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The Chemistry of Phyto Pigments

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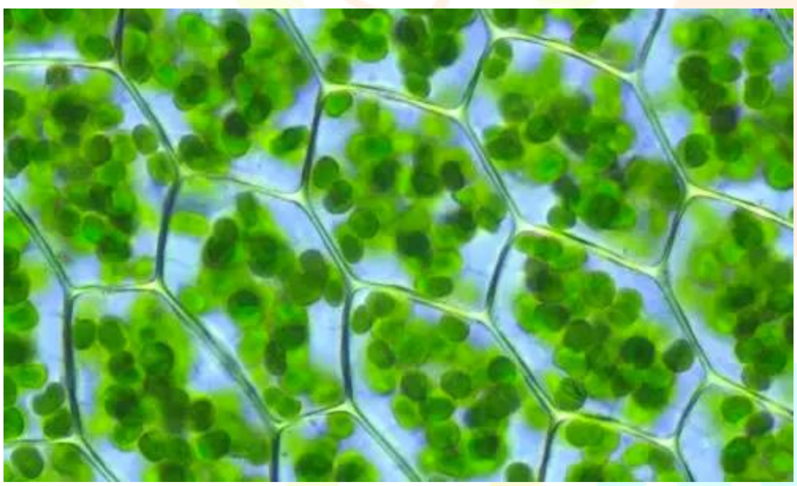
INTRODUCTION

Plant pigments is a term used to refer to coloured molecules naturally present in plant parts that not only impart colour to these parts but also help the plant perform some important metabolic activities like photosynthesis and promote plant growth. These pigments are formed by biosynthesis in plants.



All plant pigments are organic, i.e. are made up of carbon chains. The colour of the pigment depends on the ratio of absorption to scattering of light. For example, taking carotenoids, the most commonly found plant pigment, the molecules absorb the green and blue part of the visible spectrum and scatter the red light thus appearing red in colour to our eyes.

TYPES OF PLANT PIGMENTS

There are 3 main categories of plant pigments, namely

- Carotenoids: they impart red, orange and yellow colours to plant parts like leaves, vegetables, fruits etc. There are two types of carotenoids:
  - ❖ Carotenes
  - ❖ xanthophylls
- Chlorophyll: chlorophyll imparts green colour to plant parts, mainly leaves. There are five

types of chlorophylls:

- ❖ Chlorophyll a
- ❖ Chlorophyll b
- ❖ Chlorophyll c
- ❖ Chlorophyll d
- ❖ Chlorophyll e

- Anthocyanins: anthocyanins are plant pigments that are responsible for giving purple, blue and sometimes even black or red hues to plant parts. The colour changes due to different pH levels. There are six types of anthocyanins:

- ❖ Cyanidin
- ❖ Delphinidin
- ❖ Pelargonidin
- ❖ Peonidin
- ❖ Malvidin
- ❖ Petunidin

carotenoids	**chlorophyll**	**anthocyanins**
Red, orange and yellow	Green	Purple, blue, red, black
Watermelons, oranges, capsicums, carrots etc.	Leaves, stems and stalks, ripe kiwi, avocado, green capsicum	Grapes, purple cabbage,berries, currants, raspberries etc.

PLANT PIGMENTS

Carotenoids

Red, orange and yellow colours are imparted to plant parts by carotenoids. These pigments not only give colour to plant parts but also help the plant perform important metabolic processes like photosynthesis and hence help in plant growth.

Carotenoids are present in the membranes of chloroplasts. Carotenoids are responsible for imparting red, orange and yellow colours to plant parts and consist of almost 1100 compounds. They are also the most common type of pigments found in nature. All carotenoids contain 40 carbon atoms. They are responsible for giving colour to tomatoes, carrots and some red flowers like daffodils and other fruits and vegetables. They are synthesised in chloroplasts and chromoplasts of plant cells. Chromoplasts are plant cell organelles containing and pigment other than chlorophyll. A structure which contains chlorophyll is a chloroplast.

