Fascinating Organic Molecules from Nature

3. Colours in Flight – Pigments from Bird Feathers and Butterfly Wings

N R Krishnaswamy and C N Sundaresan

Among the most colourful objects found in Nature are bird feathers and butterfly wings. Their beauty is more obvious when a bird or a butterfly is in flight as the colour of the pigments present in wings and feathers is accentuated by refraction and reflection of incident light by the nano-keratinoid structural elements in the feather. Thus, when a bird or a butterfly flaps its wings the effect is kaleidoscopic. The pigments responsible for the primary colours of bird feathers and butterfly wings are discussed here.

(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
Birds of paradise, butterflies, xanthophylls, melanins, polyenals (psittacofulvins), porphyrins and pterins.

Introduction

One of the most pleasing sights in Nature is the synchronised colour display in the plumage of birds and the wings of butterflies and some moths. It is no wonder that bird feathers are treasured objects in certain communities of the world. The birds of paradise, species of which are found in New Guinea, have been hunted from ancient times for the male bird's feathers which are used by the local people for ornamentation as well as in rituals. Peacock feather is associated with Lord Krishna and Shanmukha in Hindu mythology. The totality of colour and sheen seen in bird feathers is due to a combination of pigmentation and physical phenomena such as fluorescence, refraction and reflection. The pigments responsible for colouration include oxygenated carotenoids, melanins, polyenals (psittacofulvins) and porphyrins. Pterins are the characteristic pigments of butterfly wings.

The structural material of a feather is β-pleated keratin, which is a polypeptide consisting of about 100 amino acids with a higher percentage of glycine, serine, proline, leucine and glutamic acid than other amino acids. The sheet-like β-keratin strands are further twisted and cross-linked with the help of disulphide bridges. The resulting material is tougher than the α-keratins of mammalian hair.

Structural Colour of Birds

Structural colour is common to all birds, whereas pigmentation varies from species to species. Therefore, it is essential to deal at least briefly with structural colours before moving on to specific types of colourants found in bird feathers.

Blue, and often green, etc., colours are results of interaction of incident light with the structural material of a feather. The physical phenomena involved in this process include thin film interference, multilayer interference, diffraction, photonic crystal effects and light scattering. The β-keratin polymeric structures mentioned above form a nano-scale grating material which includes air spaces. The dimensions of this nanostructure are conducive to the above optical effects. Pigment particles, particularly melanins, are also incorporated in this nano-structure. The resultant effect is spectacular as, for example, in a peacock feather (*Figure* 1). The green colour of parrot feathers is due to an overlay of a yellow psittacofulvin with a blue structural colour.

Figure 1. Each peacock feather consists of thousands of flat branches. When light shines on the feather, we see thousands of glimmering coloured spots, each caused by minuscule bowl-shaped indentations and plate-like layers called micro-lamellae.

Pigments of Plumages of Passerines – Carotenoids

Passerines, also known as perching birds, account for more than half of all birds and include a diverse variety of birds possessing colourful plumage, such as the birds of paradise, as well as song birds such as the warblers, larks, shamas, magpie robins, fantail flycatchers and skylarks. The colour seen in a passerine feather is the result of a combination of pigmentation and special structural features. Shades of white and blue are primarily due to refraction

Previous articles:

1. Some Exotic Red Pigments of Plant Origin, Vol.17, No.10, 2012.
2. The Blue of Blue Jeans and Royal Purple, Vol.17, No.11, 2012.

Box 1. Functions of Bird Feathers

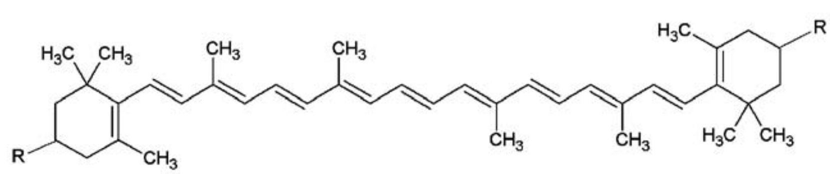
The most characteristic feature of a bird is its plumage. A feather is not just an appendage. It not only acts as an essential accessory in a bird's flight but also performs several other functions, which include providing protective cover, insulation, water-proofing, communication and display during interaction with a mate. For the last-mentioned function, colour is an essential component. Colour also helps in camouflage and social signalling. There are also indications that strong colouration in male birds reflects their immunocompetence and capacity for foraging. A female bird may therefore prefer a mate possessing a brightly-coloured plumage for the production of healthy progeny.

