CAROTENOIDS

Any of the various usually yellow to red pigments (as carotenes) found widely in plants and animals and characterized chemically by a long aliphatic polyene chain composed of eight isoprene units are termed carotenoids.

INTRODUCTION

Carotenoids are red, yellow and orange pigments that are widely distributed in nature.24 Although specific **carotenoids** have been identified in photosynthetic centers in plants, bird feathers, crustaceans and marigold petals, they are especially abundant in yellow-orange fruits and vegetables and dark green, leafy vegetables.25 Of the more than 700 naturally occurring **carotenoids** identified thus far, as many as 50 may be absorbed and metabolized by the human body.26 To date, only 14 **carotenoids** have been identified in human serum.26

Carotenoids absorb light in the 400-500 nm region of the visible spectrum. This physical property imparts the characteristic red/yellow color of the pigments. **Carotenoids** contain a conjugated backbone composed of isoprene units, which are usually inverted at the center of the molecule, imparting symmetry. Changes in geometrical configuration about the double bonds result in the existence of many cis and transisomers. Hydroxylated, oxidized, hydrogenated or ring-containing derivatives exist. Hydrocarbon **carotenoids** are classified as carotenes while those containing oxygen are known as xanthophylls

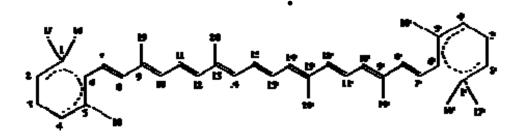
CLASSIFICATION

There are two general classes of carotenoids: carotenes and xanthophylls. Carotenes consist only of carbon and **hydrogen** atoms; beta-carotene is the most common carotene. Xanthophylls have one or more **oxygen** atoms; lutein is one of the most common xanthophylls.

CHEMISTRY

Carotenoids belong to the category of tetraterpenoids (i.e. they contain 40 carbon atoms, being built from four terpene units each containing 10 carbon atoms). Structurally, carotenoids take the form of a polyene hydrocarbon chain which is sometimes terminated by rings, and may or may not have additional oxygen atoms attached.

GENERAL STRUCTURE OF CAROTENOIDS

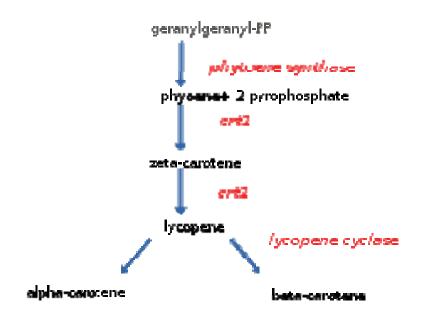


PROPERTIES

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- Carotenoids with molecules containing oxygen, such as lutein and zeaxanthin, are known as **xanthophylls**.
- The unoxygenated (oxygen free) carotenoids such as α -carotene, β -carotene and lycopene are known as **carotenes**. Carotenes typically contain only carbon and hydrogen (i.e., are hydrocarbons), and are in the subclass of unsaturated hydrocarbons.

Probably the most well-known carotenoid is the one that gives this second group its name, carotene, found in carrots (also apricots) and are responsible for their bright orange colour. Crude palm oil, however, is the richest source of carotenoids in nature in terms of retinol (provitamin A) equivalent.^[7] Vietnamese Gac fruit contains the highest known concentration of the carotenoid lycopene. Their colour, ranging from pale yellow through bright orange to deep red, is directly linked to their structure. Xanthophylls are often yellow, hence their class name. The double carbon-carbon bonds interact with each other in a process called conjugation, which allows electrons in the molecule to move freely across these areas of the molecule. As the number of double bonds increases, electrons associated with conjugated systems have more room to move, and require less energy to change states.



Simplified carotenoid synthesis pathway

This causes the range of energies of light absorbed by the molecule to decrease. As more frequencies of light are absorbed from the short end of the visible spectrum, the compounds acquire an increasingly red appearance

FLAVONOIDS

Flavonoids (or **bioflavonoids**) (from the Latin word *flavus* meaning yellow, their colour in nature) are a class of plant secondary metabolites.

Flavonoids were referred to as Vitamin P (probably due to the effect they had on the permeability of vascular capillaries) from the mid-1930s to early 50s, but the term has since fallen out of use.

FUNCTIONS OF FLAVONOIDS IN PLANTS

Flavonoids are widely distributed in plants fulfilling many functions.

Flavonoids are the most important plant pigments for flower coloration producing yellow or red/blue pigmentation in petals designed to attract pollinator animals.

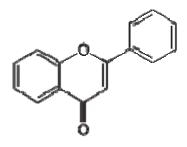
In higher plants, Flavonoids are involved in UV filtration, symbiotic nitrogen fixation and floral pigmentation.