Carotenoids are very essential for plant life as they provide photo-protection, i.e. they protect the process of photosynthesis from excess sunlight.

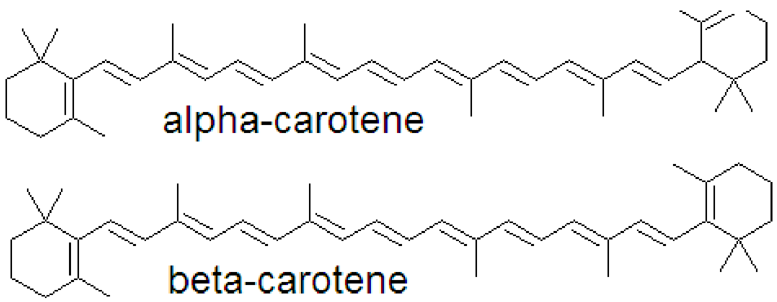
The conjugated(alternating) double bonds in carotenoids makes the compound absorb the blue and green part of the visible spectrum and reflect the red, orange part of the spectrum.

There are two main groups of carotenoids. They are carotenes and xanthophylls.
Some carotenes include α-carotene, β-carotene and lycopene. There are about 50 to 60 known carotenes.
β-cryptoxanthin, lutein, α-cryptoxanthin and zeaxanthin are some types of xanthophylls and there are over 800 known xanthophylls.
Xanthophylls contain oxygen atom(s) in the form of functional groups like hydroxyls (aldehydes, carboxyl, alcohol etc.) while carotenes do not contain oxygen. Mostly both have 40 carbon atoms with alternating double bonds. But some carotenoids have 45 to 50 carbon atoms and are known as higher carotenoids. Some carotenoids have less than 40 carbon atoms and are known as apocarotenoids.
The colour imparted also depends upon the concentration of the pigment. For example, β-carotene is yellowish-orange in colour. But high concentration of the pigment imparts red colour.

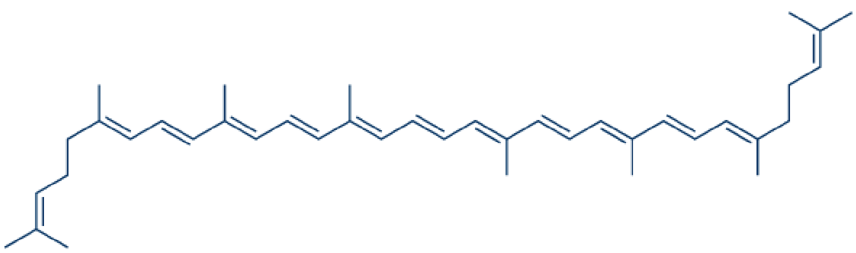
Carotenes

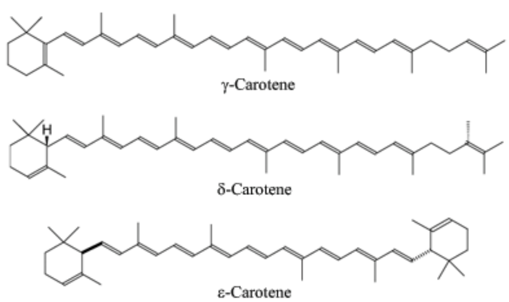
Carotenes are a group of carotenoids which do not contain oxygen. They chiefly impart red and orange colours and sometimes even yellow colours in low concentrations. Carotenes are sources of vitamin A and are present in all orange fruits and plant parts. The molecular formula of all carotenes is $C_{40}H_{56}$. All the carotenes are isomers of each other as their structure is different but their molecular formula is the same. They occur in many forms like alpha (α), beta (β), gamma (γ), delta (δ), epsilon (ε), and zeta (ζ) and lycopene.

α-Carotene and β-carotene are the most common types of carotenes along with lycopene. α-carotene is the positional isomer of β-carotene as the molecular formula is the same($C_{40}H_{56}$) but the position of a double bond in the second end ring is different.



