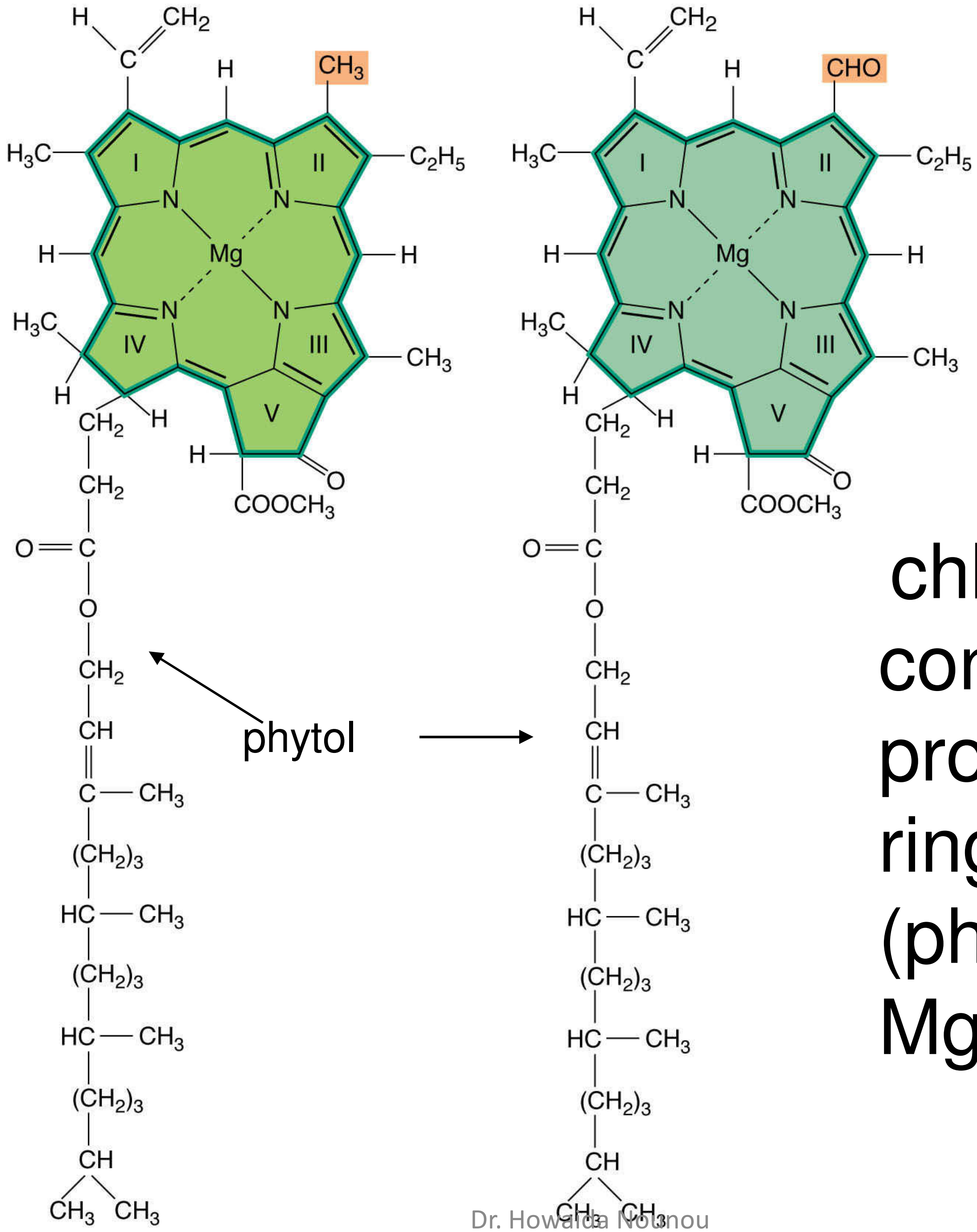
Chloropyll Synthesis

Dr. Howaida Nounou



Chlorophyll *a*   Chlorophyll *b*

chlorophyll consists of protoporphryin ring, alcohol (phytol) and Mg2+

Porphyrin

Porphyrins serve as prosthetic groups for proteins that function in oxygen transport (hemoglobin and myoglobin), breakdown of peroxide (catalase), electron transport (cytochromes a, b and c), hydroxylation (cytochrome P450) and light absorption (chlorophyll).

The porphyrins are heterocyclic ring structures that include four pyrrole rings joined together through methylene bridges ($-CH_2-$)

The most abundant porphyrins in nature are found in hemoglobin and the chlorophylls

In the center of porphyrins a metal atom binds to the nitrogen atoms of the pyrrole units.

In heme and related porphyrins this atom is iron. In chlorophyll the metal atom is magnesium.

