a variety of skin abrasions caused by cuts, insect bites, burns, etc.

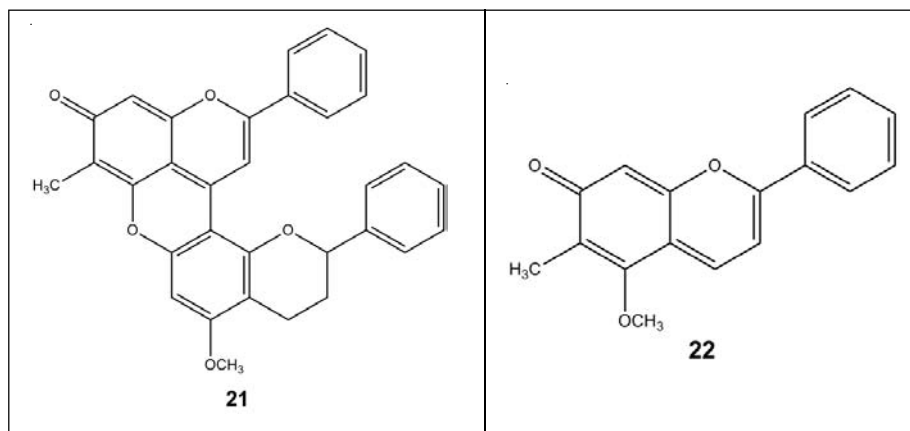
Pigments of the Dragon's Blood

In the 15th century, voyagers to the Spanish territory of Canary Islands off the North West coast of Africa brought back to Europe a deep red-coloured plant resin which they called Dragon's blood. This is a resin exuded by wounded trunk or branches of the tree *Dracaena draco*. Another species of *Dracaena*, *D.cinnabari*, also yields the pigment which is usually collected in the form of dried garnet-red globules. *D.cinnabari* is a native of the Socotra Archipelago, a group of four islands in the Indian Ocean. This isolated Yemeni territory is unique in the sense that it has fauna and flora not seen anywhere else. It has therefore been compared to the Galapagos Islands¹.

The chemistry of the two major pigments of Dragon's blood, namely, dracorubin and dracorhodin were elucidated by Brockmann and A Robertson and their co-workers. Dracorubin is a dimeric flavan derivative having the structure (21). Its colour is due to the presence of the quinonoid chromophore which is also present in dracorhodin (22). FT-Raman spectra have been used to characterize these pigments isolated from different specimens of Dragon's blood.

¹ If you wish to travel to the Canary Islands you can fly from Spain or Morocco. The Socotra islands, though nearer to us, are not that easily accessible; you will have to go to Sa'ana (Yemen) and take a flight from there.





