# Biochimica delle sostanze naturali A.A. 2022-2023

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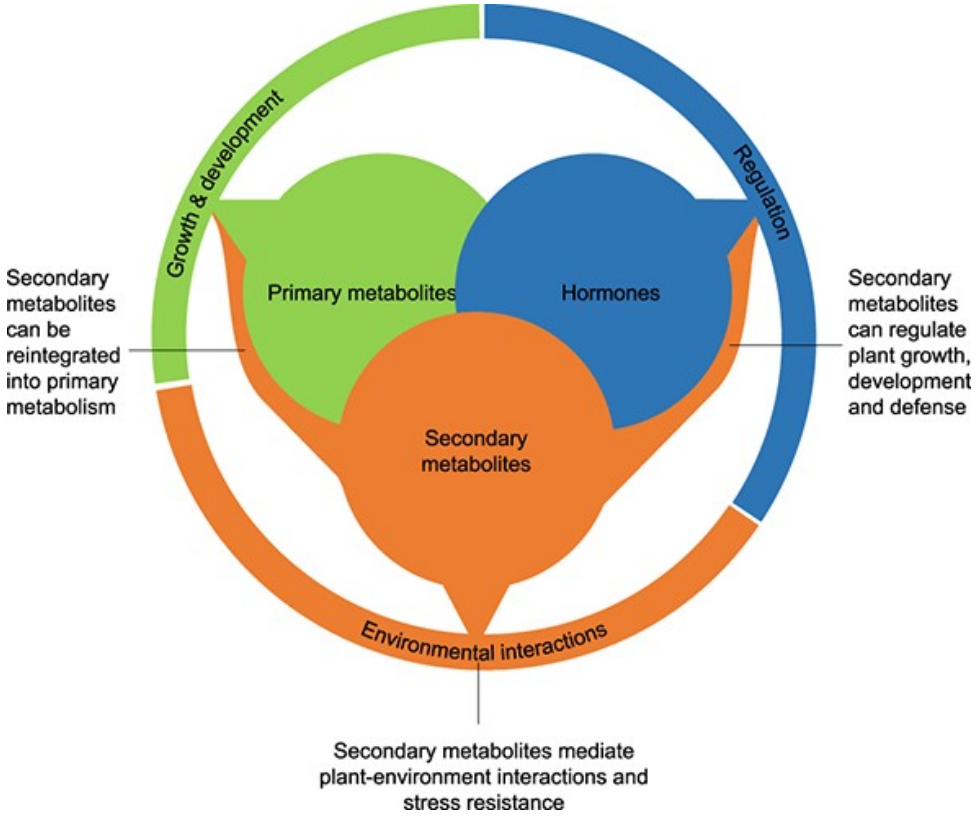
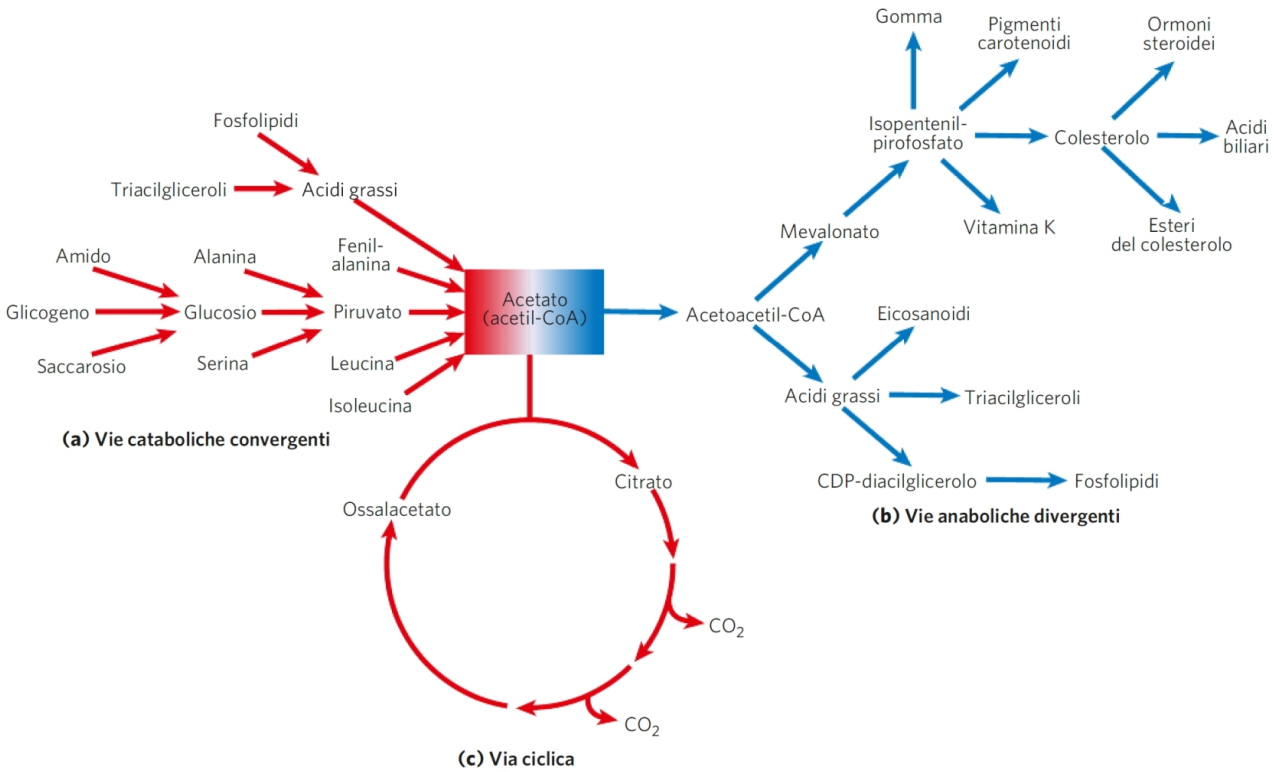
# Classification of low molecular weight compounds in plants