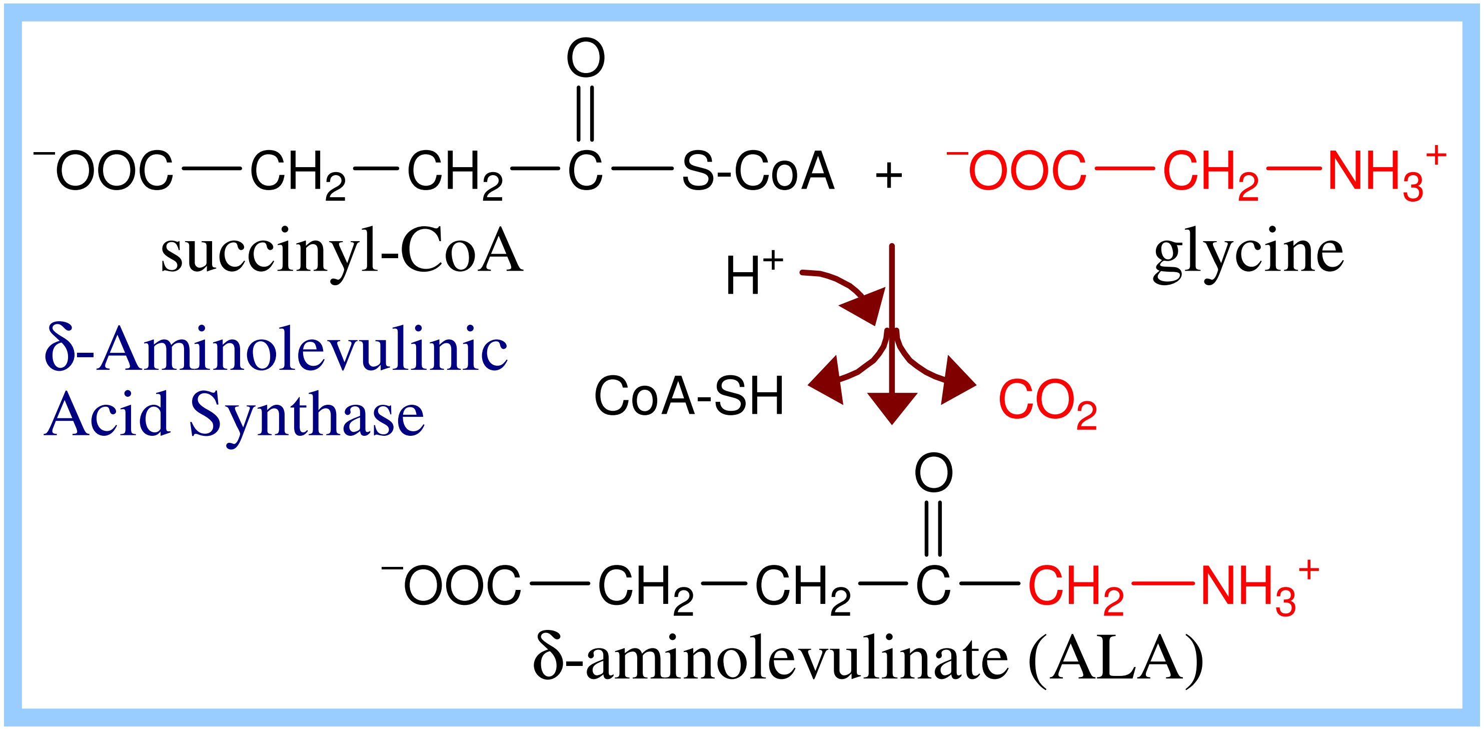
Porphyrin Synthesis

The first and rate limiting reaction in porphyrin synthesis is the reaction catalyzed by **δ-aminolevulinate synthase in the mitochondria**:

glycine + succinyl CoA --> NH_3^+-CH_2-CO-CH_2-CH_2-COO+CO_2+CoA

δ -aminolevulinate (ALA)

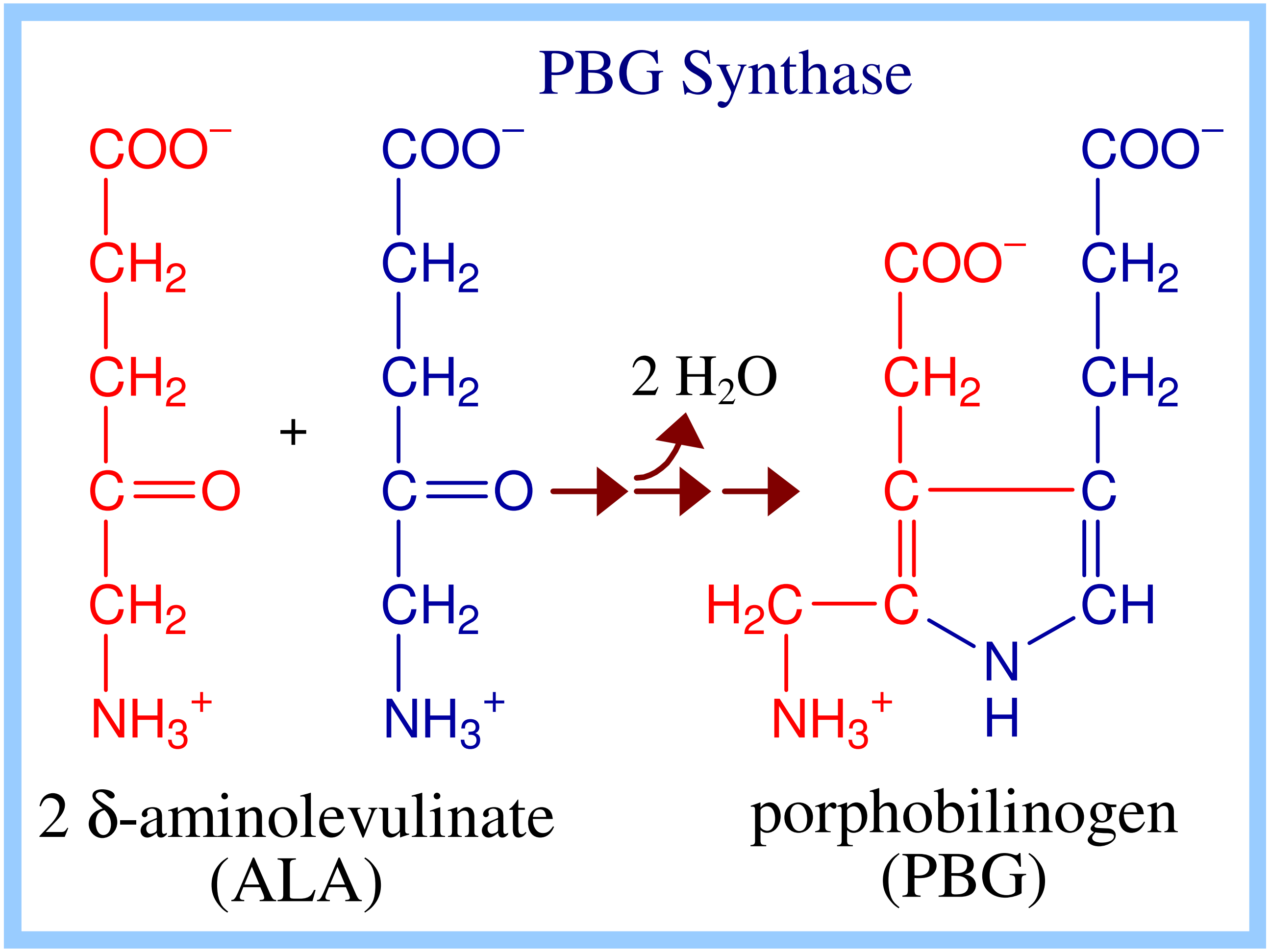
Pyridoxal phosphate is a cofactor for δ-aminolevulinate synthase.