Lycopene is another carotene with the same molecular formula but different structural formula. Lycopene is a red pigment found in large quantities in watermelons, tomatoes and pink guavas. Lycopene is converted to α-Carotene and β-carotene through addition of cyclic end groups.





Ɣ(gamma), ε(epsilon), δ(delta) and ζ(zeta) carotenes are positional isomers of β-carotene, i.e. a double bond in their end group differ in position.

Carotenes are an excellent source of vitamin A, especially α-Carotene and β-carotene. They are also applied as food dyes and cosmetic colourants.

Carotene	**colour**	**food**
β-carotene	Orange, yellow	Tomato, mango, papaya
α-carotene	Orange, yellow	Carrot, sweet potato, apricot, pumpkin.
Lycopene	Red	Watermelon, pink guava, tomato

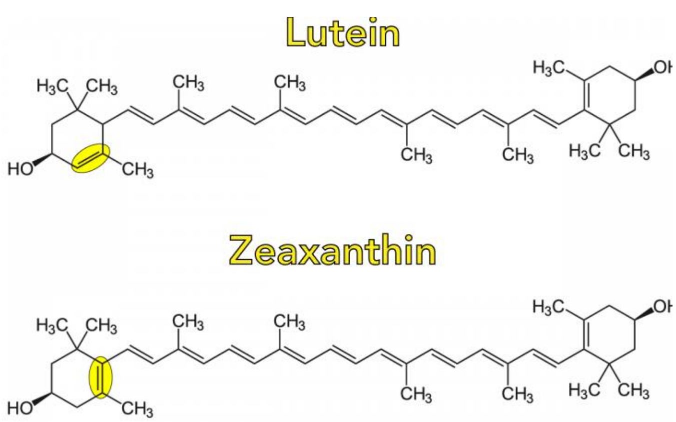
Xanthophylls

Xanthophylls are a group of naturally occurring carotenoids which impart yellow colour to plant parts. While carotenes are composed for carbon and hydrogen only, xanthophylls also contain other elements like oxygen in the form of functional groups.

Xanthophylls are very commonly occurring. Egg yolk, corn, pumpkins and most fruits with yellow pulp contain xanthophyll pigments like lutein and zeaxanthin. The yellow spot(macula lutea: area of best vision in the eye) in the iris of our eyes contains xanthophyll pigments.

Some common xanthophyll pigments include lutein, zeaxanthin, α-cryptoxanthin and β-cryptoxanthin.

Xanthophylls have similar structures to carotenes but they contain oxygen, unlike carotenes which are pure hydrocarbons. The oxygen is present in the form of hydroxyl group (alcohol-OH, Aldehyde-CHO, carboxylic acid-COOH). The presence of oxygen in xanthophylls gives it a polar property stronger than that of carotenes. Lutein is the most commonly found xanthophyll.



Lutein and zeaxanthin are isomers as they have the same molecular formula of $C_{40}H_{56}O_2$ but the position of a double bond in the end group is different. Similarly α-cryptoxanthin is isomeric with β-cryptoxanthin where their molecular formula is $C_{40}H_{56}O$ but the position of double bond in the end group differs.

Lutein is present in plants in the form of fatty acid esters. It absorbs blue light to appear yellow in low concentration and reddish orange in high concentrations.

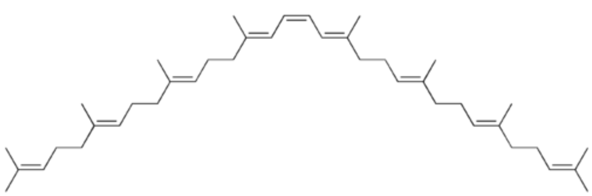
Xanthophylls are organic pigments that act as temporary light harvesting structures. They also provide photoprotection to the plants.