- The plant kingdom produces hundreds of thousands of low molecular weight organic compounds (less than 3000 da).
- Based on the assumed functions of these compounds, the research community has classified them into three overarching groups:

➢ primary metabolites, which are directly required for plant growth;
➢ **secondary (or specialized) metabolites, which mediate plant–environment interactions**;
➢ hormones, which regulate organismal processes and metabolism.



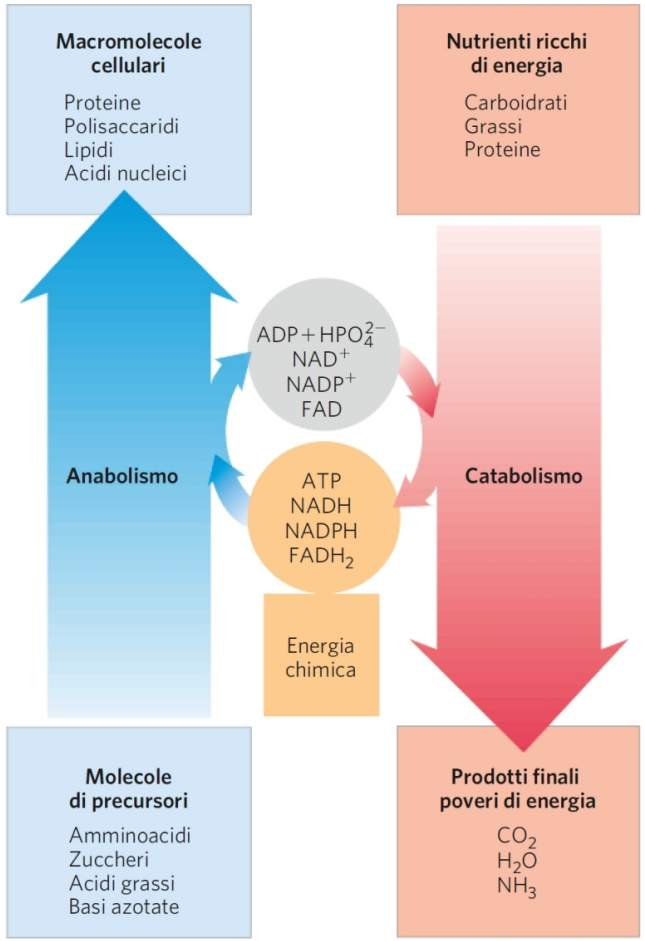




**Figura 2** **Quadro generale delle relazioni energetiche tra vie anaboliche e vie cataboliche.** Le vie cataboliche generano energia in forma di ATP, NADH, NADPH e $FADH_2$. Queste molecole sono poi usate nelle vie anaboliche per convertire piccoli precursori in macromolecole.

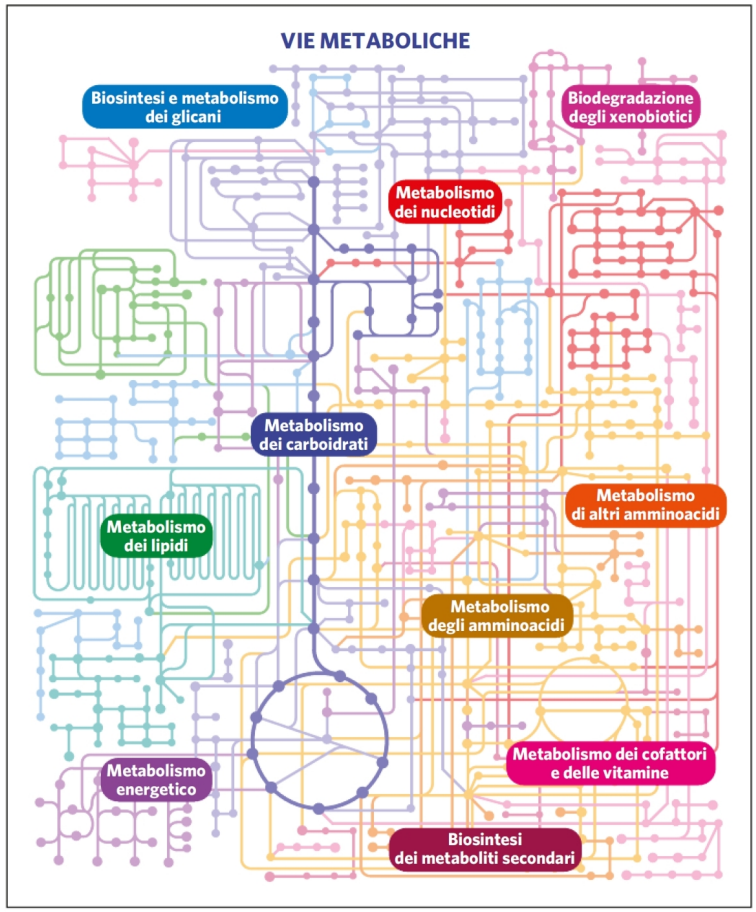
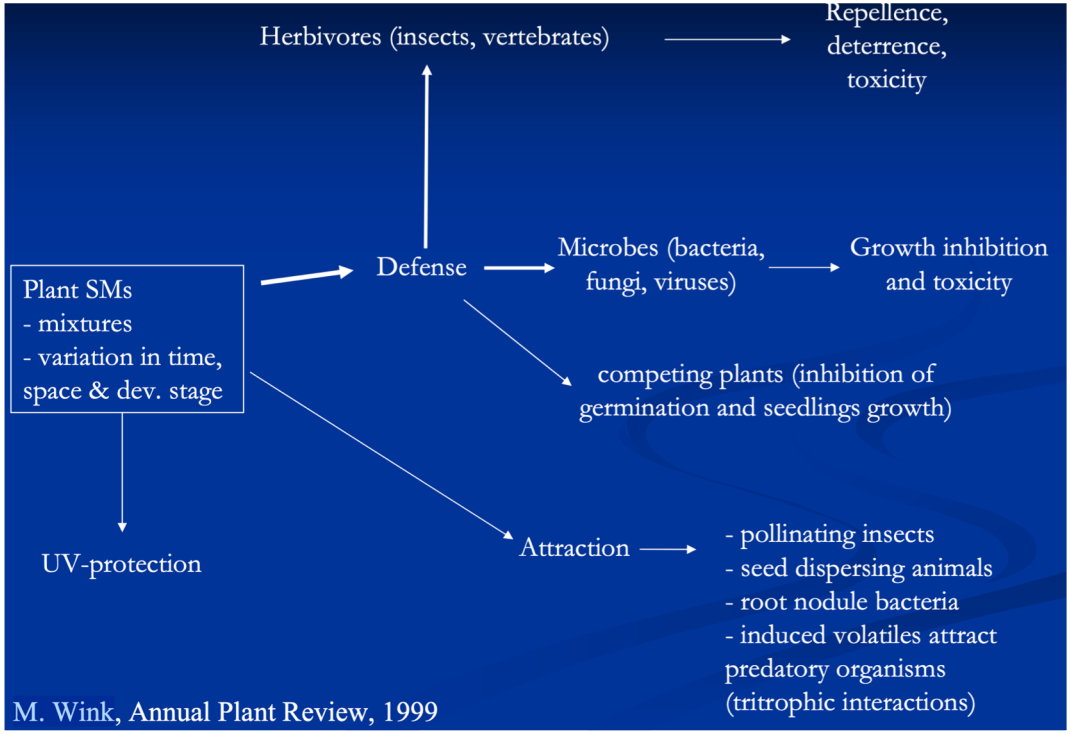


