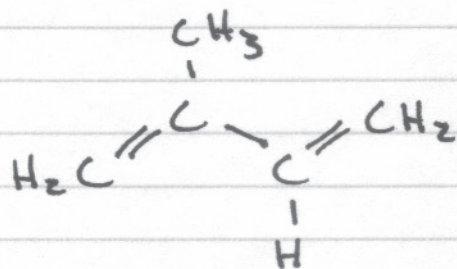


PIGMENTS OF PHOTOSYNTHESIS

There are three major groups:

CAROTENES / (carotenoids)
 BILINS and XANTHOPHYLLS
 CHLOROPHYLLS.

Carotenoids are synthesized from a basic 5-carbon isoprene unit.



These are condensed into a long (40-carbon) linear molecule phytoene: with few conjugated bonds, phytoene is colorless.

Subsequent desaturation effects double bond conjugation so that the molecule absorbs in the visible wavelengths.

Hydroxyl-containing derivatives are called xanthophylls.

(Mercur & Goodwin)

(or other oxygen-containing groups)

Carotenoids absorb maximally at about 530 nm. They function in protecting the photosynthesis apparatus from oxidation by singlet oxygen, superoxide, hydrogen peroxide.

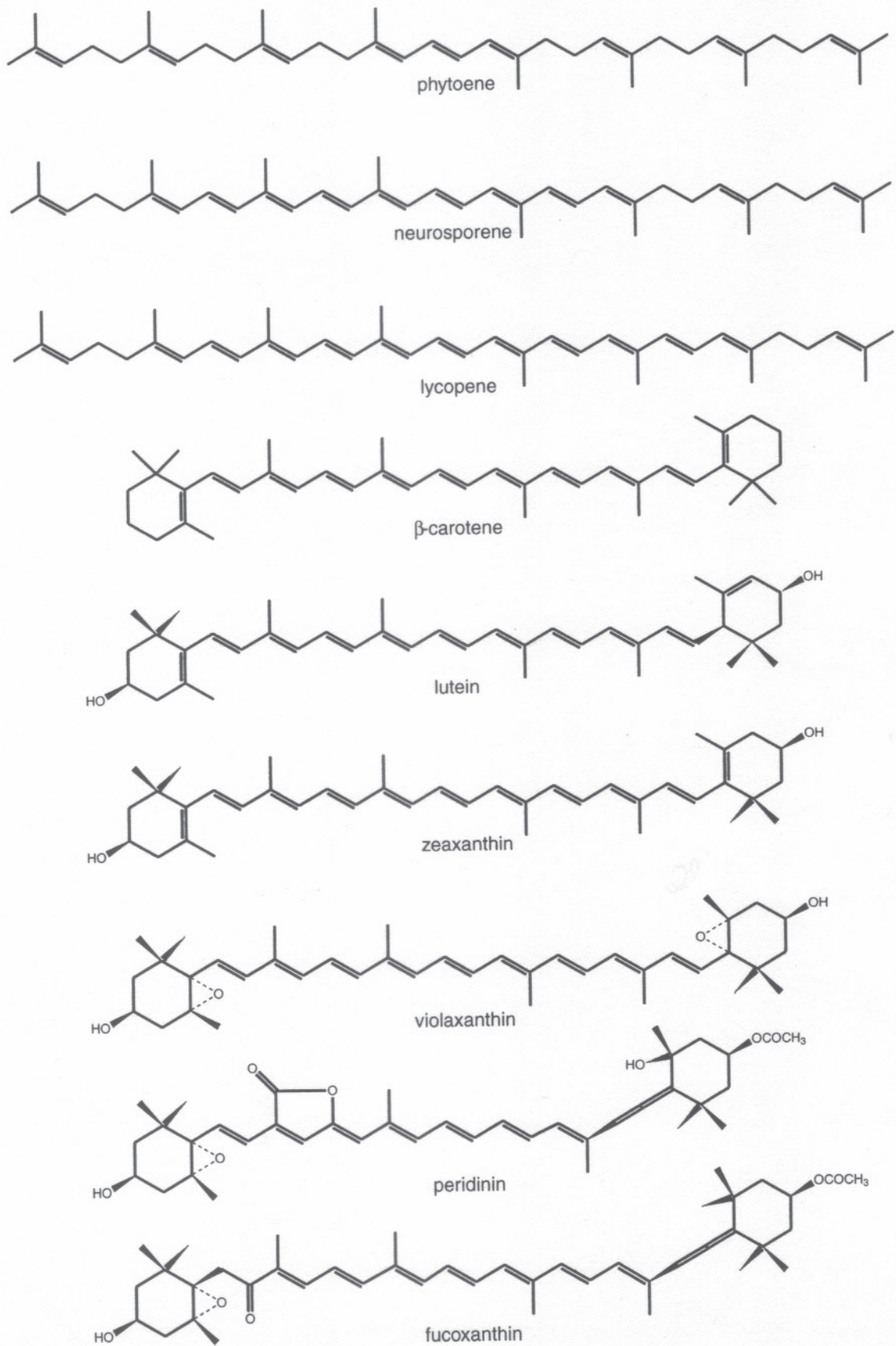
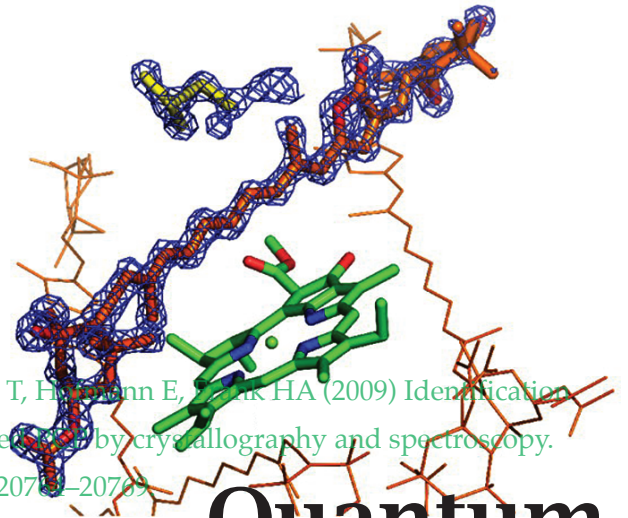
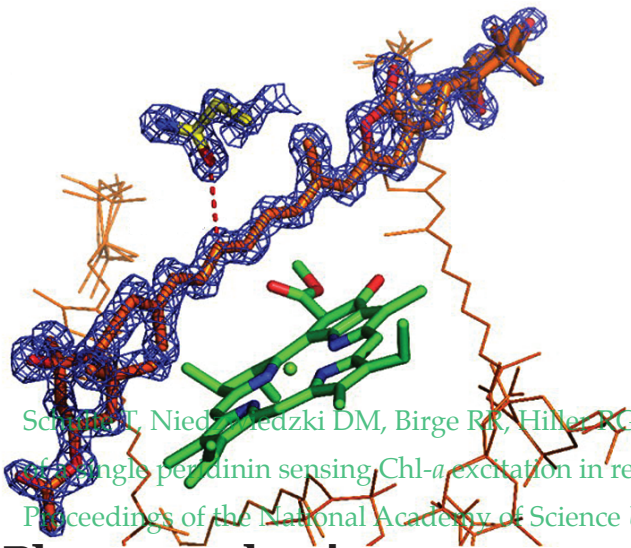
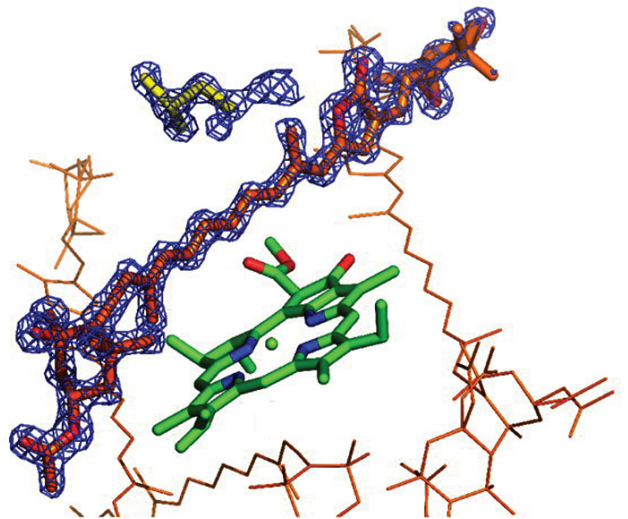
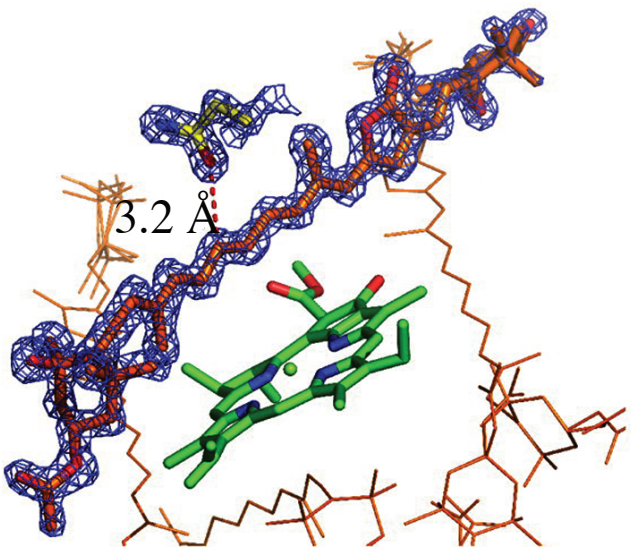
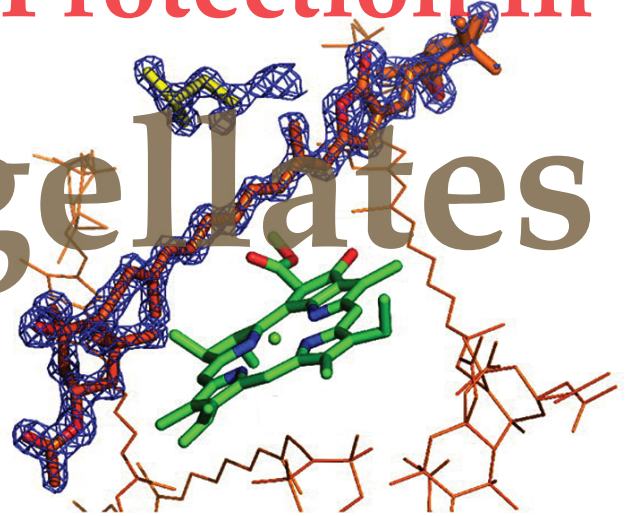
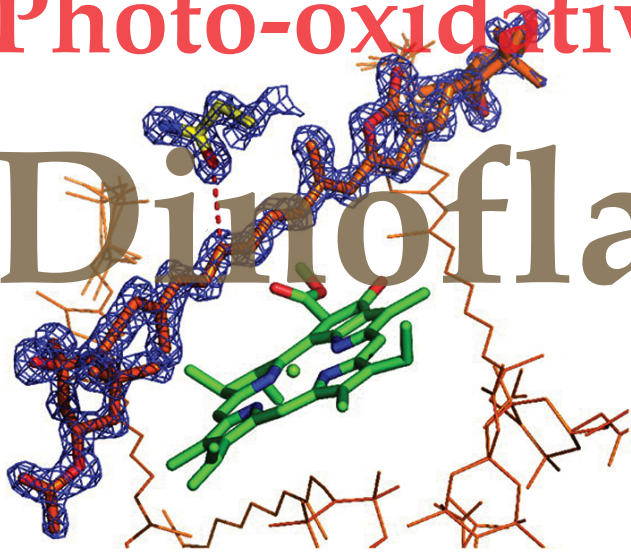


Figure 4.10 Structures of several carotenoids and carotenoid precursors important in photosynthetic systems.