Biosynthesis of carotenoids (flowchart will be added in handwritten copy)

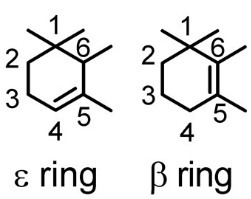
The process by which carotenoids are synthesised in plants is known as the **carotenoid biosynthesis pathway or carotenogenesis**. Carotenoids are synthesised by all organisms which perform photosynthesis. There is a core method by which carotenoids are synthesised, however some plants and fungi have special methods. The core method is as follows:

(note: ***synthase*** refers to an enzyme which acts as a catalyst in the synthesis of a compound)

1. The first reaction is that of *glyceraldehyde-3-phosphate*($C_3H_7O_6P$) and *pyruvate*($C_3H_4O_3$). The reaction takes place in the presence of 1-deoxy-D-xylulose-5-phosphate synthase(DXS) **synthase** to produce 1-deoxy-D-xylulose-5-phosphate(DXS)
2. The second reaction involves the production of IPP(isopentenyl diphosphate) and DMAPP(dimethylallyl diphosphate).
3. Condensation of 3 molecules of IPP and 1 molecule of DMAPP takes place in the presence of Geranygeranly diphosphate(GGPP) **synthase** to produce the compound Geranylgeranyl diphosphate(GGPP) which is composed of a carbon chain which 20 carbon atoms.
4. 2 molecules of GGPP are condensed in the presence of phytoene **synthase** to produce phytoene, the prime precursor to all carotenoids. Phytoene comprises of 40 carbon atoms(20 from each GGPP molecule)



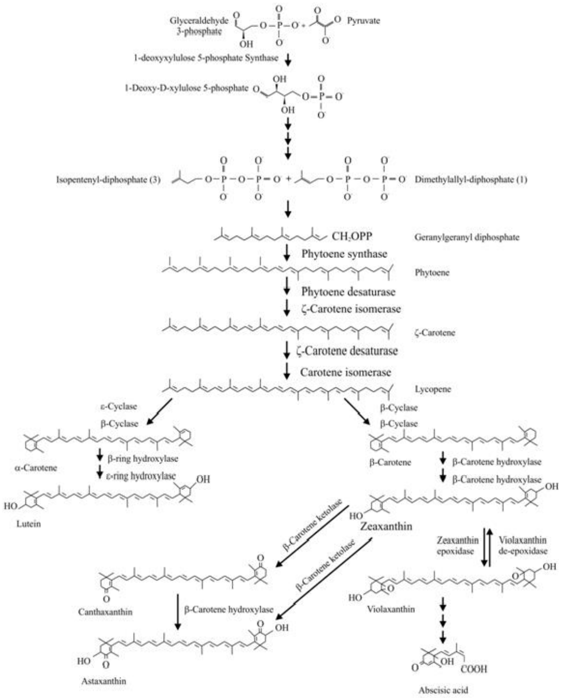
5. Phytoene undergoes several processes like desaturation(removal of hydrogen atoms to form double bonds) and isomerization to produce lycopene, the red carotene.



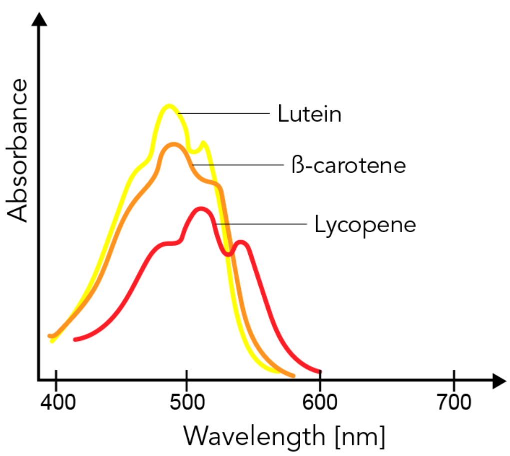
6. The next process known as cyclisation of lycopene takes place. The enzyme lycopene β cyclase initiates the formation of β rings on either ends of the lycopene molecule. Likewise, the formation of α-carotene requires lycopene α cyclase and lycopene ε cyclase to initiate the formation of a β ring at one end of the lycopene molecule and an ε ring at the other end.

compound	First end ring	Second end ring
β carotene	Beta ring	Beta ring
α carotene	Beta ring	Epsilon ring