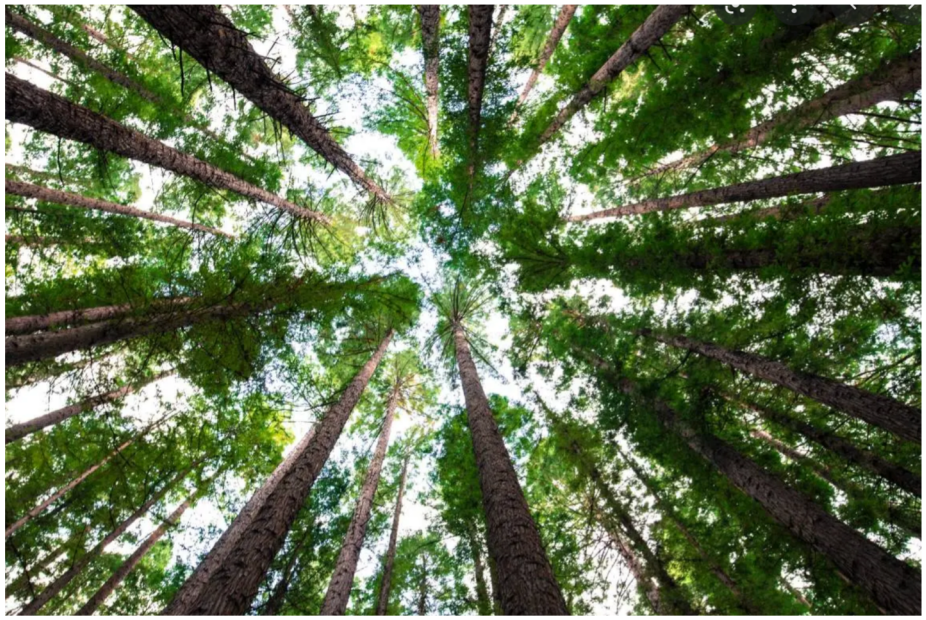

**Figura 13.28 Il metabolismo può essere rappresentato come un reticolo tridimensionale.** Una cellula eucariote è in grado di sintetizzare circa 30 000 differenti proteine, che catalizzano migliaia di reazioni in cui sono coinvolte molte centinaia di metaboliti, la maggior parte dei quali partecipa a più di una via metabolica. In questa visione globale molto semplificata delle vie metaboliche, ciascun puntino rappresenta un intermedio e ogni linea di connessione rappresenta una reazione enzimatica. Per un'immagine più realistica, ma al tempo stesso anche molto più complicata del metabolismo, *vedi* la banca dati online KEGG PATHWAY (www.genome.ad.jp/kegg/pathway/map/map01100.html). In questa mappa interattiva, si può cliccare su ciascun puntino per ottenere ulteriori dati sul composto corrispondente a quel puntino e agli enzimi di cui esso è substrato. [Fonte: www.genome.ad.jp/kegg/pathway/map/map01100.html.]