Photo-oxidative Protection in Dinoflagellates

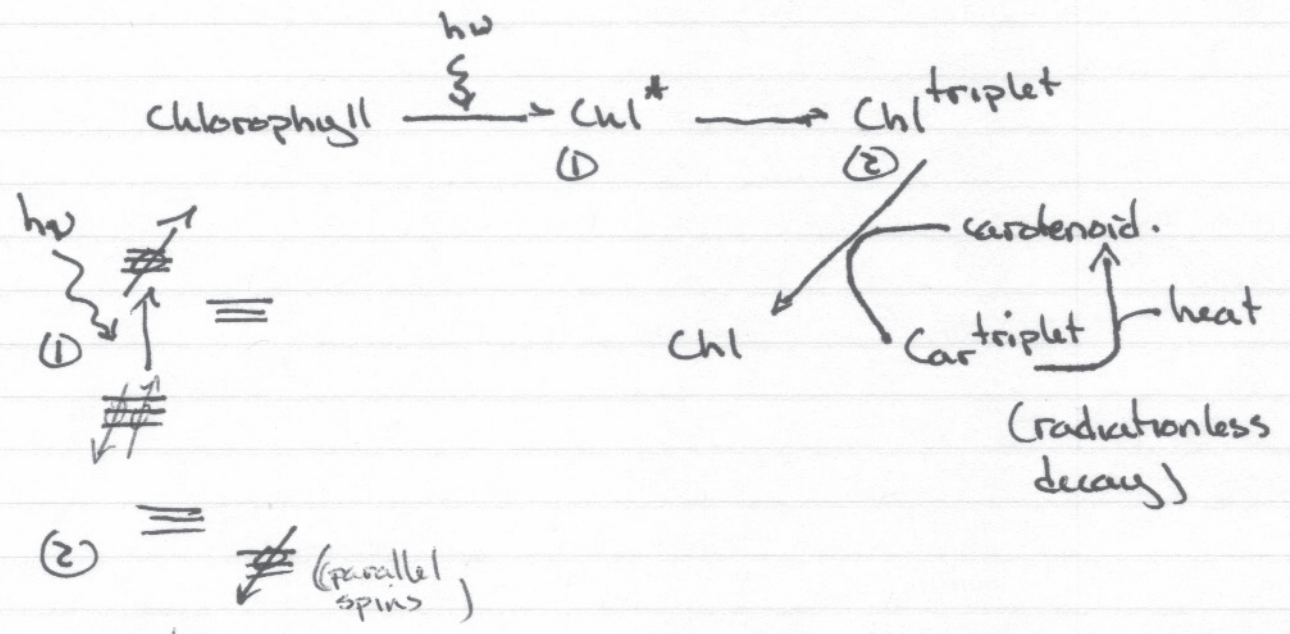


Schirmer T, Niedzwiedzki DM, Birge RK, Hiller RG, Polivka T, Hildebrand E, Frank HA (2009) Identification of a single peridinin sensing Chl-*a* excitation in reconstituted PSII by crystallography and spectroscopy. Proceedings of the National Academy of Science USA 106:20759–20769

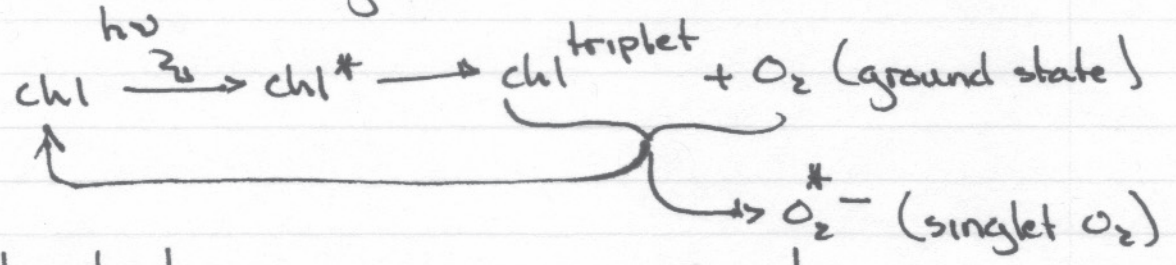
Photosynthesis
SC/BIOL 4160

Quantum
Photosynthesis

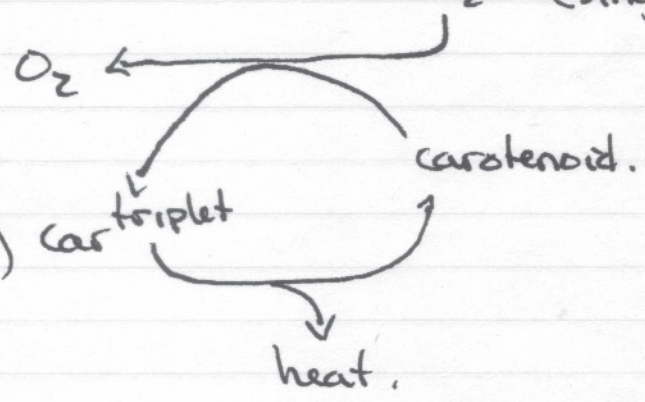
In one reaction, a triplet excited state of chlorophyll can be "de-excited" if a carotenoid is nearby and at the correct orientation for excitation transfer



The triplet refers to the e^- in the opposite state. This is fairly stable, and capable of reacting with O_2 in its ground state



Alternatively, the carotenoid can react directly with singlet O_2 ($O_2^* \text{ -}$)



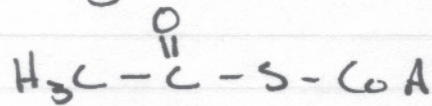
Finally, the xanthophyll cycle⁽⁴⁾ (enzyme-mediated) offers another alternative for quenching excited state O₂ derivatives.

Mutations in carotenoid biosynthesis cause cellular damage during photosynthesis due to the absence of protection from photooxidation.