7. The production of xanthophylls involves the hydroxylation(addition of hydroxyl group) of α-carotene to produce zeinoxanthin($C_{40}H_{56}O$), an isomer of alpha and beta cryptoxanthin which is further hydroxylated to produce lutein, the most commonly found xanthophyll.
8. For the production of zeaxanthin, beta carotene($C_{40}H_{56}$) is acted upon by beta carotene hydroxylase which helps add OH^- ions to the compound and beta cryptoxanthin($C_{40}H_{56}O$) is produced. Beta cryptoxanthin is further hydroxylated to produce zeaxanthin with two oxygen atoms ($C_{40}H_{56}O_2$).



flowchart similar to this will be hand-drawn



The absorption spectrum of carotenoids is 400 nm to 600 nm (nm=nanometer) which include the blue and green spectrum of visible light. The red part of the spectrum including the red, orange and yellow light is scattered.

Chlorophyll

Chlorophyll is one of the most significant and commonly known plant pigments. Chlorophyll appear green in colour as they absorb the red and blue spectrum of the visible light which are essential for photosynthesis and scatter the green light. Chlorophyll is a photoreceptor that absorbs light and helps in the process of photosynthesis.

Chlorophyll is found in plastids known as chloroplasts. Specifically, they are found in the membranes of thylakoids(thylakoids are flat coin like structures stacked atop each other inside the chloroplast).

There are five types of chlorophylls each with different molecular formulas:

Chlorophyll a	$C_{55}H_{72}O_5N_4Mg$

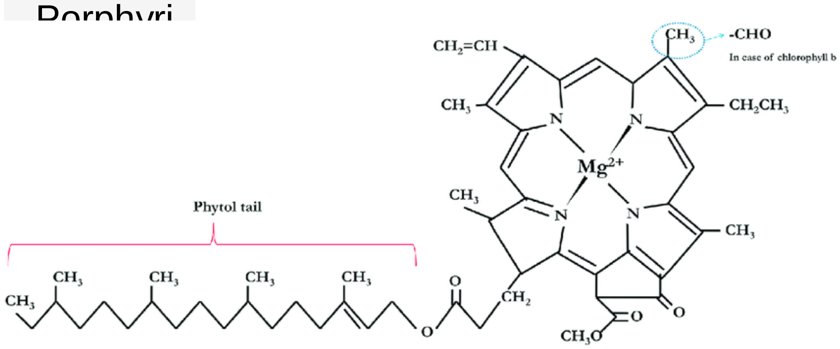
Chlorophyll b	$C_{55}H_{70}O_6N_4Mg$
Chlorophyll c	$C_{35}H_{30}O_5N_4Mg$
Chlorophyll d	$C_{54}H_{70}O_6N_4Mg$
Chlorophyll e	Not known yet

The most common type of chlorophyll is chlorophyll a followed by chlorophyll b.

Structure of chlorophylls

Chlorophyll has a central magnesium atom surrounded by four nitrogen atoms. The nitrogen is a part of a ring known as the pyrrole ring. There are four pyrrole rings and the four pyrrole rings along without magnesium is known as the porphyrin ring and with magnesium it is known as the porphyrin head.