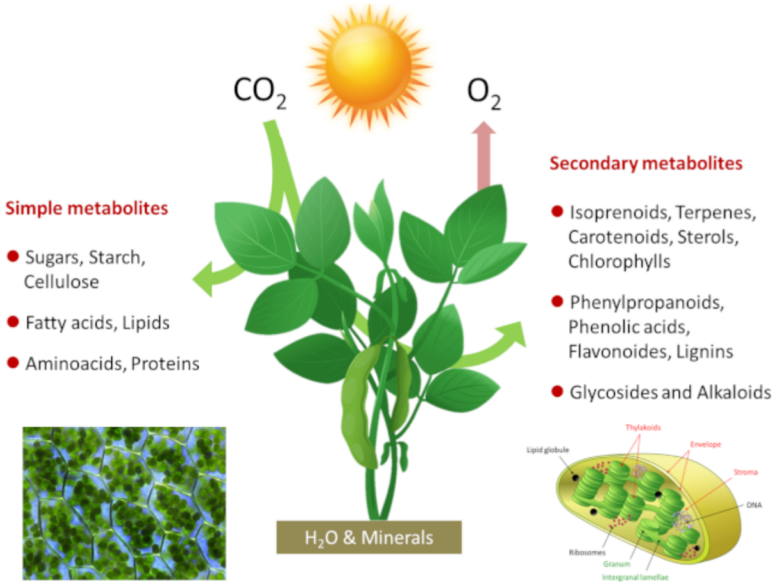
# Functions of secondary metabolites




- Compounds are generally characteristic of a particular species or family (specific taxonomic distribution )
- Classified as "secondary metabolites" in contrast to "primary metabolites
- No nutritional or structural function
- Functional roles may include:
  - - color (attraction or repulsion)
  - - sexual attraction
  - - defense (e.g., plant toxins and antibiotics)
  - but many still have unknown function in the organism in which they are found.

# Secondary metabolites in plants






Secondary metabolites are grouped into classes on structural basis, biosynthetic pathways, or types of plants that produce them. The broadest classes are **terpenoids**, **phenolics** and **alkaloids**.

# Main groups of secondary metabolites

29,000 terpenes- derived from the C5 precursor isopentenyl diphosphate (IPP)

12,000 alkaloids- derived from amino acids

8,000 phenolics- shikimate pathway or malonate/acetate pathway

# Main secondary metabolites

Nitrogen containing:

- Alkaloids (12,000)
- Non protein amino acids (600)
- Amines (100)
- Cyanogenic glycosides (100)
- Glucosinolates (100)

# Main secondary metabolites

Without nitrogen:

- Terpenoids (29,000):
mono- 1000
sesquiterpene- 3000
diterpenes-1000
triterpenes, steroids, saponines- 4,000

- Phenolics (8,000):
Flavonoids- 2000
Polyacetylens-1000
Polyketides- 750
Phenylpropanoids- 500