⁽⁴⁾ Blankenship Ch. 5 P. 92
Lawlor Ch. 4 P. 47.

Digression: carotenoid biosynthesis

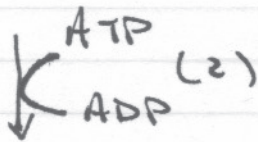
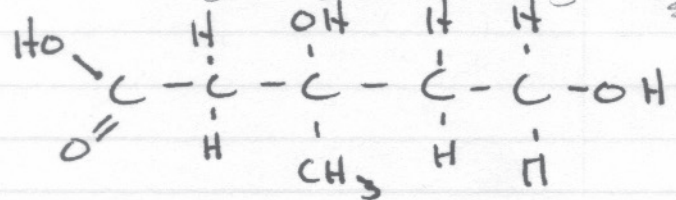
(a) Acetyl-CoA



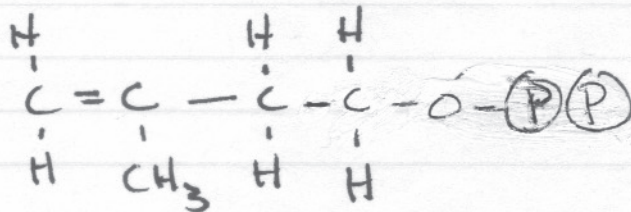
condensation
reduction

+ Acetyl-CoA transferred to enzyme hydroxymethylglutaryl CoA synthase

mevalonic acid.



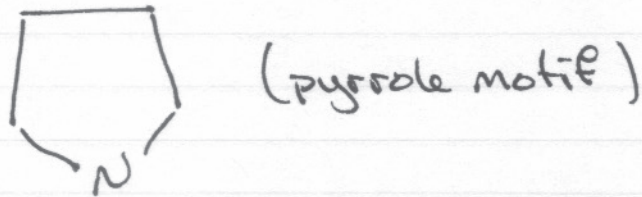
isopentenyl pyrophosphate



5-carbon backbone
condense to 10-C, 15-C etc.

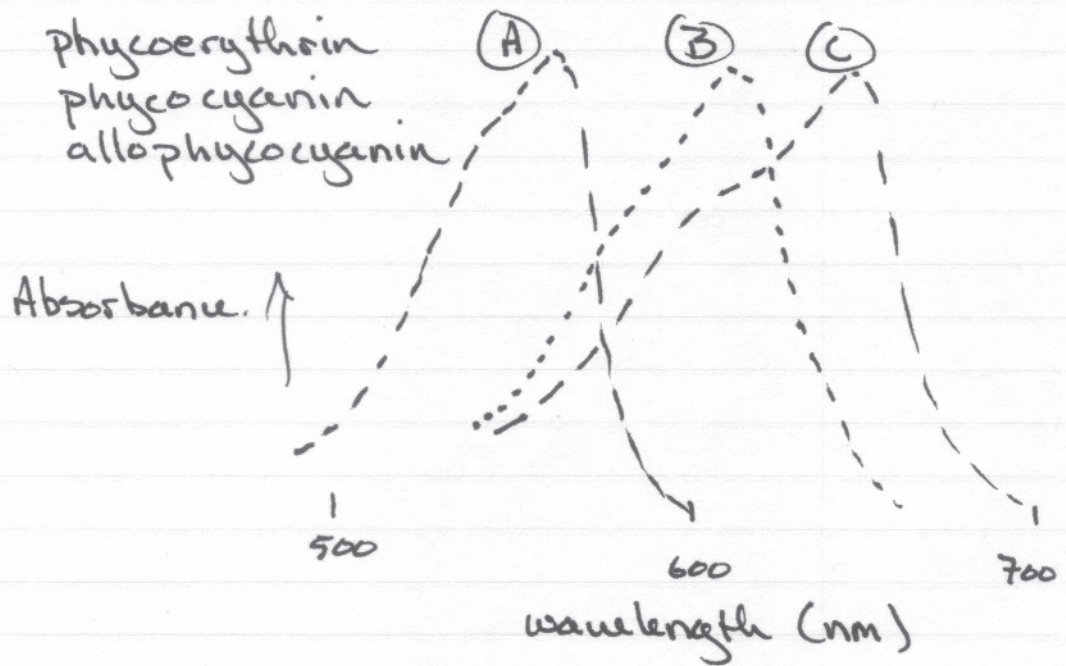
BILINS

Bilins are linear tetrapyrroles, made of four pyrroles:



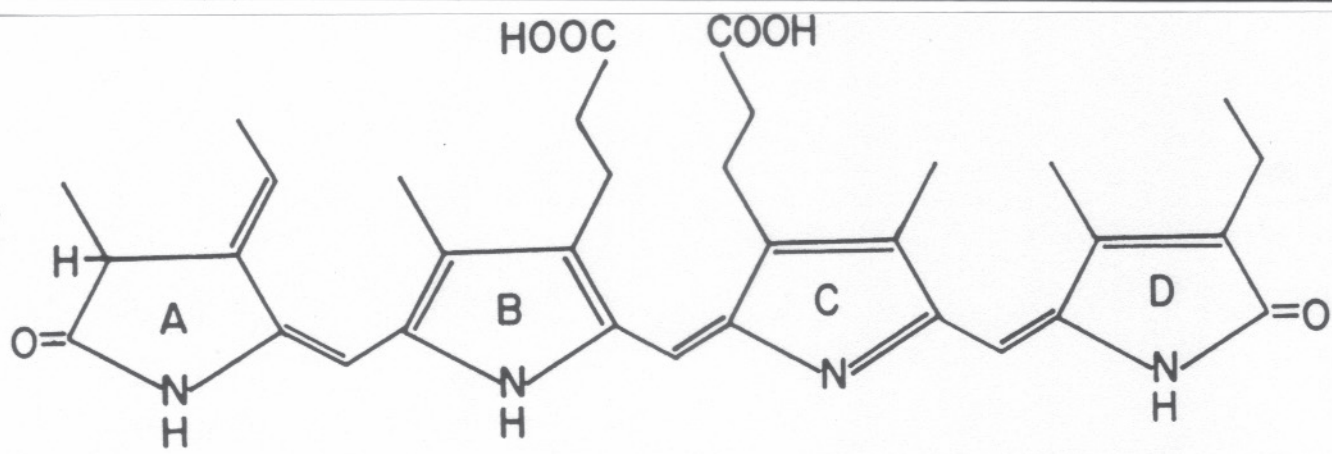
They are found in cyanobacteria and Rhodophyta (Red algae). Three common bilins are:

- (A) phycoerythrin
- (B) phycocyanin
- (C) allophycocyanin

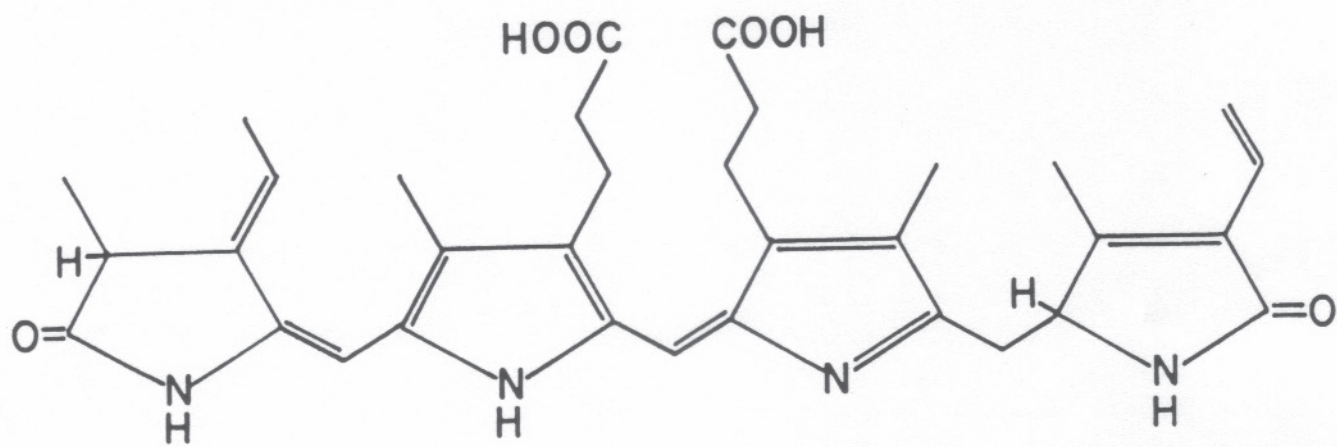


They are actually synthesized from the cyclic tetrapyrrole protoporphyrin IX, a precursor of chlorophyll synthesis.

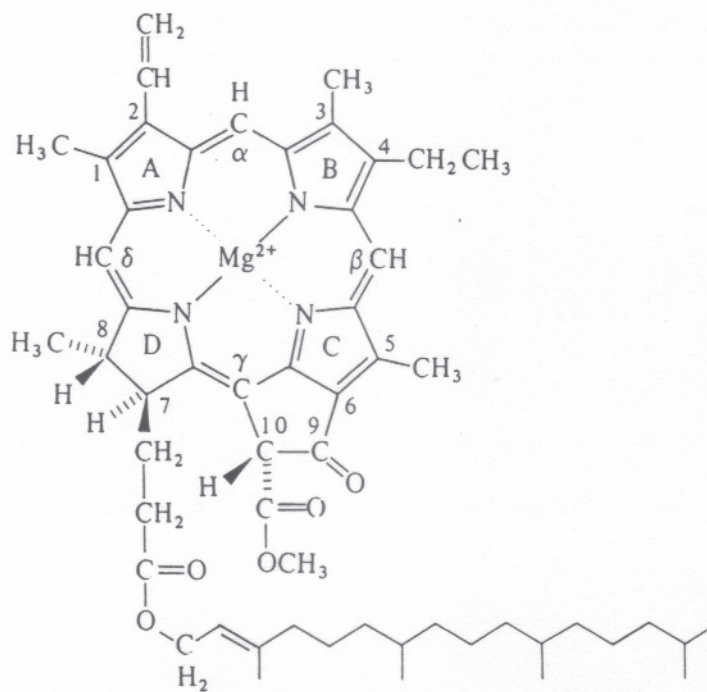
They are covalently linked to proteins to form phycobilisomes