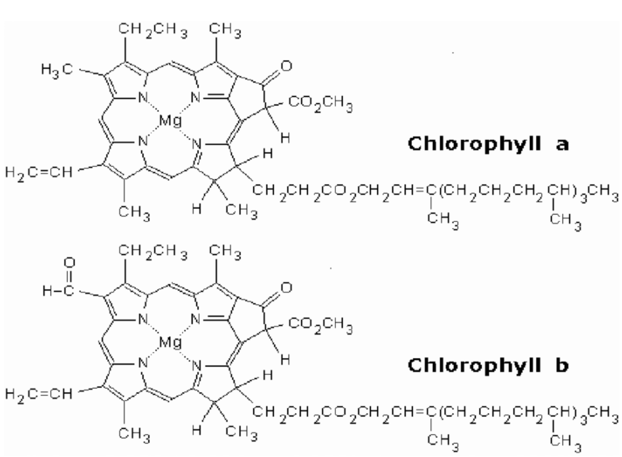
Porphyri



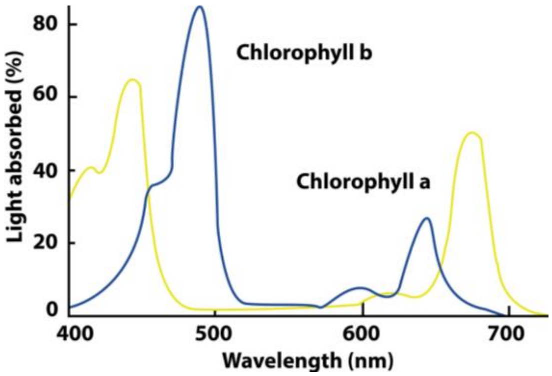
(add a formation diagram in sequence: pyrrole→porphyrin ring→porphyrin head)

Attached to the porphyrin head is the phytol tail.

Chlorophyll a and chlorophyll b differ only in the substituent present in the porphyrin. In the case of chlorophyll a, the substituent present is a methyl group→ CH_3 and for chlorophyll b the substituent is aldehyde→ CHO.



The porphyrin head is hydrophilic while the phytol tail is hydrophobic which allows the molecule to plant itself in the thylakoid membrane.



The different types of chlorophyll differ slightly in structure due to which different wavelengths of light are scattered and the colour varies. For instance chlorophyll a appears greenish-blue in colour while chlorophyll b appears greenish-yellow in colour.

When a leaf is boiled the bright green colour turns dull and sometimes even brown. This happens because on heating, the magnesium ion in the centre of the porphyrin ring is replaced by a hydrogen ion due to which the green shade is lost.

During photosynthesis, chlorophyll a, chlorophyll b and beta carotene are mainly used. In reality, plants do not really require chlorophyll b and can perform photosynthesis with just chlorophyll a. Hece, chlorophyll b is called an accessory pigment.

Anthocyanins

Anthocyanins are plant pigments which are found in vacuoles of cells and give purple, red, blue or black colour based on the pH of the vacuole content. They are water soluble pigments belonging to the parent group of molecules known as flavonoids. They are the most commonly found flavonoids

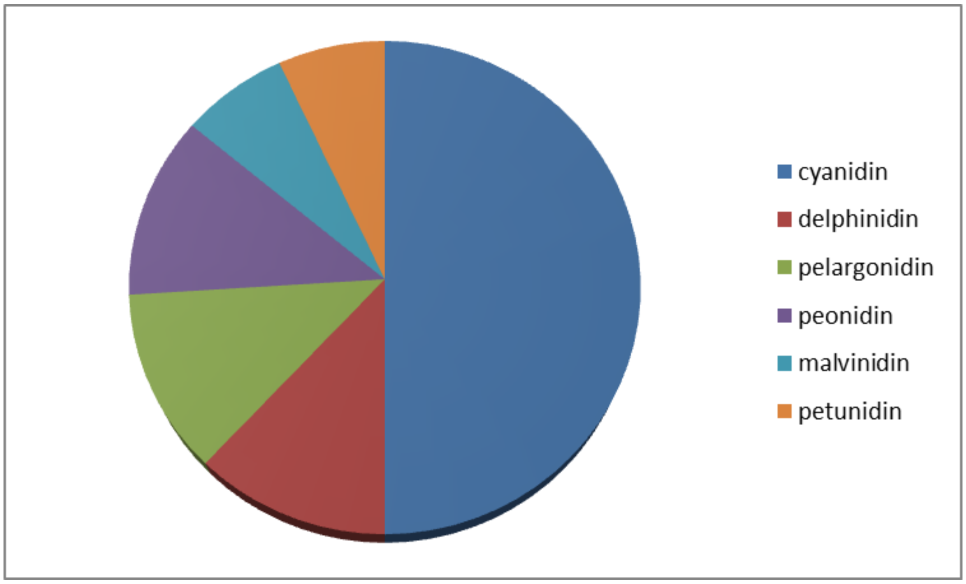
They are mainly found in flowers, fruits/vegetables and some tubers.