CLASSIFICATION

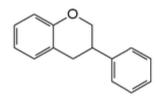
According to the IUPAC nomenclature, they can be classified into:

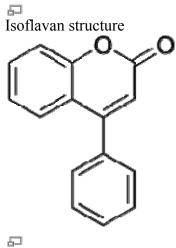
- *flavones*, derived from 2-phenylchromen-4-one (2-phenyl-1,4-benzopyrone) structure (examples: quercetin, rutin).
- *isoflavonoids*, derived from 3-phenylchromen-4-one (3-phenyl-1,4-benzopyrone) structure
- *neoflavonoids*, derived from 4-phenylcoumarine (4-phenyl-1,2-benzopyrone) structure.

The three flavonoid classes above are all ketone-containing compounds, and as such, are flavonoids and flavonols. This class was the first to be termed "bioflavonoids." The terms flavonoid and **bioflavonoid** have also been more loosely used to describe non-ketone polyhydroxy polyphenol compounds which are more specifically termed flavanoids, flavan-3-ols (or catechins).



Solution Structure of the flavone backbone (2-phenyl-1,4-benzopyrone)

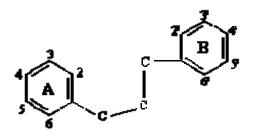




Neoflavonoids structure

GENERAL STRUCTURE OF FLAVONOIDS

The flavonoids are polyphenolic compounds possessing 15 carbon atoms; two benzene rings joined by a linear three carbon chain.

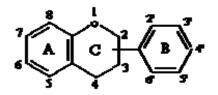


The skeleton above, can be represented as the

C₆ - C₃ - C₆ system.

Flavonoids constitute one of the most characteristic classes of compounds in higher plants. Many flavonoids are easily recognised as flower pigments in most angiosperm families (flowering plants). However, their occurence is not restricted to flowers but include all parts of the plant.

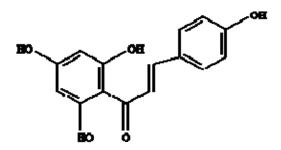
The chemical structure of flavonoids are based on a C_{15} skeleton with a CHROMANE ring bearing a second aromatic ring B in position 2, 3 or 4.



Various subgroups of flavonoids are classified according to the substitution patterns of ring C. Both the oxidation state of the heterocyclic ring and the position of ring B are important in the classification.

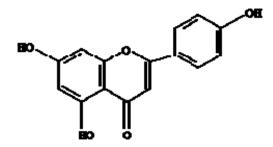
Examples of the 6 major subgroups are:

1. Chalcones



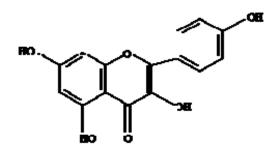
2. Flavone (generally in herbaceous families, e.g. Labiatae, Umbelliferae, Compositae). Apigenin (Apium graveolens, Petroselinum crispum).

Luteolin (Equisetum arvense)

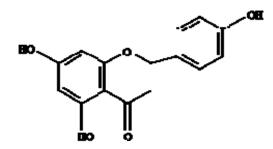


3. Flavonol (generally in woody angiosperms)Quercitol (Ruta graveolens, Fagopyrum esculentum, Sambucus nigra)Kaempferol (Sambucus nigra, Cassia senna, Equisetum arvense, Lamium album, Polygonum bistorta).Myricetin

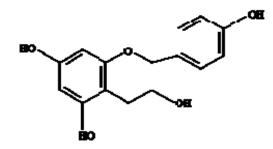
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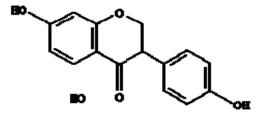
4. Flavanone



5. Anthocyanins

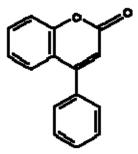


6. Isoflavonoids



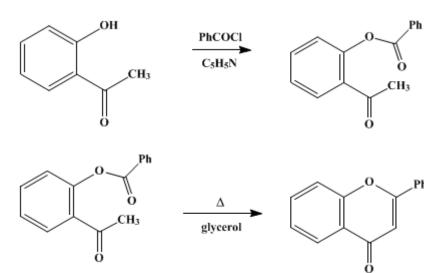
Most of these (flavanones, flavones, flavonols, and anthocyanins) bear ring B in position 2 of the heterocyclic ring. In isoflavonoids, ring B occupies position 3.

A group of chromane derivatives with ring B in position 4 (4-phenyl-coumarins = NEOFLAVONOIDS) is shown below.



The Isoflavonoids and the Neoflavonoids can be regarded as ABNORMAL FLAVONOIDS.

SYNTHESIS OF FLAVONE



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