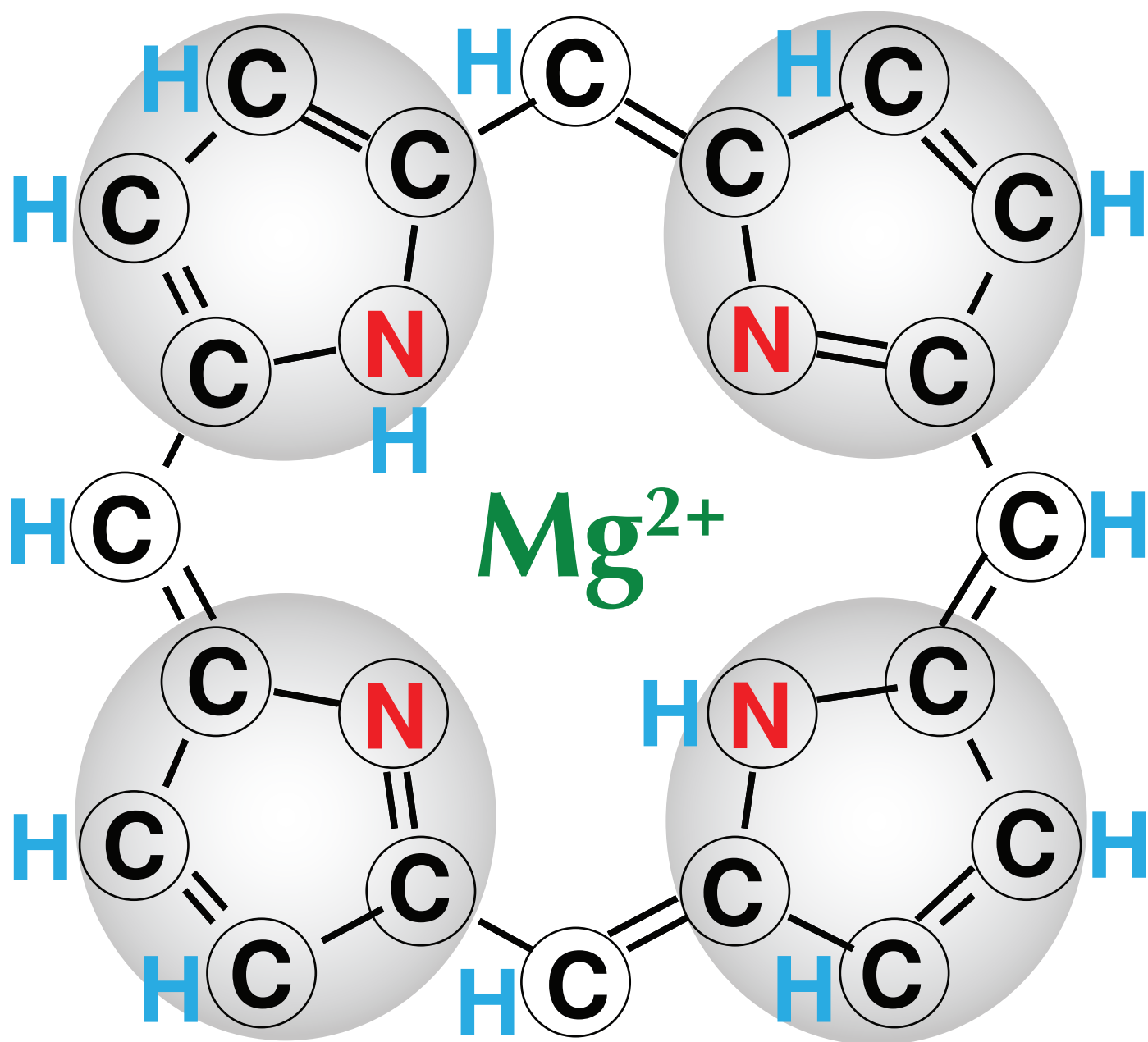


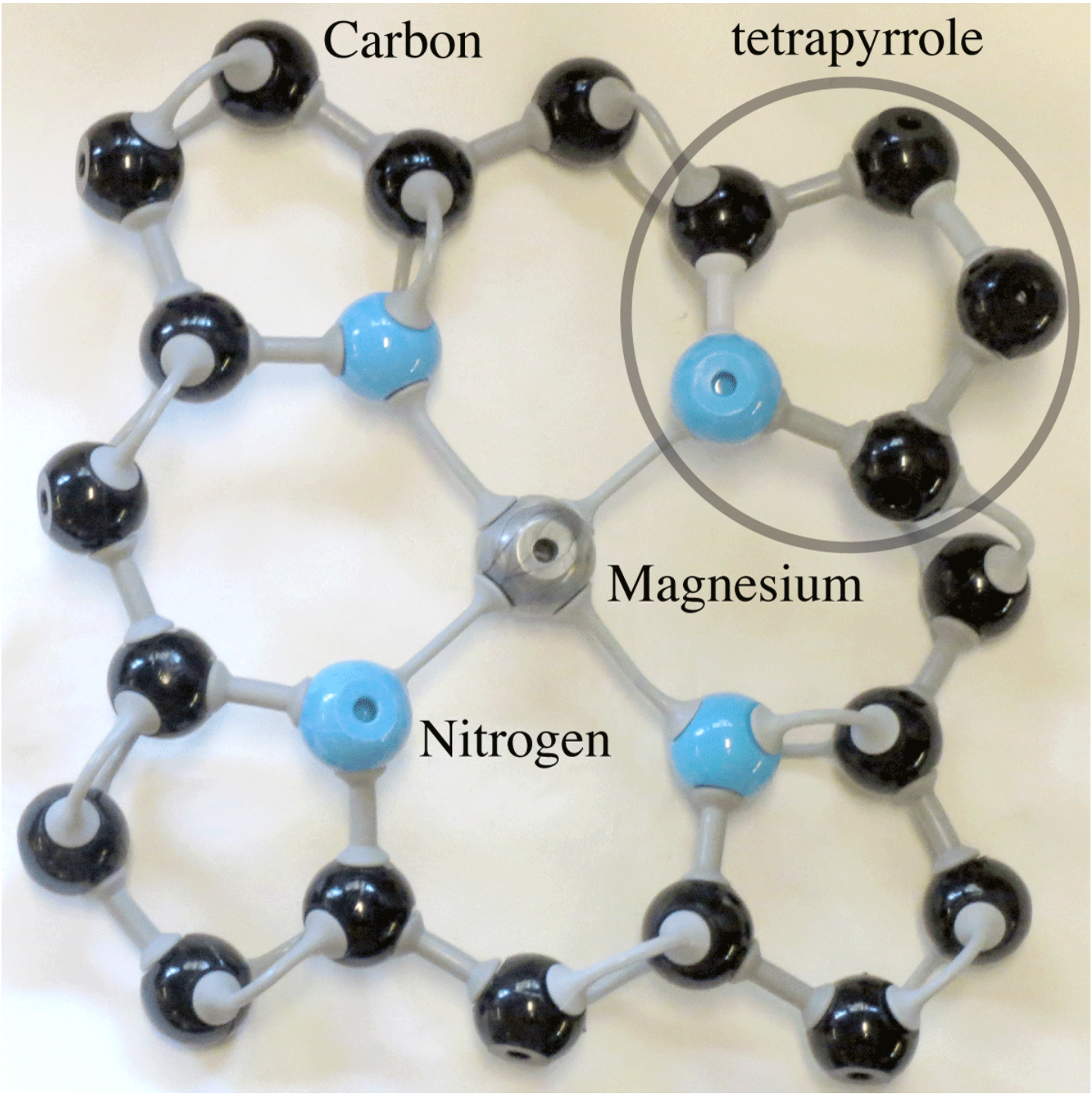
Phycocyanobilin



Phycoerythrobilin







CHLOROPHYLLS

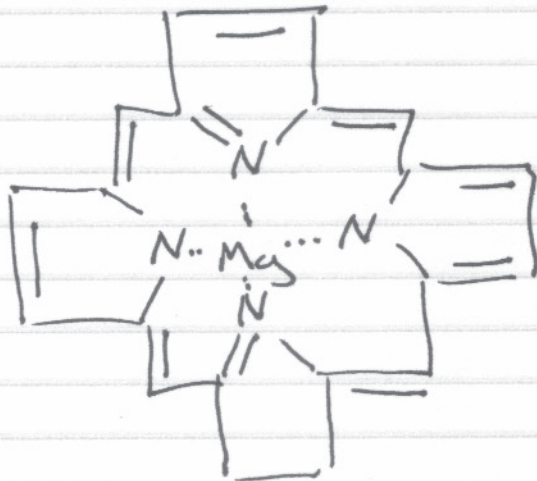
Chlorophylls are the principal light-absorbing pigments of photosynthesis.