They appear red in colour in acidic conditions and blue in colour in alkaline conditions and are purple in colour in neutral conditions.

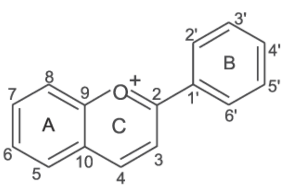
There are six types of anthocyanins, namely Cyanidin, delphinidin, pelargonidin, peonidin, malvidin, and petunidin.

Their composition in fruits and vegetables is:

cyanin	50%
delphinidin	12%
pelargonidin	12%
peonidin	12%
malvidin	7%
petunidin	7%

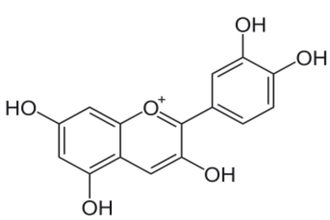


Structure and types of anthocyanins



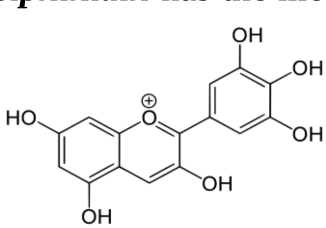
The base structure for all the anthocyanins is the flavylium cation($C_{15}H_{11}O^{+}$). The addition of hydroxyl and/or methoxy substituent(s) to the flavylium ions result in the formation of anthocyanins. The different positions taken by these molecules in the flavylium ion determine the different types of anthocyanins. However, all anthocyanins have hydroxyl substituents in positions 3, 5 and 7.

Cyanidins are formed by the addition of hydroxyl substituents to positions 3', 4', 3, 5 and 7 of the flavylium cation. It has the molecular formula $C_{15}H_{11}O_{6}^{+}$. They are found in many fruits such as raspberry(most cyanidin dense fruit), black raspberry, blueberry, blackberry, cherry, purple grapes, cranberry and also in vegetables like red cabbage and onion.



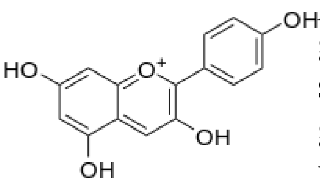
In nature cyanidin is found in the form of glycosides and other forms. For example, the most commonly found anthocyanin is cyanidin-3-glucoside also known as chrysanthemin. In black raspberries and blackberries they are found in the form of antirrhinum or cyanidin-3-rutinoside. In red onions they are found in the form of cyanidin-3,4'-di-O-β-glucopyranoside and cyanidin-4'-O-β-glucoside.

Delphinidin has the molecular formula is $C_{15}H_{11}O_{7}^{+}$ and is formed by the addition of hydroxyl substituents to positions 3', 4', 5', 3, 5 and 7 of the flavylium cation. It occurs in several berries and brinjals and wine. It also colours several flowers like roselle and flowers from the plant family of violet like viola and are also found in larkspur which are also known as "delphinium".

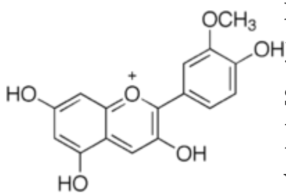


Nasunin or delphinidin-3-p-coumaroyl rutinoside-5-glucoside is the delphinidin which gives the purple colour to brinjals. The 3-glucoside and 3-rutinoside of delphinidin, myrtillin and tulipanin respectively are found in blackcurrants.

Pelargonidin ($C_{15}H_{11}O_5^+$) is the flavonoid cation with hydroxyl substituents in positions 4’, 3, 5, and 7 and is mostly red or orange. The 3-glucose of pelargonidin is found in large quantities in strawberries along with chrysanthemin (cyanidin-3-glucoside). They are found in a variety of flowers like red and pink roses and red geraniums. Its strong orange colour enables us to use it as industrial dyes. It is also present in Rajma beans or kidney beans. Pelargonidin also happens to be the most simple anthocyanin.