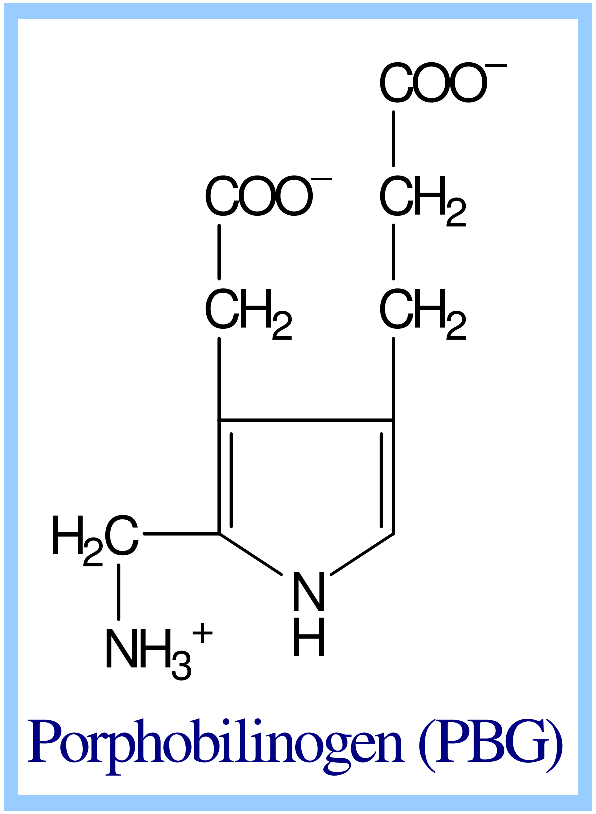


porphyrin synthesis begins with condensation of glycine & succinyl-CoA, with decarboxylation, to form **δ-aminolevulinic acid** (**ALA**).

- In the **second reaction** of porphyrin synthesis, two molecules of δ-aminolevulinate condense to form the monopyrrole, porphobilinogen **by δ-aminolevulinic acid dehydratase** (ALA dehydratase) or **Porphobilinogen Synthase in the cytosol.**

- **Porphobilinogen Synthase** is inhibited **by lead** that combine with the S H- group of the enzyme.





PBG Synthase (Porphobilinogen Synthase), also called ALA Dehydratase, catalyzes condensation of **two** molecules of **δ-aminolevulinate** to form the pyrrole ring of **porphobilinogen** (**PBG**).

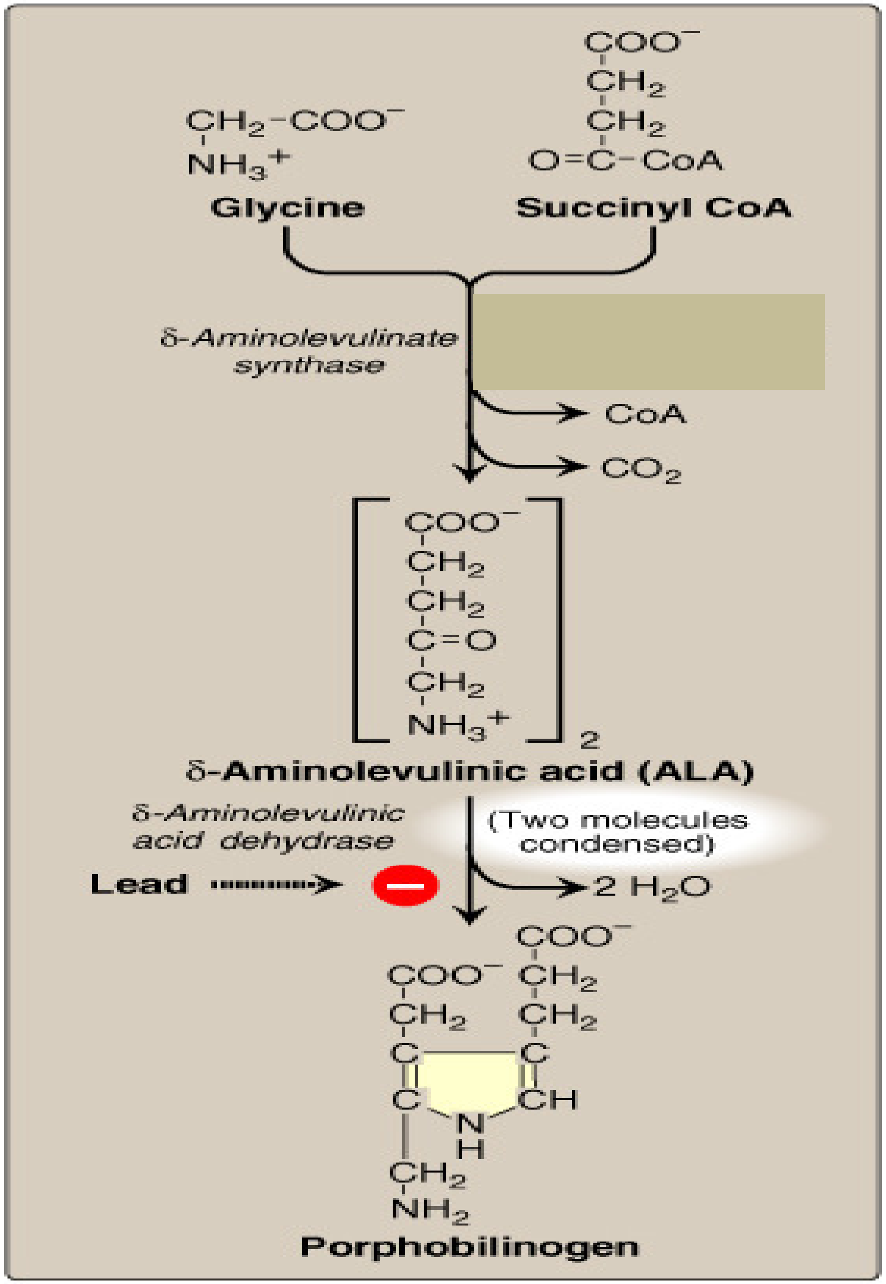
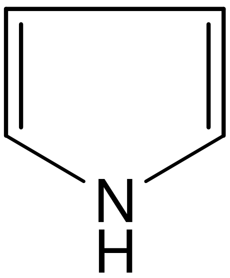
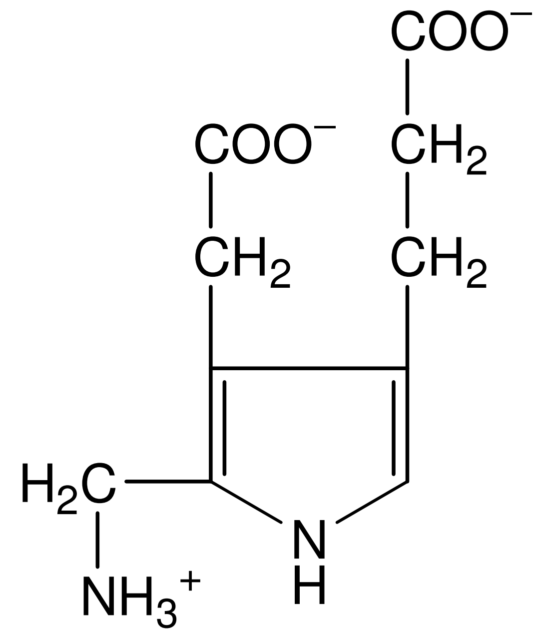