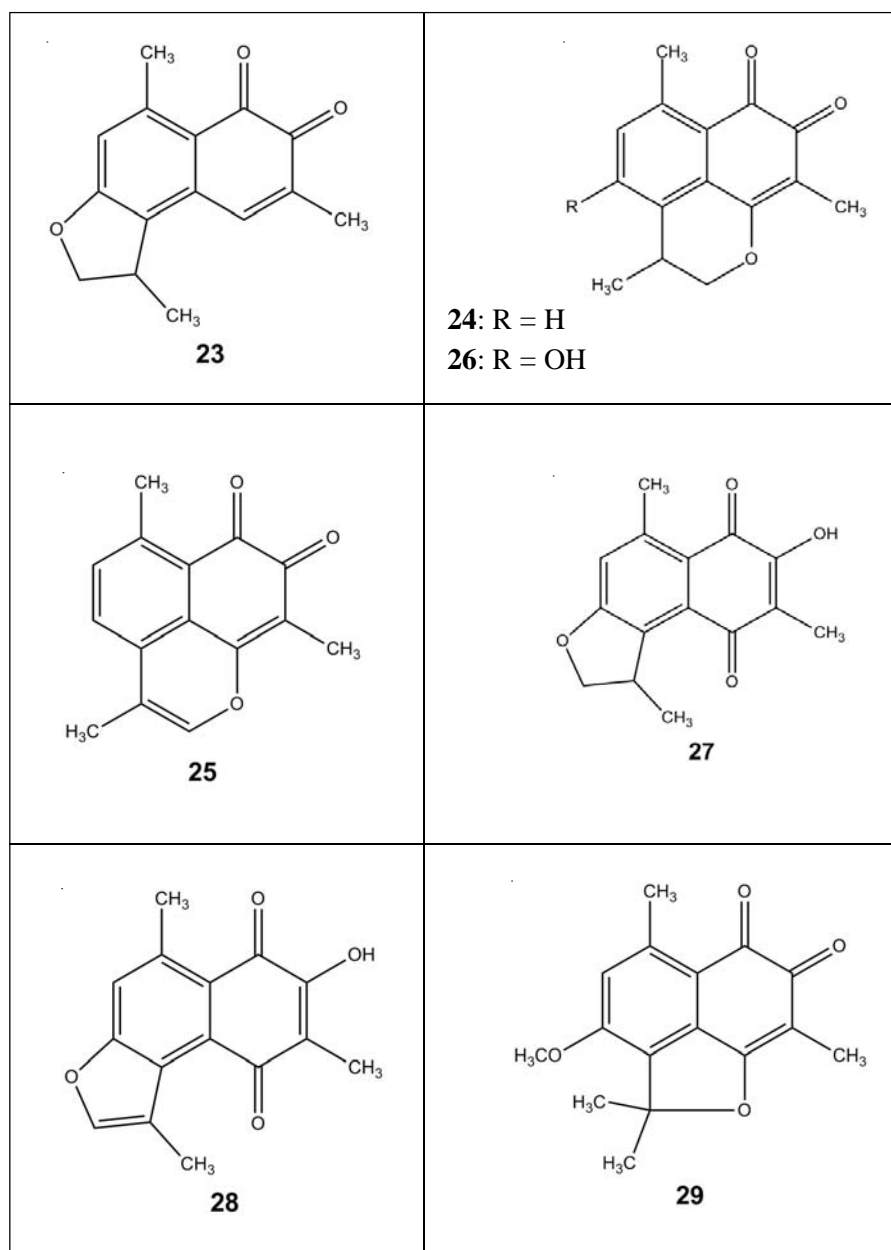
Pigments of the Miro Wood (*Thespesia populnea*)

To collect this wood, also known as the Portia tree, we need not have to undertake an overseas journey; the tree, also known as the Indian Tulip tree (Sanskrit: Plaksa) is a native of India. However, it is a very popular tree in many of the Pacific Islands, including Hawaii, Fiji, Pitcairn Islands, Marshall Islands, Tonga and Samoa. It is known as Miro wood in the Pitcairns and as Milo in Hawaii. It is also known as Pacific Rosewood. In Oceania, it is a much valued wood used for making carved curios and bowls, etc. This small tree was once common on the Pitcairn Islands. But, due to excessive cutting of the trees it has become a rarity on these islands. However, since the wood continues to be in great demand, the Pitcairn islanders sail to the Henderson Islands to collect the wood. If this practice continues the tree may soon become an endangered plant species in these islands. Several adventurers have travelled with the Pitcairn islanders to the Henderson Islands and their accounts make interesting reading and one is tempted to visit these distant islands!

In South India, the wood ('Hoovarasi' in Kannada and 'Poovarasu' in Tamil) is used for making the percussion instrument, Thavil, which is played in conjunction with the wind instrument, nadaswaram (similar to the shehnai and the clarinet). The pigments of the wood have been characterized as quinonoid compounds derived from a cadalene type sesquiterpene structure.

In New Zealand, the native Maoris use the miro wood for the construction of houses, though it is not a durable wood.

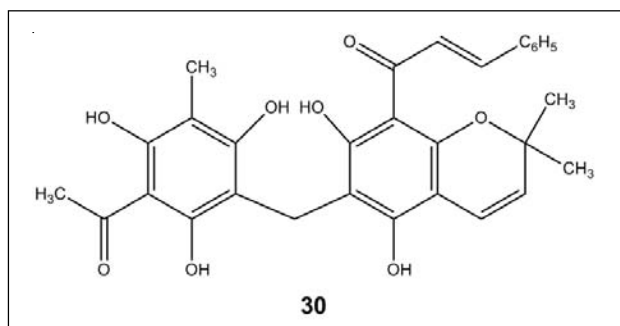
These include mansonone D (**23**), mansonone E (**24**), mansonone F (**25**), mansonone H (**26**), thespesone (**27**), thespesenone (**28**), and dehydrooxoperezinone-6-methyl ether (**29**). These compounds are together responsible for the rich orange colour of the miro wood.