[1] Carotenoids are also classified as tetraterpenes as they are biosynthesised from the same primary precursors as other terpenoids. The first member of this group of pigments is lycopene which is responsible for the red colour of ripe tomatoes.

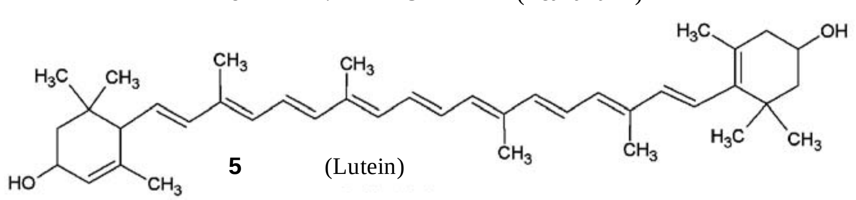
[2] Oxygenation is a key step in the biosynthetic conversion of carotenes into xanthophylls. Molecular oxygen and light are require for this process which is catalysed by the enzymes, hydroxylases and epoxidases. Along with flavonoids, xanthophylls are responsible for the autumnal colouring of leaves.

of incident light by the keratin fibrils which form the structural material. On the other hand, dietary carotenoids[1] are responsible for the yellow, orange and red colours. An overlay of these pigments with the blue colour produced by refraction results in green colour. Xanthophylls[2], which are oxygenated carotenoids, form complexes with proteins and this is responsible for the iridescence seen in many feathers.

The carotenoid pigments seen in bird feathers are, by and large, of dietary origin. Therefore, if the diet is not of the right kind or inadequate, the feather colour is less intense as has been observed in the case of flamingos which lose their pink colour if the diet is deficient in carotenoids. The pigments imparting bright yellow, orange, red and occasionally violet colours to bird feathers are mainly oxygenated carotenoids (xanthophylls). Canaries and chicken require diets rich in xanthophylls; they are unable to utilise dietary β-carotene (**1**). On the other hand, flamingos can efficiently absorb this yellow-coloured compound and convert it to the more deeply-coloured astaxanthin (**2**) to impart the characteristic pink colour to their plumage. The feathers of male house finches are coloured by a combination of carotenoids which include β-carotene, the orange-coloured iso cryptoxanthin (**3**) and the red-coloured echinenone (**4**). Another widely occurring

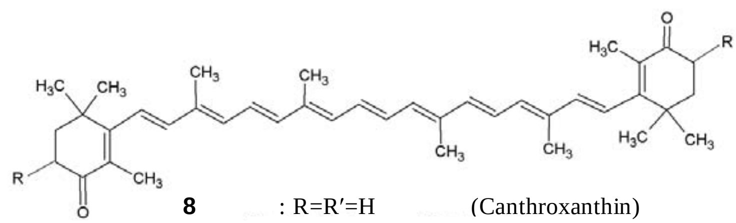


1 : R=R′=H (β-Carotene)
3 : R=OH; R′=H (Cryptoxanthin)
6 : R=R′=OH (Zeaxanthin)

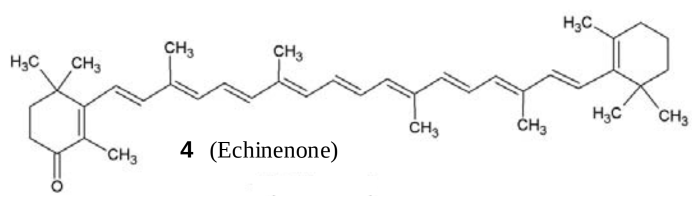


5 (Lutein)