Figure 21.3
Pathway of porphyrin synthesis:formation of porphobilinogen. (Continued in Figure 21.4.)



pyrrole

Porphobilinogen (PBG) is the first pathway intermediate that includes a **pyrrole** ring.



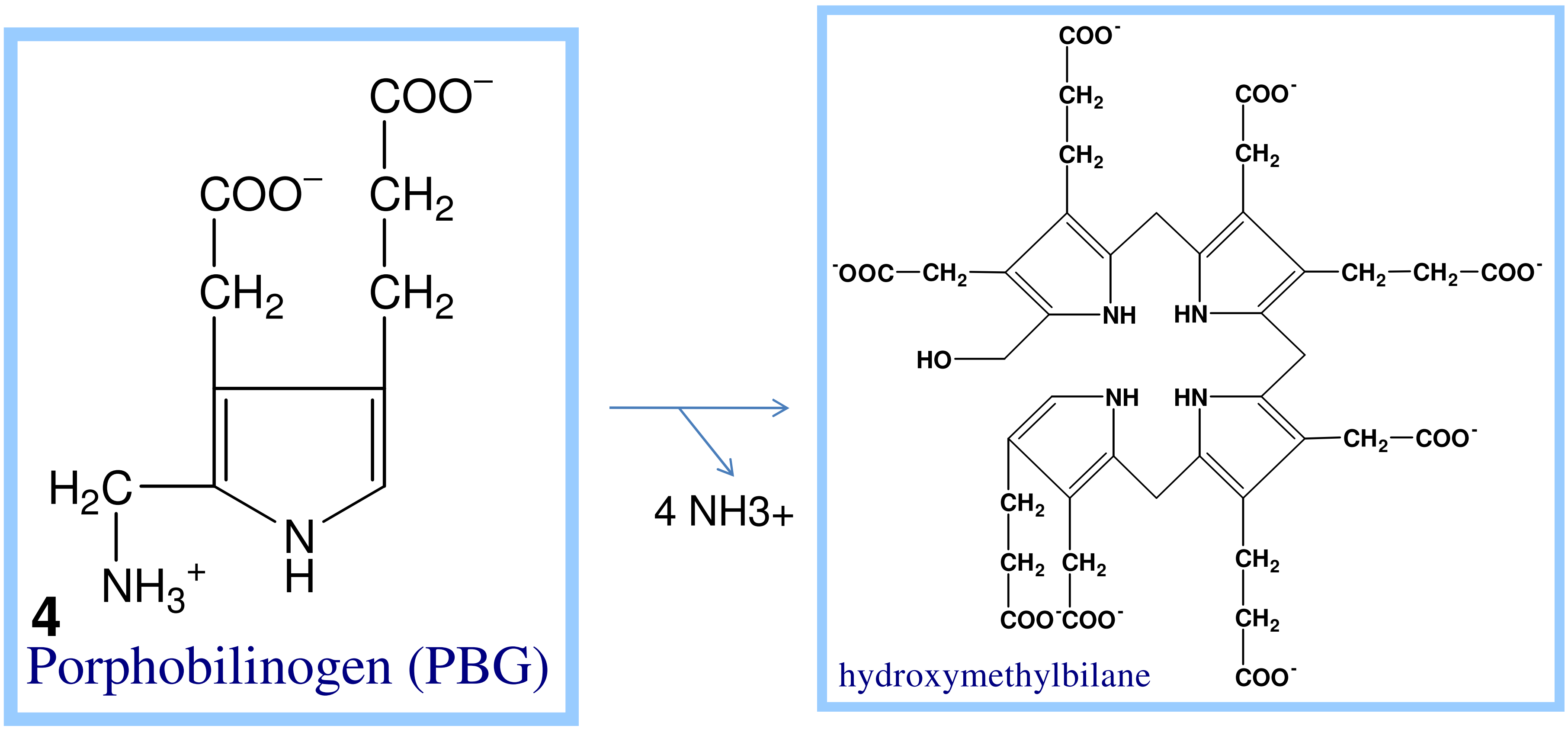
Porphobilinogen (PBG)