These are cyclic tetrapyrroles, porphyrins, with a Mg^{2+} complexed in the center.

The complete ring structure is flat with extensive conjugation: all conjugated bonds corresponding to a λ_{max} of ~ 472 nm

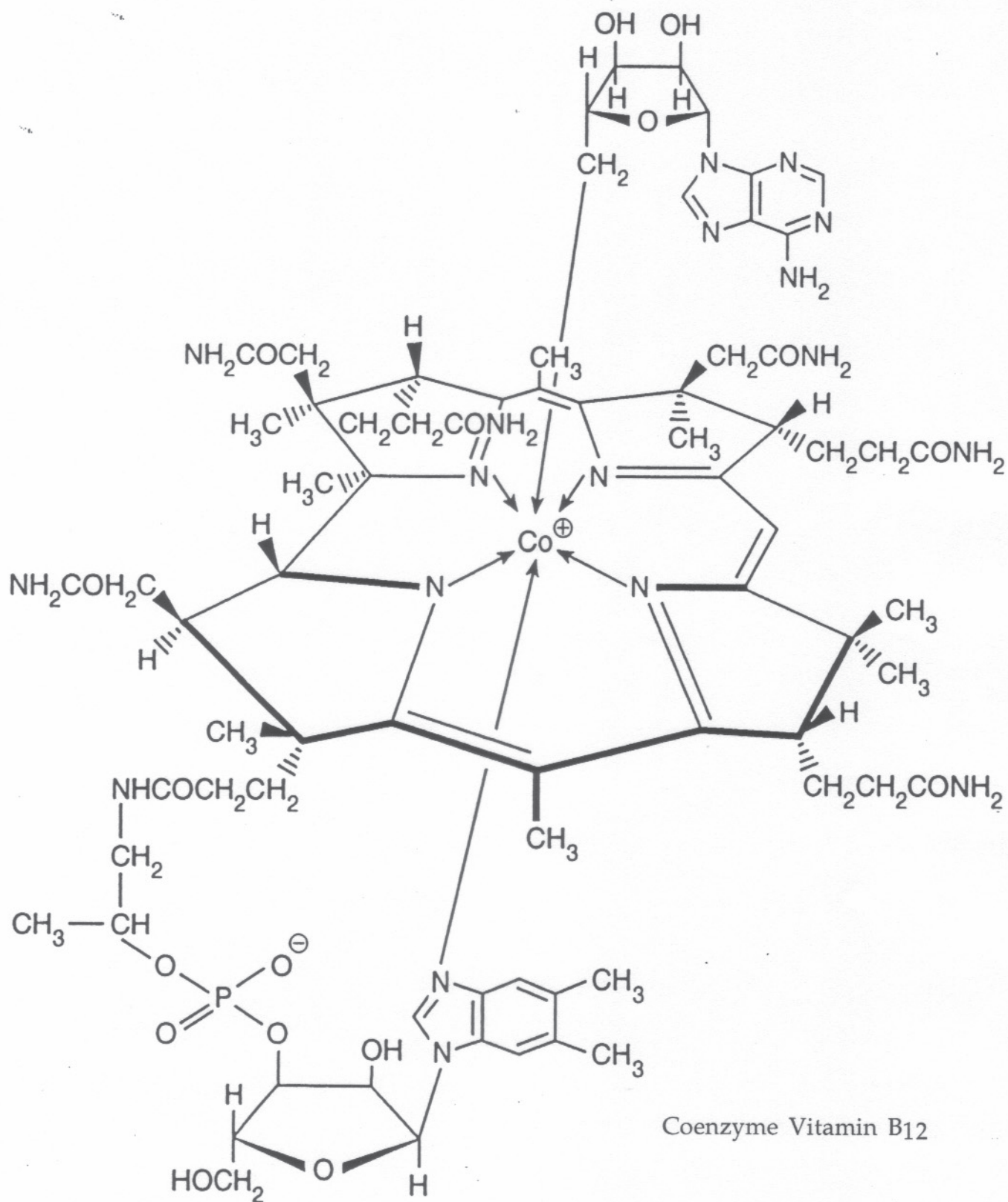
As noted before, they have two major absorbance bands: Soret & Q.