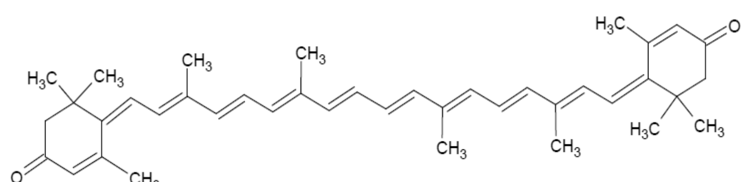
plumage cartenoid is lutein (**5**). Birds absorb this pigment from a wide variety of diets including seeds of vegetables, flower petals and insect larvae. Zeaxanthin (**6**), which is an isomer of lutein, is also a common dietary carotenoid and it imparts a warmer shade of yellow compared to lutein. The bright red-coloured rhodoxanthin (**7**) is responsible for the red, violet and blue (overlay of rhodoxanthin with structural colour) colours seen in the feathers of fruit pigeons. Other carotenoid pigments contributing to plumage colour include canthaxanthin (**8**) (which is di-dehydroxyastaxanthin), adonirubin (**9**) and canary xanthophyll-A (**10**). The primary colours of these individual carotenoids are



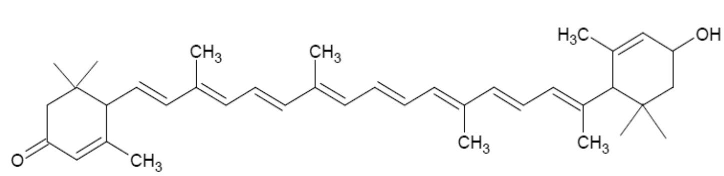
8	: R=R′=H	(Canthroxanthin)
9	: R=OH; R′=H	(Adonirubin)
2	: R=R′=OH	(Astaxanthin)



4 (Echinenone)



7 (Rhodo xanthin)



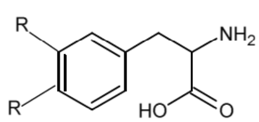
10 (Canay Xanthophyll)

modified, accentuated and made iridescent by co-pigmentation, combination with structural colours and by complexation with proteins. The result is, indeed, spectacular and eye-catching.

Melanins

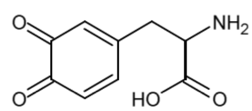
Apart from carotenoids, melanins[3] are the most common among bird feather pigments and are widely distributed. They are responsible for black, brown, yellow and shades of these colours. There are two types of melanins, namely eumelanin and phaeomelanin. These polymeric molecules are biosynthesized from the amino acid tyrosine (**11**). The partial structure of eumelanin is (**12**) whereas phaeomelanin is represented by the structure (**13**). In the formation of melanins, the first step is the oxidation of tyrosine to dihydroxytyrosine (dopa) (**14**). In the next step, the catechol unit in (**14**) is oxidised to the corresponding o-quinone, dopaquinone (**15**). The oxidation is catalysed by

[3] Melanins are responsible for the colour of skin and hair in animals. They also strengthen bird feathers and render them resistant to bacterial attack.



11 : R= R′=H

14 : R=R′=OH



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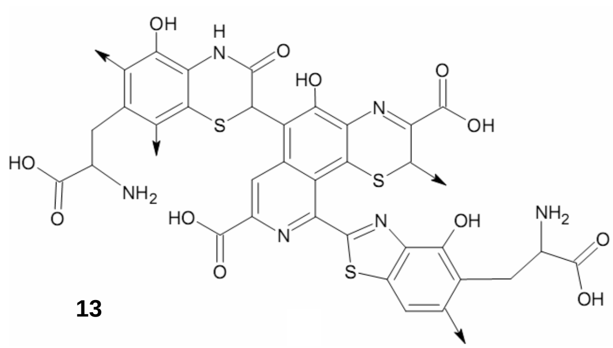

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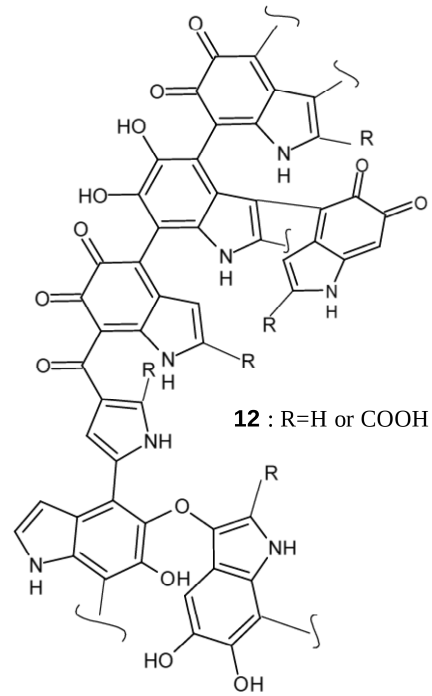
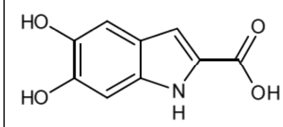


12 : R=H or COOH

the copper-containing enzyme, tyrosinase. Intramolecular Michael-type addition of the amino group to the quinine moiety in (**15**) results in leucodopachrome (**16**). The latter is oxidized to dopachrome (**17**). Subsequent polymerization of (**17**) as well as that of (**15**) results in the formation of an acidic eumelanin. On the other hand, dopachrome can undergo oxidative decarboxylation to yield 5,6-indolequinone (**18**), which on polymerization, yields a eumelanin without the carboxyl groups.