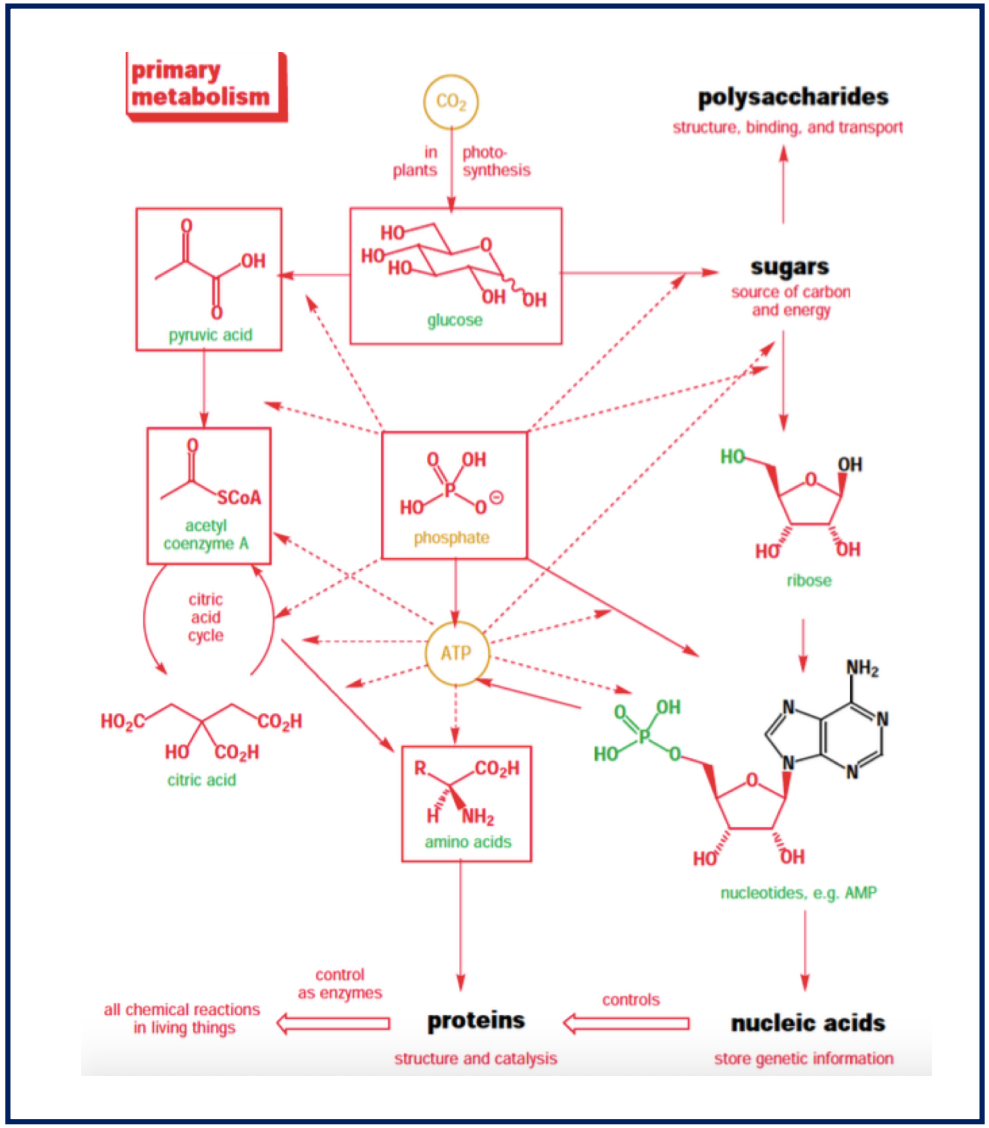
- **The most common roles for secondary metabolites in plants are ecological roles that govern interactions between plants and other organisms.**
- Many secondary metabolites are brightly colored pigments such as anthocyanins which color red, blue and yellow flowers. These attract pollinators and fruit and seed dispersers.
- Nicotine and other toxic compounds protect plants from herbivores and microbes.