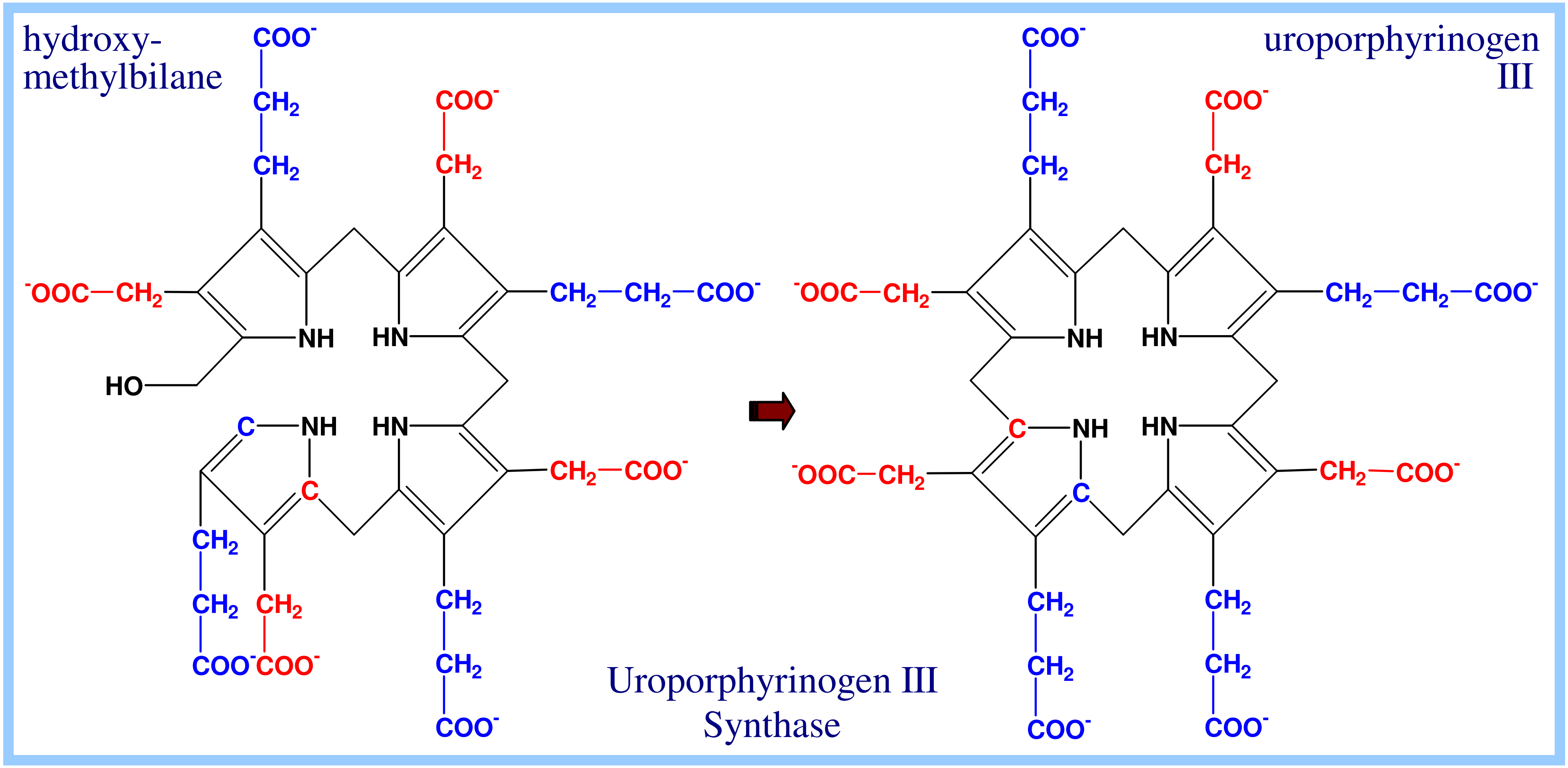
The **porphyrin** ring is formed by condensation of **4** molecules of **porphobilinogen**.

Porphobilinogen Deaminase (hydroxymethylbilane synthase) catalyzes successive PBG **condensations**.

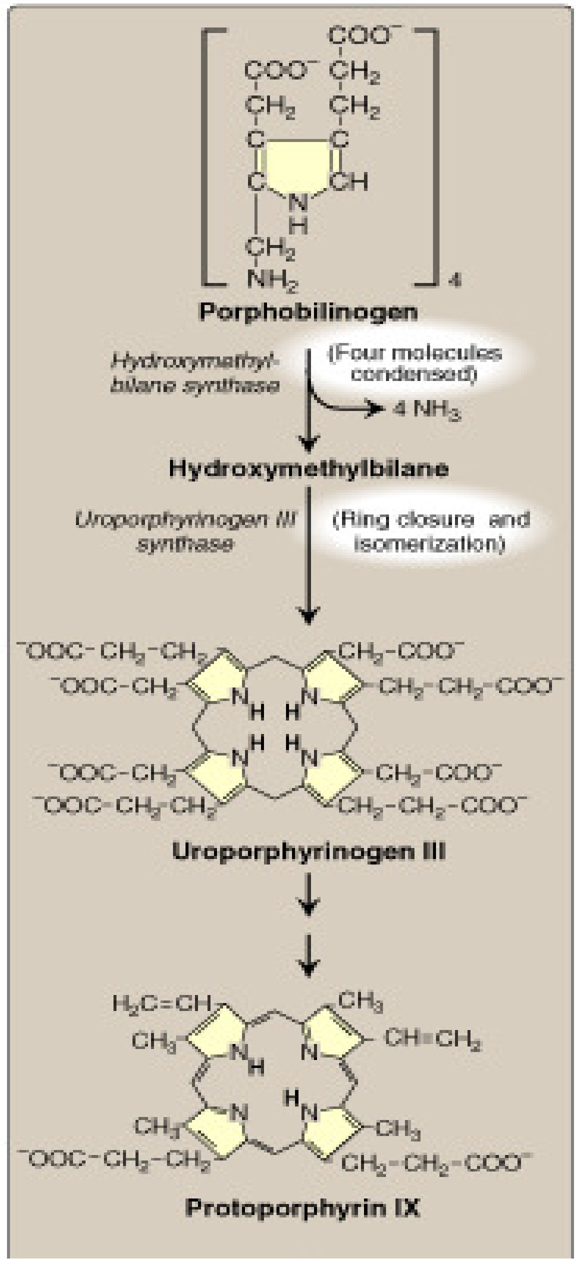
The combination of four porphobilinogen molecules gives a linear tetrapyrrole hydroxymethylbilane, it is accompanied by the **loss of four molecules of ammonia**