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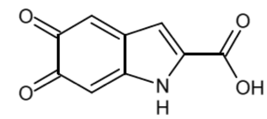

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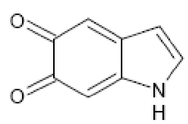
The biosynthesis of phaeomelanins takes a different route from dopaquinine onwards. Combination of (**15**) with the amino acid cysteine gives a mixture of 2-S-cysteinyldopa (**19**) and 5-S-cysteinyldopa (**20**). The latter, which is the major product, undergoes conversion to cysteinyldopaquinone (**21**) by way of a redox exchange with dopaquinone. An intramolecular Schiff base formation occurs due to amino group interaction with the quinone moiety in (**21**) which results in the transient intermediate quinoimine (**22**). The latter readily tautomerises to the more stable benzothiazine-3-carboxylic acid derivative (**23**). If the transformation is accompanied by decarboxylation, the product is 7-(2-amino-2-carboxyethyl)-4-hydroxybenzothiazine (**24**). These



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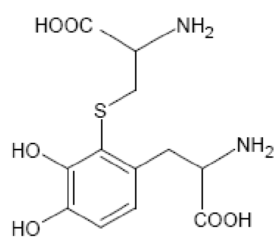

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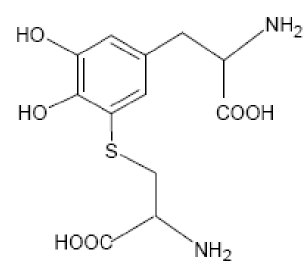

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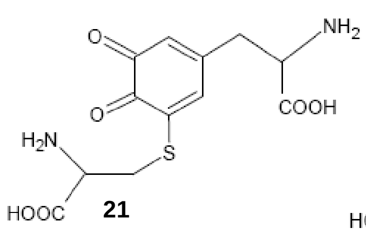

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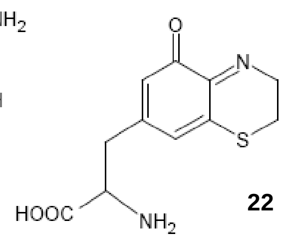

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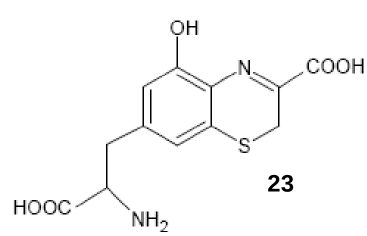