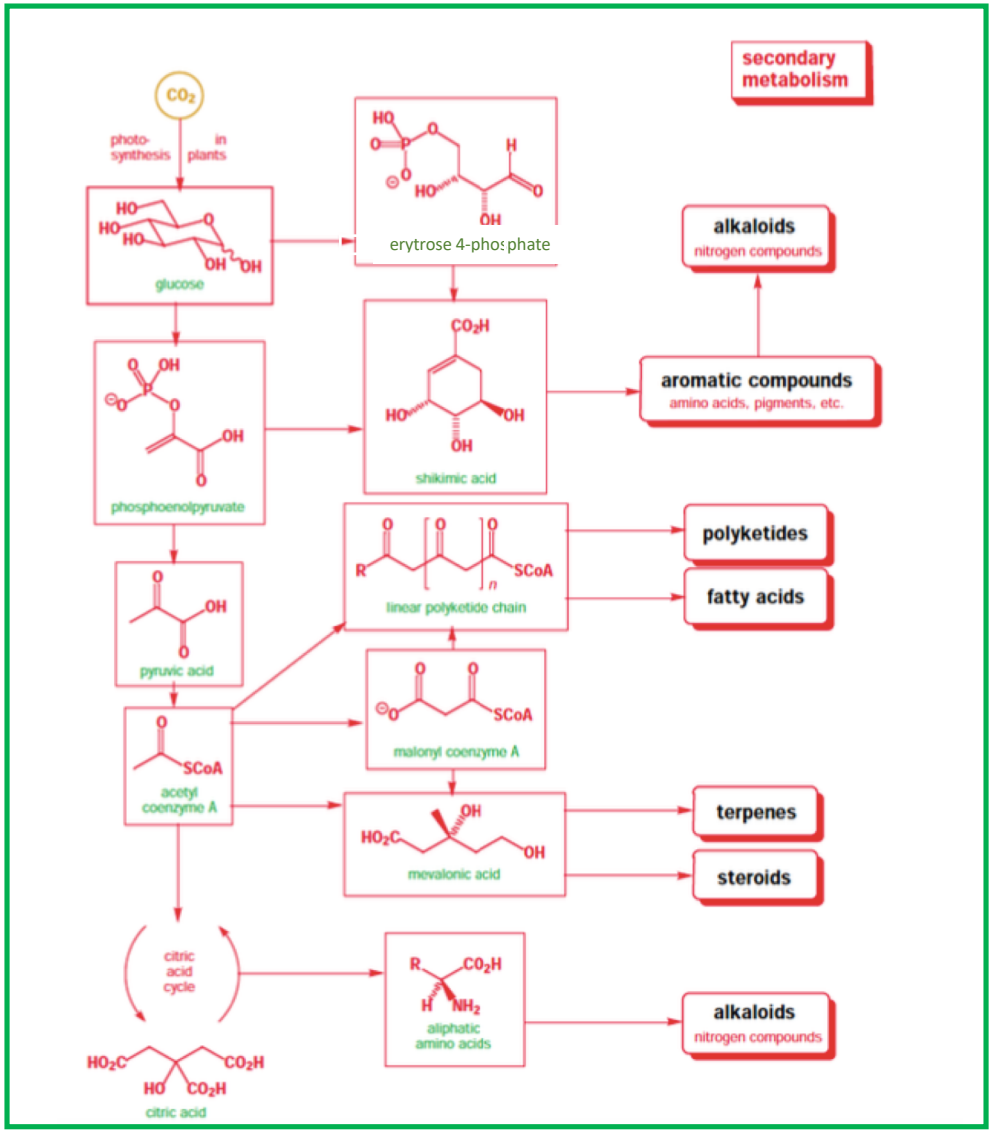
# Secondary metabolites as regulators of plant defense

Larrea tridentata, il cespuglio di creosoto

- In 1977, David Rhoades studied the properties of creosote bush (Larrea spp.) leaf resin (high levels of phenylpropanoid derivatives, lignans);
- This resin absorbs ultraviolet radiation, reduces evaporative water loss.
- It has also the capacity to form complexes with proteins, reducing the digestibility of plant materials for herbivores.