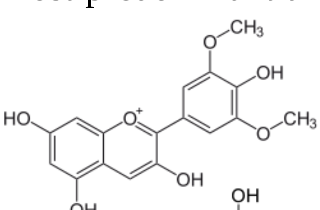


Peonidin ($C_{16}H_{13}O_6^+$) is the flavonoid cation with hydroxyls in 4’, 3, 5, 7 and methoxy substituent in position 3’. Peonidin is derived from cyanidin as it is the 3’ methoxy derivative of cyanidin meaning in cyanidin, position 3’ is occupied by a methoxy substituent instead of the hydroxyl substituent.

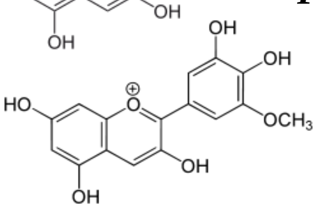


It imparts magenta colour but it can change according to pH value in the vacuole content. Cranberries are rich in peonidin. The 3-glucoside of peonidin is found in grapes and onions and purple corn. It is found in peony flowers where peonidin is pinkish in colour due to different pH levels. Peonidin is derived from cyanidin.

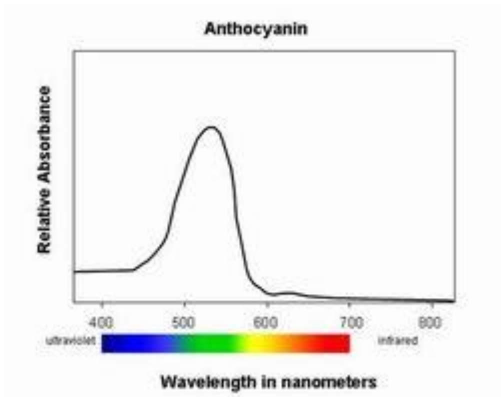
Malvidin ($C_{17}H_{15}O_7^+$) is derived from delphinidin as it is the 3’,5’ methoxy derivative of delphinidin. In most grape varieties, the 3-glucoside of malvidin is the most predominant anthocyanin and hence is found in large quantities in red wine. Malvidin and delphinidin derivatives are the most abundant anthocyanins in blueberries. The main source of malvidin is vitis vinifera or the common grape vine.



Petunidin ($C_{16}H_{13}O_7^+$)is also the methoxy derivative of delphinidin. It is the 5’ methoxy derivative of delphinidin. It is found in many red berries and grape varieties. Since it is predominantly found in petunia, the pigment has been named as petunidin. Petunidin is being used as food colouring in the food industry.



These are found in the form of glycosides(bonded with sugar molecules) in plants. For example, cyanidin-3-glucoside, delphinidin-3-glucoside and peonidin-3-O-glucoside. In nature, cyanidin, delphinidin and pelargonidin glycosides are the most commonly found. Cyanidin-3-glucoside is the most commonly found anthocyanin. Anthocyanins have been used as natural pH indicators. They turn blue in alkaline conditions and red in acidic conditions.



Anthocyanins are very healthy when consumed due to their anti-cancer and anti-diabetic properties and they have been known to prevent cardiovascular diseases as well. Anthocyanins can be consumed as anthocyanin-rich foods or by supplements.

CONCLUSION

The chemistry of plant pigments continues to attract biochemists and researchers to study them more closely, to understand how they are formed and how they function. The formation of each plant pigment requires hundreds of chemicals which the plant needs to obtain and then apply them to the process. The pigments are one of the most important components of plants as without chlorophyll, photosynthesis cannot be performed at all and without the accessory pigments like carotenoids, the amount of light absorbed is very less. Without carotenoids and anthocyanins, flowers will not have their bright and vibrant colours which will cause a complete decline of pollination as pollinating agents like insects and small birds are not attracted towards the flowers, hence reducing plant population considerably.