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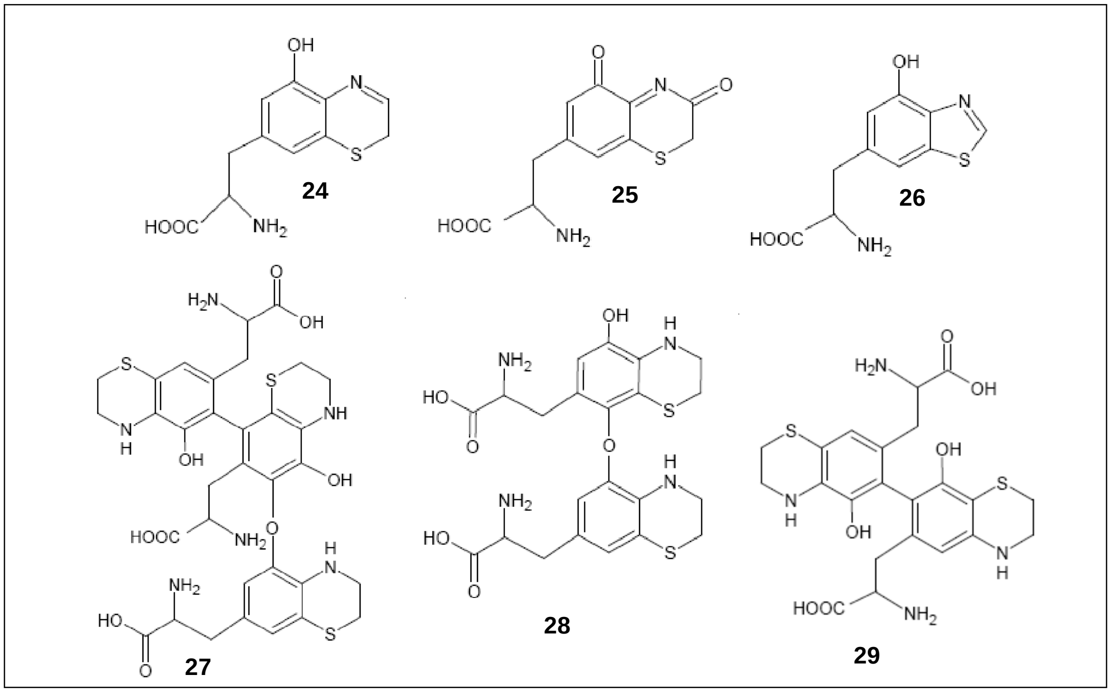
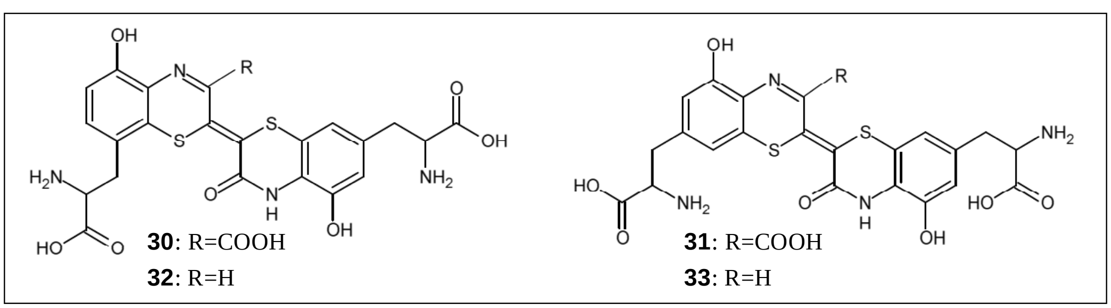
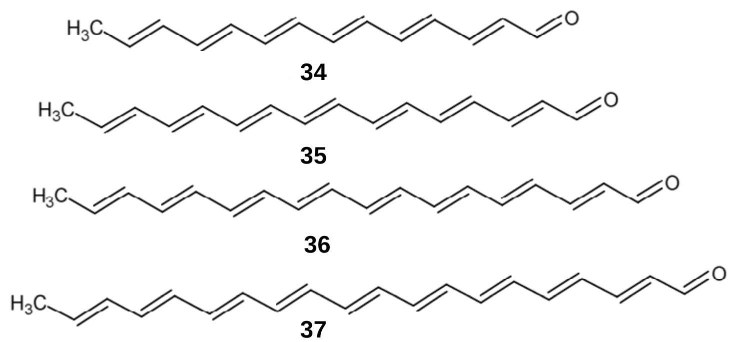


two compounds are the major monomeric precursors for the formation of phaeomelanins. However, two minor monomeric compounds also get incorporated in the polymeric pigment. These are 7-(2-amino-2-carboxyethyl)-5-hydroxy-3-oxo-3,4-dihydro-2H-1,4-benzothiazine (**25**) and 6-(2-amino-2-carboxyethyl)-4-hydroxy-benzothiazole (**26**). Several oligomers formed during this polymerization process have been isolated and characterized. The structures of three of them are **27**, **28**, and **29**.These contain C-C and C-O linkages arising as a result of phenolic oxidative coupling. In this context, also of interest are the trichromes B (**30**), C (**31**), E (**32**) and F (**33**), which have been isolated from some bird feathers.