# Connection


primary metabolism
CO2
in plants
photo-synthesis
polysaccharides
structure, binding, and transport
pyruvic acid
glucose
sugars
source of carbon and energy
acetyl coenzyme A
phosphate
ribose
citric acid cycle
ATP
citric acid
amino acids
nucleotides, e.g. AMP
control as enzymes
all chemical reactions in living things
proteins
structure and catalysis
controls
nucleic acids
store genetic information

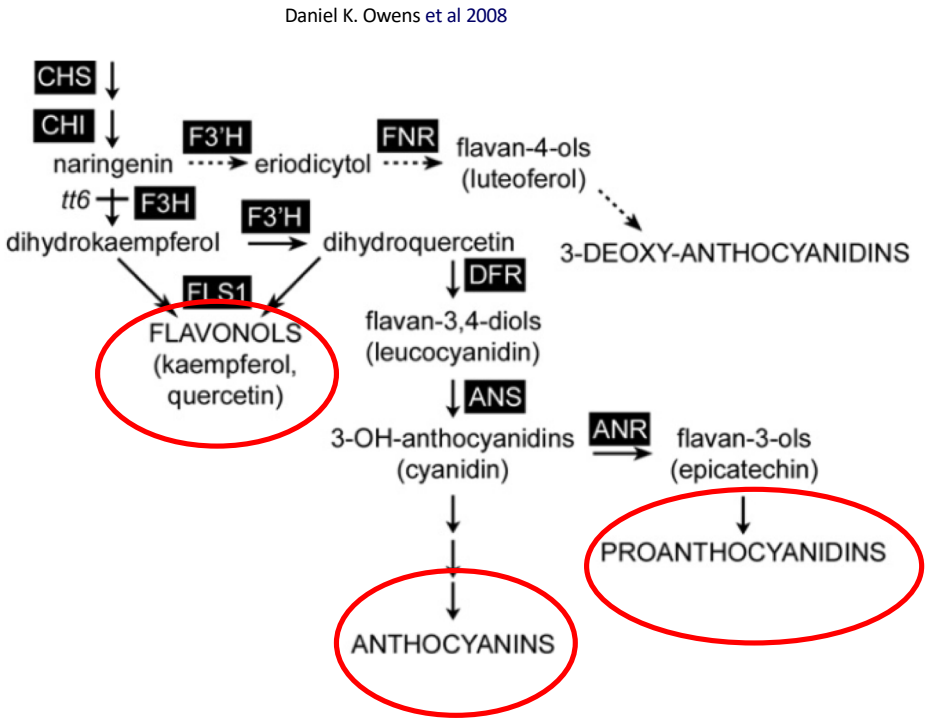

secondary metabolism
CO2
photo-synthesis
in plants
glucose
erythrose 4-phosphate
alkaloids
nitrogen compounds
aromatic compounds
amino acids, pigments, etc.
shikimic acid
phosphoenolpyruvate
polyketides
fatty acids
linear polyketide chain
pyruvic acid
malonyl coenzyme A
acetyl coenzyme A
terpenes
steroids
mevalonic acid
citric acid cycle
aliphatic amino acids
alkaloids
nitrogen compounds
citric acid

# Secondary Metabolites: other functions?

- Whereas primary metabolites are highly conserved, secondary metabolites evolve dynamically and are inherently variable in structure and production.
- Evidence for **secondary metabolites that contribute to primary metabolism**, is emerging.
- Secondary metabolites may serve as primary metabolite precursors.
- Degradation of many different secondary metabolites has been observed under specific environmental conditions and alterations in primary metabolites are observed in various plants with altered secondary metabolism.

# Secondary Metabolites: other functions?

Schematic of flavonoid biosynthesis in Arabidopsis




*Arabidopsis thaliana*

- In Arabidopsis, plants with mutations in the flavonoid pathway (FLAVANONE-3-HYDROXYLASE, F3H) show a reduction in the respiratory cofactor ubiquinone (coenzyme Q).
- Ubiquinone levels can be restored by adding dihydrokaempferol or kaempferol to the mutants.
- Labeling experiments demonstrate that the aromatic ring of kaempferol is integrated into ubiquinone, and that heme-dependent peroxidases likely use kaempferol to produce 4-hydroxybenzoate as a substrate for ubiquinone.

**Flavanone 3β-hydroxylase** (**F3H**; EC 1.14.11.9) is a 2-oxoglutarate dependent dioxygenase that catalyzes the synthesis of dihydrokaempferol, the common precursor for three major classes of 3-hydroxy flavonoids, the **flavonols**, **anthocyanins**, and **proanthocyanidins**.