Rottlerin – The Red Pigment from ‘Kamala’

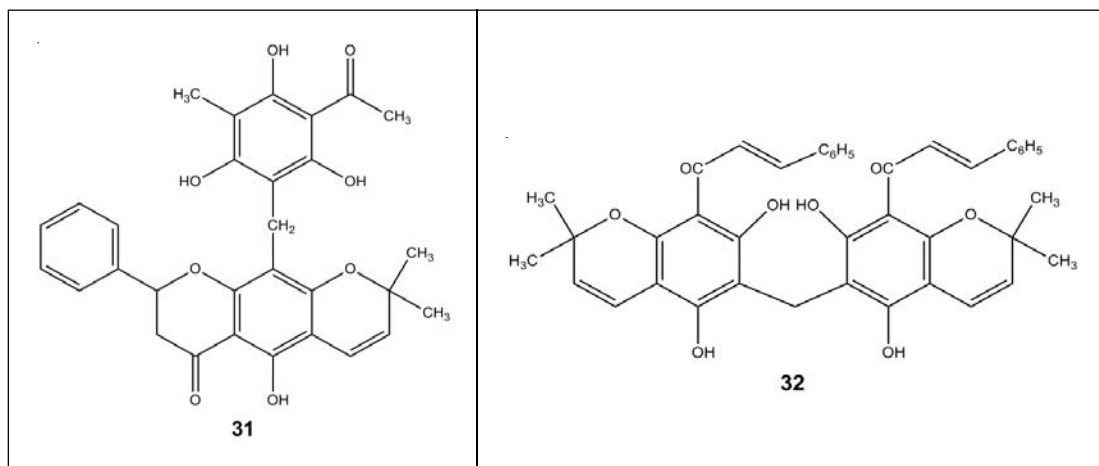
We shall conclude this article with a brief account of the chemistry of rottlerin which is the major colouring principle of the Kamala dye. This red dye, obtained from the seeds of *Mallotus phillippinensis* syn. *Rottlera tinctora* belonging to the spurge family Euphorbiacea, was used extensively in the past in India and other South East Asian countries to dye silk. The traditional method in India involved brushing off the red powder from the seed coats and boiling it with a solution of sodium carbonate to obtain a durable red dye. In India it has also been used as an anthelmintic drug.

The pigment was first isolated by H Telle in 1906. After some preliminary studies by A G Perkin and his co-workers, who obtained rottlerin in a pure form, along with isorottlerin, extensive studies on the structure of rottlerin were made by Brockmann, A Robertson and their co-workers. It has the molecular formula $C_{30}H_{28}O_8$ and is phenolic in nature as shown by the colour given with alcoholic ferric chloride and ready solubility in dilute aqueous alkali. On hydrogenation over palladium it yields a tetrahydro derivative. On alkaline fusion, rottlerin gives benzoic acid and cinnamic acid, whereas the tetrahydro derivative gives only dihydrocinnamic acid. On distillation with zinc dust, rottlerin yielded dihydrocinnamic acid and C-methylphloroglucinol. This was a crucial evidence for the presence of a C-methylphloroglucinol moiety in the pigment. Following these early leads, Robertson and his co-workers carried out further analytical as well as synthetic studies based on the results of which the



The name ‘Kamala’ is derived from the fruit coat which resembles the colour of lotus flowers. The red powder is brushed off the ripe fruits.

Arthur George Perkin (1861–1937) was the second son of W H Perkin, Sr. Under the tutelage of Prof. J J Hummel, he was attracted to the study of natural pigments and dyes. He was Professor of colour chemistry at the University of Leeds from 1892 to 1926. There is an oil painting (by Richard Jack) of this outstanding natural products chemist in the University of Leeds.



well as synthetic studies based on the results of which the structure of rottlerin was deduced as **30**. When heated in high boiling solvents, rottlerin gets converted into isorottlerin (**31**), as in a chalcone to corresponding flavanone transformation. This change involves an intramolecular Michael-type addition. Another interesting reaction of rottlerin is its conversion into rottlerone (**32**) on treatment with aqueous sodium carbonate. Try to figure out a mechanism for this intriguing transformation.

Suggested Reading

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