Psittacofulvins



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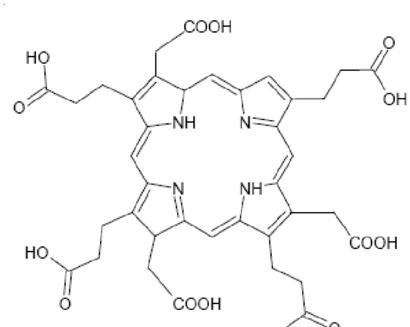
Psittacines, commonly known as parrots, possess multi-coloured plumages with vivid shades of yellow, orange, red, and green colours. The pigments responsible for these colours are known as psittacofulvins[4], which are unique to the psittacines. Four of these compounds (**34-37**) have been characterized as highly conjugated polyenals containing 14 to 20 carbon atoms. Kruckenberg (1882) was the first to isolate these pigments from the feathers of several psittacines including the scarlet Macaw. Early studies showed that though they are lipophilic like the carotenoids, their spectral characteristics are different. Unlike the carotenoids which show three absorption maxima in their UV– visible spectra, the psittacofulvins show only one maximum in the 420–450 nm region. Unlike the carotenoids, the psittacofulvins are not obtained from the bird's diet but are synthesised endogenously in the growing feather, presumably from the corresponding fatty acids. The green colour in parrots is due to the combination of a yellow psittacofulvin with a blue structural colour.

[4] The psittacofulvins are unique to birds of the parrot family. These lipid-soluble pigments also protect the feathers from being eaten away by bacteria such as *Bacillus licheniformis.*

Porphyrins

Colouration by porphyrin pigments is seen in the feathers of several species of birds such as rock doves, owls, pheasants, etc. Usually they produce shades of brown though occasionally a porphyrin colour could be a bright red or even green. The red-coloured turacin and the green turacoverdin are found only in the African turacos commonly known as banana eaters, go-away birds and louries. Turacin is a copper complex of uroporphyrin III (**38**). Turacoverdin is an oxidised metabolite of turacin.



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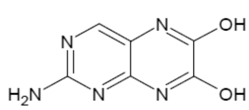
Turacin was first isolated from the tail and wing feathers of several species of the African turaco bird by A H Church in 1889. He found that this alkali-soluble red pigment contained 7% copper. In 1924, Hans Fischer (winner of Nobel Prize for his studies on haemin) and J Hilger showed that the non-metallic part of the pigment was a porphyrin. However, the correct identification of the porphyrin as uroporphyrin III was made several years later by Rimington.

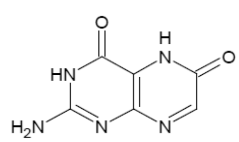
Pterins

Butterfly wing colours are partly due to structural factors and partly due to the presence of pigments, particularly those known as pterins. F G Hopkins[5], a pioneer in biochemical research, was the first to study the chemistry of this class of pigments. Not all pterins are coloured compounds. Leucopterin (**39**), for example is a white pigment exhibiting a pale blue fluorescence which gives a pearl-like appearance to the material in which it occurs. This is a common feature of many butterfly wings, such as those of the cabbage white. Xanthopterin (**40**) is yellow in colour and emits a greenish-yellow light. Erythropterin (**41**) is a red pigment, whereas sepiapterin (**42**) is yellow in colour. This compound, exhibiting orange fluorescence, is present in the wings of the alfalfa butterfly. The red-coloured pterorhodin (**43**) is used by some species of butterflies for colouring their wings.

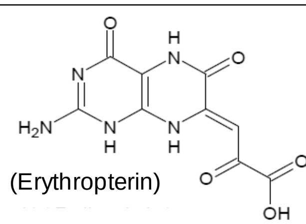
[5] Sir F G Hopkins (1861–1947) was popularly known as the father of Biochemistry. He discovered the amino acid tryptophan and tripeptide glutathione. He was awarded the Nobel Prize in Medicine/Physiology in 1929 which he shared with C Eijkman for his pioneering studies on vitamins. He was the President of the Royal Society from 1930 to 1935.



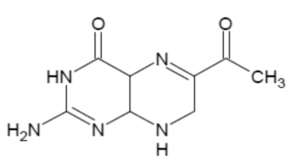
39 (Leucopterin)



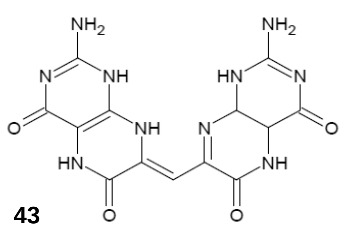
40 (Xanthopterin)



41 (Erythropterin)



42 (Sepiapterin)



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Suggested Reading

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