Carotenoids and Feather Pigmentation

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What are Carotenoids?

Carotenoids are a group of compounds composed of relatively simple molecules.

Between 500-600 specific carotenoids have been identified

Noncarotenoid Plumage Colour

Not all plumage colours are due to carotenoids:

- feather structure and light refraction
- microscopic air cells in the barbs of the feather are the sites where refraction occurs
- feather diseases: upset air cells and disrupt refractive process
  - green feathers to appear yellow
  - blue feathers to appear white.
- blue and white colours: structural elements influence organization and positioning of keratin fibrils
- green feathers result from yellow pigmentation and the refraction of blue light.

Source of Carotenoids

Synthesised only by plants

Animals (insects, molluscs, crustaceans, fish) concentrate and metabolise

- provide a rich food source for birds

Carotenoids vs. Xanthophylls

a) Carotenoids:

- unmodified cyclohexenyl rings
- α- and β-carotene
- utilised by flamingos
- not preferred by canaries and chickens

b) Xanthophylls:

- oxycarotenoids with alcohol, keto or ester groups on terminal cyclohexenyl rings.
- lutein, zeaxanthin, astaxanthin, rhodoxanthin, capsanthin.
- utilised by canaries and chickens
- not readily utilised by flamingos. Flamingos transform β-carotene to astaxanthin but do not utilise it in its pure form.

Molecular Characteristics of Carotenoids

Long chains linking the two ends groups
- differ only in the presence and number of oxygen atoms
- differences dictate the physical and chemical properties of each carotenoid.

Chromophore
- chain in all three molecules has a series of alternating double bonds
- responsible for colour

Position and type of oxygen groupings varies
- zeaxanthin: the oxygen is part of a grouping formed by oxygen and hydrogen
- astaxanthin: characterized by two identical hydroxyls that are found next to an oxygen, which is linked to carbon by a double bond.

End group conjugation:
- double bonds in the end groups do not alternate directly with double bonds in chain
- β (beta): end group conjugated with a double bond. (β-carotene, zeaxanthin and astaxanthin are all β,β-carotenoids)
- ε (epsilon): end group double bonds spaced further apart not conjugated with chain
- β,ε-carotenoids and ε,ε-carotenoids are commonly found in plumage

As conjugation length increases, reflected colour shifts from yellow to violet:

- e,ε-carotenoids (canary xanthophylls) appear to be lemon yellow
- β,ε-carotenoids (lutein) appear golden yellow
- β,β-carotenoids (β-carotene, β-cryptoxanthin and zeaxanthin) appear orange

Position of carbonyl (C=O):
- adjacent to the final double bond
- increases the conjugation by one unit
  - Echinenone: orange-red (oxo),
  - Canthaxanthin, Astaxanthin: definite reds (di-oxo)
  - Rodoxanthin: 14 double conjugated bonds, appears as brilliant reddish purple.

Expression of Carotenoids in Plumage

Direct deposit:

- yellows of orioles, some tits, wagtails and the reds and pinks of flamingo and scarlet ibis
- yellow pigmentation is common in many Passeriformes,
  - can result from ingested carotenoids without modification (lutein and zeaxanthin)

Metabolic transformation:

- may shift orange to yellow during oxidation (zeaxanthin to canary xanthophylls).

Picolfulvins:

- optical properties that differ radically
- resemble lutein, zeaxanthin and β-cryptoxanthin
- differ in the absence of double bonds adjacent to the end group β.
- responsible for yellow pigments in some American and Asian woodpeckers.

Red plumage:

- direct ingestion (astaxanthin, rodoxanthin)
- metabolic oxidation: conjugation extends to the carbonyl group
  - colour to shifts from yellow to red.

Therefore:
β-carotene ➢ echinenone ➢ cathaxanthin
Lutein ➢ α-doradoxanthin
Zeaxanthin ➢ adonixanthin ➢ astaxanthin
β-cryptoxanthin ➢ 3-hydroxy-echinenone ➢ adonirubin
Rubixanthin ➢ 4-oxo-rubixanthin

Often only the male undergoes these transformations.

Rodoxanthin:

- reddish-purple coloured molecule
- yew tree’s seed-coat or aril and also occurs in several conifers
- never been identified in European Passeriformes
- responsible for red colouring in American varieties of waxwing and tanagers.

Metabolic Destiny of Carotenoids

- β-carotene: not utilised in its pure form
- oxidised to echinenone > canthaxanthin, both of which are absorbed
- further oxiudation of echinenone > 3-hydroxy-echinenone > adonirubin > astaxanthin
- further oxidation of canthaxanthin > adonirubin > astaxanthin. Alternatively, echinenone can undergo hydroxylation to form 3-hydroxy-echinenone.

Lutein:forms the basis of various tones of yellow, green, orange and red.

- common in green parts and seeds of vegetables,
- some flower petals
- many insects (especially in the larval form)
- absorbed in its pure or oxidized form.
- if oxidised to α-doradexanthin it forms reds and if canary xanthophylls it forms yellow.

Zeaxanthin: common in vegetables and arthropods

- present in smaller quantities than lutein
- particularly rich in certain varieties of corn and some insect larvae.
- pure state it provides warmer shades of yellow compared with lutein-based yellow
- oxidized and dehydrogenized to form the reds and yellows of most insectivorous birds.

The red carotenoids astaxanthin and rodoxanthin can be absorbed directly.

Case Studies

Bee-eaters:

- supplemented with Canthaxanthin
- birds faded to lighter colours
- supplemented with mixed carotenoids, pigmentation maintained.
- metabolic transformation of lutein in order to maintain red pigmentation?

Bald Eagle:

- provided with whole prey raised on grains
- do not represent the full spectrum of carotenoids required by these birds
- bright yellow beak and feet faded.
- Injection of mixed carotenoids into prey

Helmeted Honeyeater:

- inhouse mix of honey and eggs maintained colour
- commercial mixes: faded
- lutein and zeaxanthin from corn fed to chickens > egg yolks

- possible antagonism of carotenoid uptake by high vitamin A

Environment:

- balanced diet, regular exercise and balanced sexual stimuli
- male Crossbill and Pine Grosbeak require an environment that mimics the wild habitat
- stress associated with restricted spaces or other negative factors inhibits the oxidation process that turns yellow ingested carotenoids to red
- may overcome by providing carotenoids similar to those formed in the wild as these may be absorbed directly without undergoing metabolism.

Parrots and Carotenoids

Parrot pigments differ in structure from carotenoids

Endogenous and not exogenous (carotenoids are exogenous pigments because birds cannot construct them internally and must absorb them from outside through the diet. Endogenous pigments are melanin)

Red plumage of the Scarlet Macaw (*Ara macao*):

- linear polyenal structure comparable with the molecules tetradecahexenal, hexadecaheptenal, octadecaoctenal and eicosanonenal.

Carotenoids and Vitamin A

Pro vitamin A from carotenoids

Conversion of carotenoids to vitamin A varies, lycopene has no vitamin A activity.

Animals are able to regulate the conversion of carotenoids to vitamin A, thus avoiding any potential vitamin A toxicities.

Conversion of specific carotenoids to vitamin A may be species specific.

Carotenoids and Antioxidant Activity

Astaxanthin protects mitochondria of vitamin E deprived cells from damage by Fe2+-catalysed lipid peroxidation

- inhibitory effect is stronger than that of α-tocopherol
- antioxidant activity of astaxanthin in iron-containing vesicles may be derived from its rigidifying effect in membranes and inherent scavenging ability.