Porphobilinogen Deaminase





Uroporphyrinogen III Synthase catalyzes ring closure and isomerization, converts the linear tetrapyrrole hydroxymethylbilane to the macrocyclic **uroporphyrinogen III in the cytosol.**


Porphobilinogen
Hydroxymethyl-bilane synthase
(Four molecules condensed)
4 NH3
Hydroxymethylbilane
Uroporphyrinogen III synthase
(Ring closure and isomerization)
Uroporphyrinogen III
Protoporphyrin IX

- Further intermediates in the synthesis of chlorophyll are **coproporphyrinogen III, protoporphyrinogen IX and protoporphyrin IX.**

- **Uroporphyrinogen III** → **coproporphyrinogen III** + 4 CO_2

  Uroporphyrinogen III decarboxylase
  (Cytosol)

coproporphyrinogen III ↓ **protoporphyrinogen IX** + 2 CO_2

coproporphyrinogen III oxidase (mitochondria)
Oxidative decarboxylation

protoporphyrinogen IX → **protoporphyrin IX** + 6 H

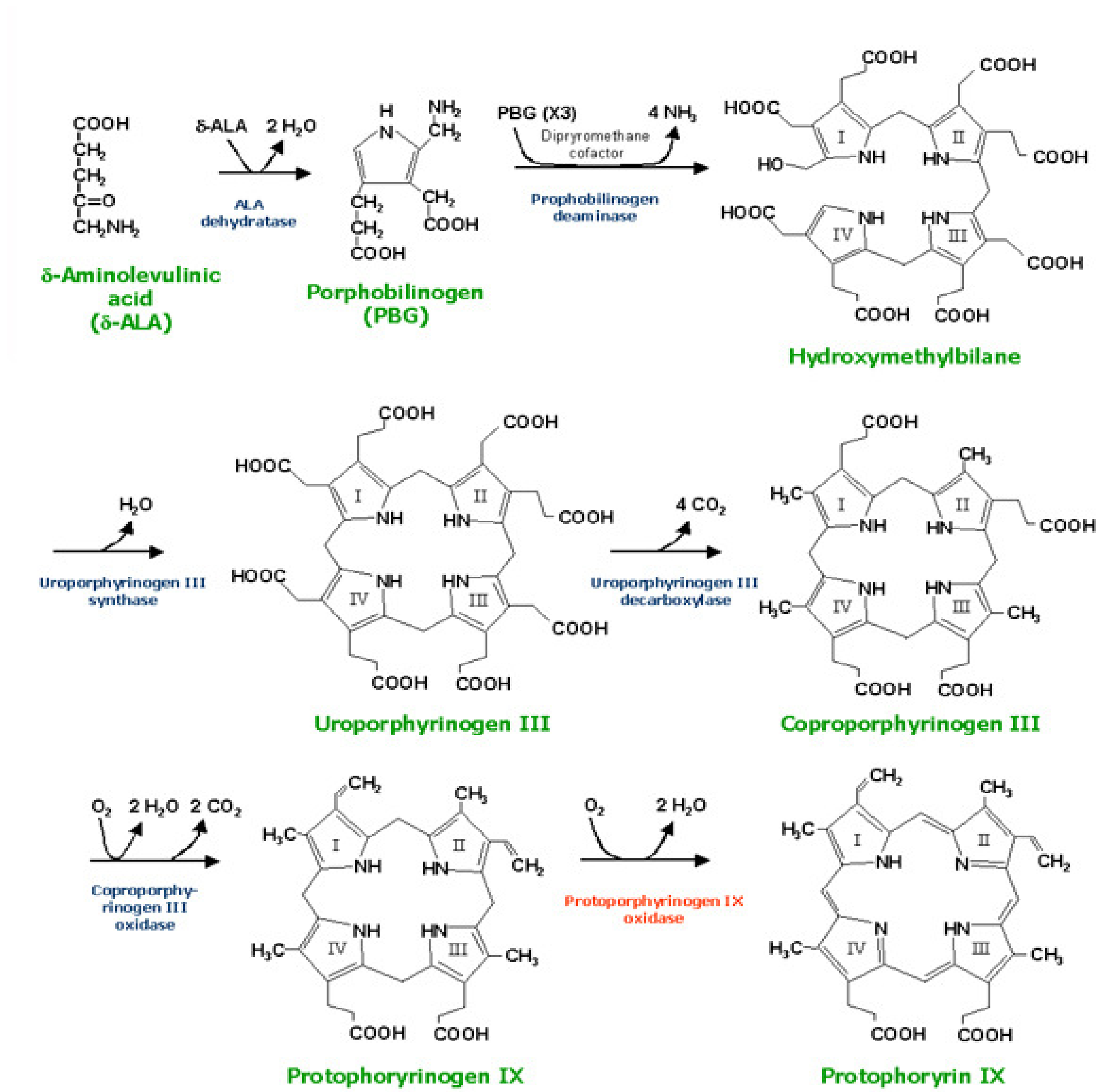
protoporphyrinogen IX oxidase (mitochondria)

protoporphyrin IX ↓ **Mg- protoporphyrin**

Mg 2+

Mg- protoporphyrin → **Chlorophyll**

series of reactions

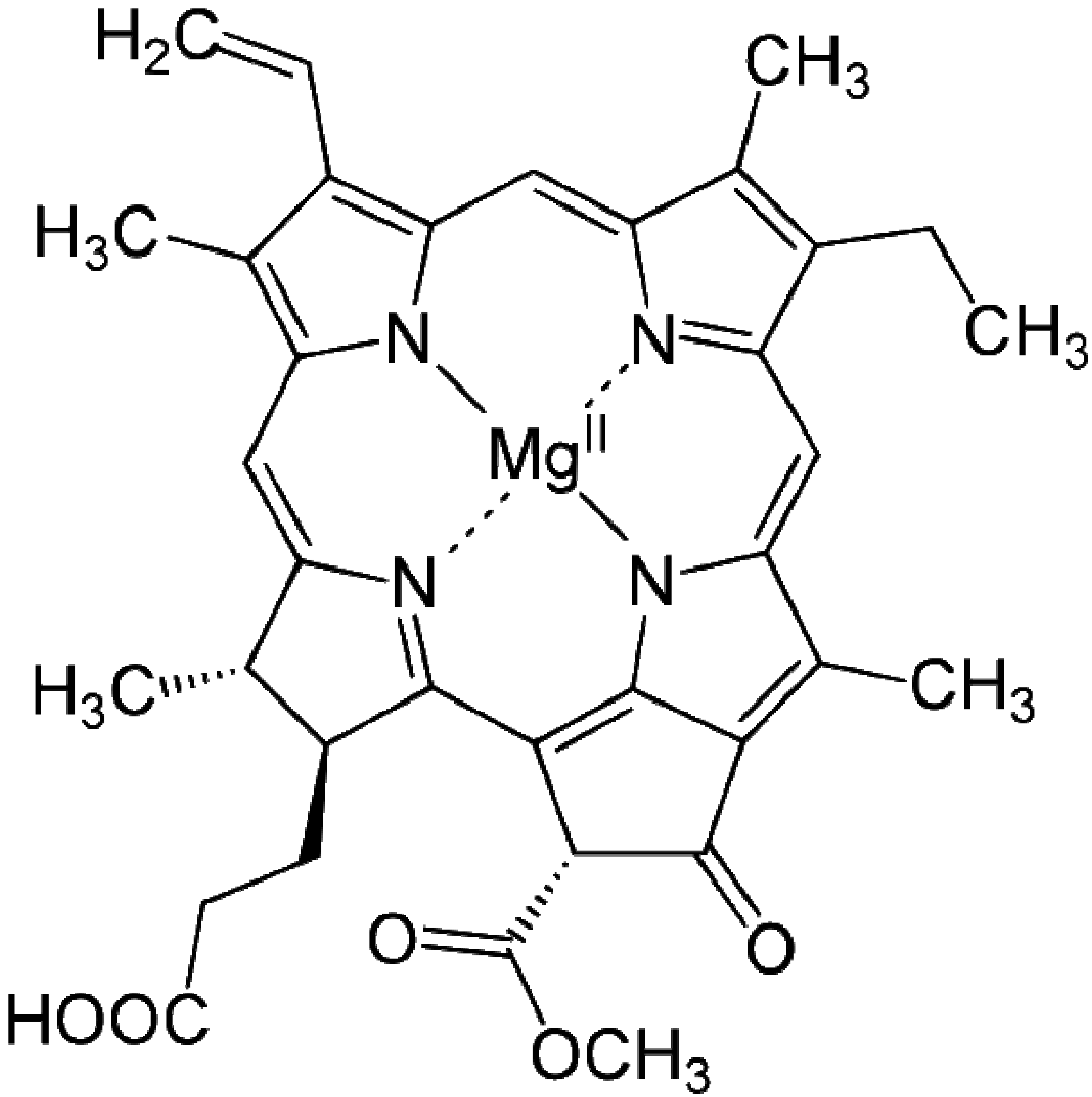


The last step, catalyzed by the enzyme protoporphyrinogen IX oxidase, is inhibit by herbicides from several chemical families.

- After Mg2+ is added to protoporphyrin to form **Mg- protoporphyrin** which is a substrate for series of reactions that terminates in chlorophyll synthesis.
- These reactions involve **additional changes in the side chains** and finally **the partial reduction of one of the pyrrole rings**

- The first reaction and the last two reactions of protoporphyrin III synthesis occur in mitochondria with the other reactions being in the cytosol

Protochlorophyllide



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- **Protochlorophyllide**, or **monovinyl protochlorophyllide**, is an immediate precursor of chlorophyll *a* that lacks the phytol side-chain of chlorophyll.
- Unlike chlorophyll, protochlorophyllide is highly fluorescent; it glow red if irradiated with blue light.
- In Angiosperms, the last step, conversion of protochlorophyllide to chlorophyll, is light-dependent, and such plants are pale (etiolated) if grown in the darkness.
- Gymnosperms, algae, and photosynthetic bacteria have another, light-independent enzyme and grow green in the darkness as well

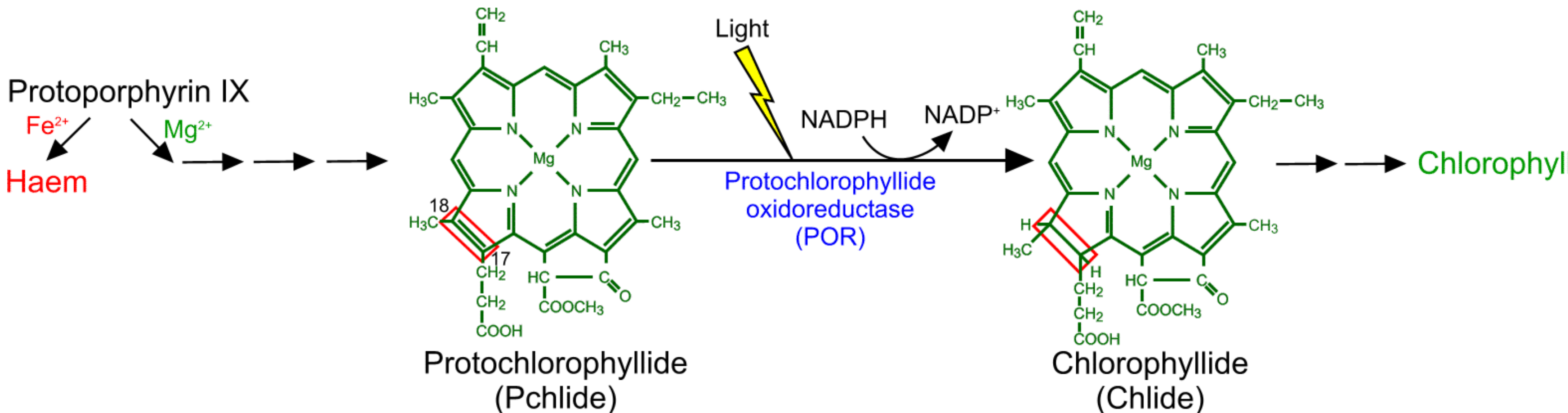
Conversion of Protochlorophyllide to chlorophyll

- The enzyme that converts protochlorophyllide to chlorophyll is **protochlorophyllide reductase**.

- There are two structurally unrelated proteins with this activity: the light-dependent and the dark-operative. The light-dependent reductase needs light to operate.

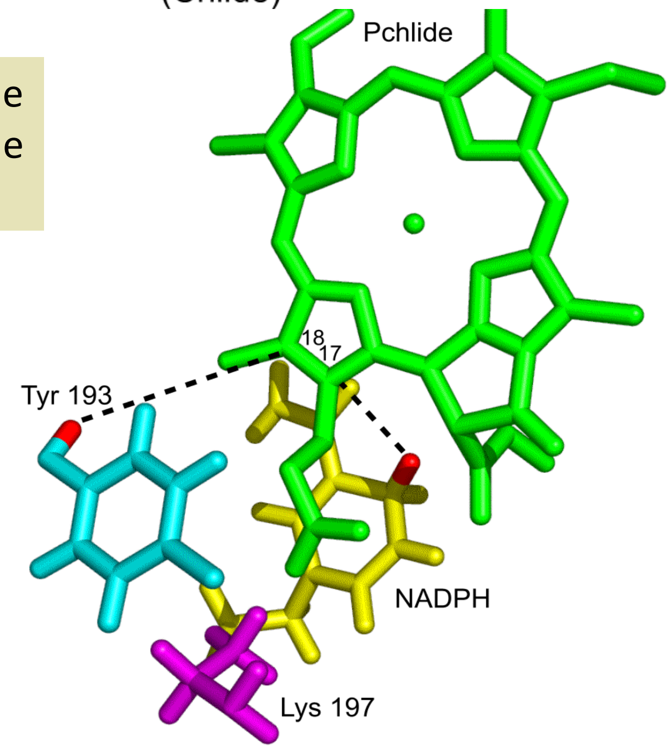
- The dark-operative version is a completely different protein, consisting of three subunits that exhibit significant sequence similarity to nitrogenase, which catalyzes the formation of ammonia from dinitrogen

Light-driven step in the biosynthesis pathway of chlorophyll

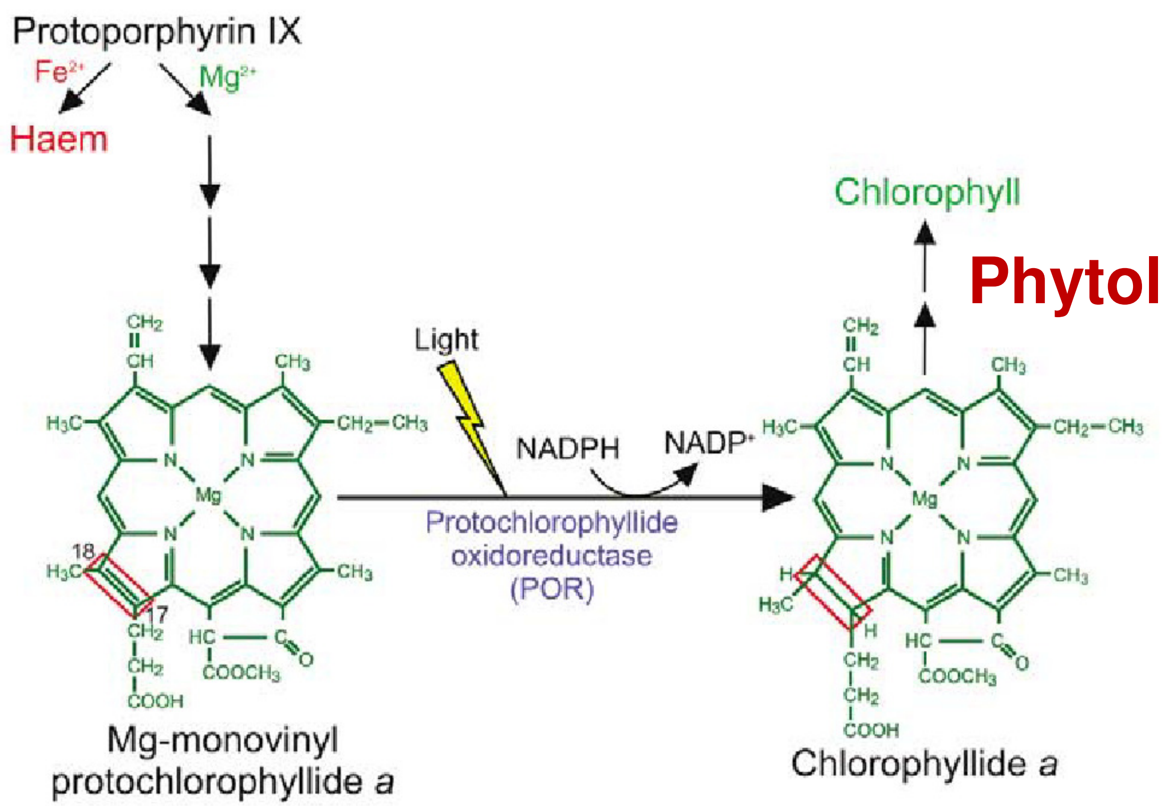


POR catalyses the light-driven reduction of the C17-C18 double bond of protochlorophyllide (Pchlide) to form chlorophyllide (Chlide).

The reaction involves hydride transfer from NADPH to the C17 position of the Pchlide molecule.



PChlide to Chlide conversion



Chlorophyll synthesis

– Most higher plants require light for chlorophyll synthesis, some can synthesis chlorophyll in the dark (Many algae) .

Control of chlorophyll synthesis :

- ALA synthetase is the rate limiting step in the process , ALA synthetase is inducible enzyme (Photo inducible) i.e. formation of this enzyme increase in light.
- Enzymes From ALA to protoporphyrin are constitutive (not induced) i. e. conc .remain fairly constant and not regulated .
- Some kind of RNA synthesis is required for large scale production of chlorophyll.

- An inhibitor of DNA metabolism [Fluorodeoxy- uridine] - actinomycin D, an inhibitor of DNA – dependent RNA synthesis , blocks greening of illuminated grown leaves of maize i.e. block chlorophyll synthesis , so even if the plant is put in light (illuminated) it dose not become green.