The general motif:



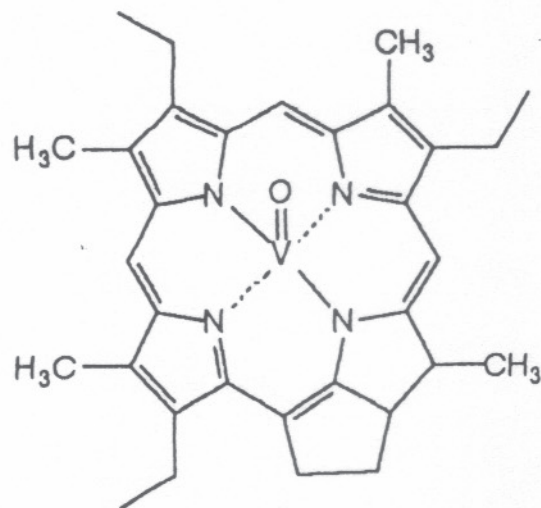
is repeated time & time again in biology. Iron complexed porphyrins are hemes, function in e^- transport & oxygen binding. Copper-complexed porphyrins are found in insects. A cobalt-complexed porphyrin is Vitamin B₁₂.

Even vanadyl-complexed porphyrins are known from oil deposits.



Coenzyme Vitamin B12

from: Lionel R. Milgrom. 1997. *The Colours of Life: An introduction to the chemistry of porphyrins and related compounds*. Oxford University Press.



Vanadyl DPEP from Venezuelan crude oil.

The major metalloporphyrin in petroleum and oil shale is *vanadyl deoxyphylloerythroetiopyrin* (VODPEP) which was first discovered by Alfred Treibs (of the same Munich school of porphyrin chemistry as Hans Fischer) in 1934. Treibs quickly realised that his discovery strongly implied a biological origin for coal and oil. But he went further and developed a scheme of chemical (as opposed to biochemical) reactions that could have occurred to convert chlorophyll in green plants into VODPEP.

Since Treibs' time, modern analytical techniques have unearthed a vast number of petroporphyrins, in the light of which Treibs' original scheme has had to be modified. Nevertheless, the basic principles that he enunciated still hold, so that a knowledge of the main petroporphyrin types in any particular sample of coal or oil, and their relative concentrations, can provide geologists with accurate information about the thermal stresses and sedimentological history of the environment the material has been exposed to. This, in turn, gives geologists vital clues about the difficulties likely to be encountered in obtaining non-renewable resources.

from: Lionel R. Milgrom. 1997. *The Colours of Life: An introduction to the chemistry of porphyrins and related compounds*. Oxford University Press.

The differences between the various chlorophylls.

Chl a, b, c & d
 Bchl a, b, d, e, and g

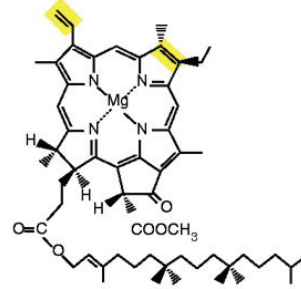
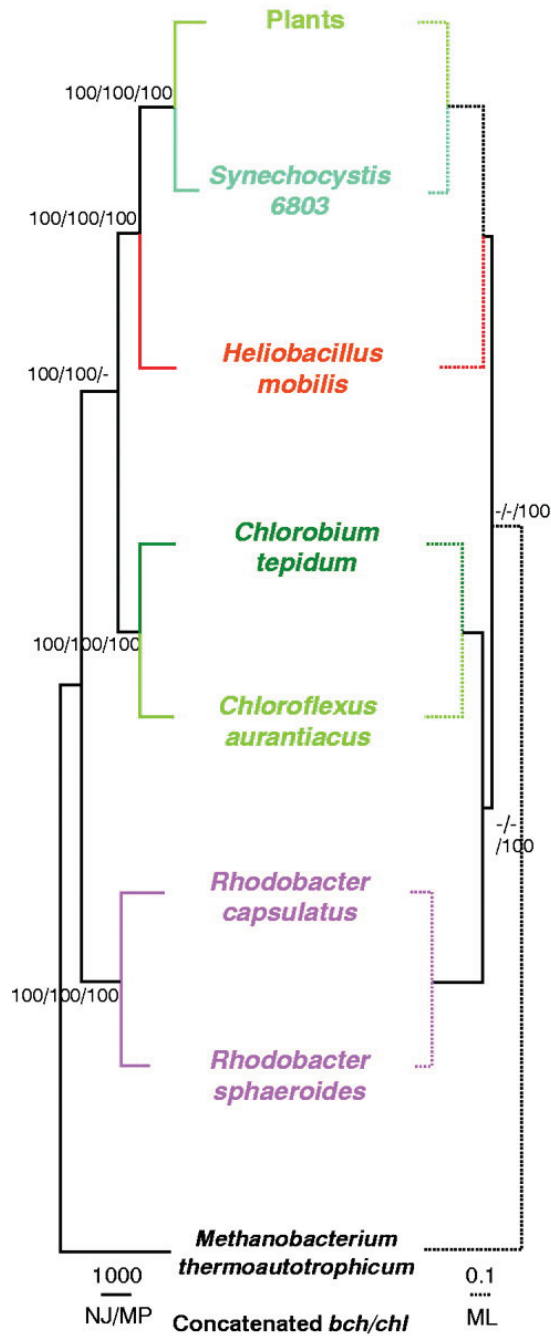
are relatively minor substitutions, which do, however have significant effects on the absorbance spectra. Especially bacteriochlorophylls which absorb in the far-red (750-800 nm)

The synthesis of chlorophylls can be divided into two ^(three) steps.

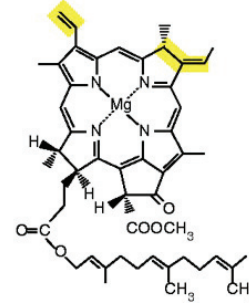
1. The synthesis of the pyrrole (porphobilinogen)
2. Followed by condensation to the cyclic tetra-pyrrole (porphyrin) and.
3. Mg complexation.

The immediate precursor of the porphobilinogen is δ -aminolevulinic acid.

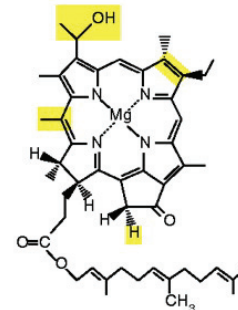
C



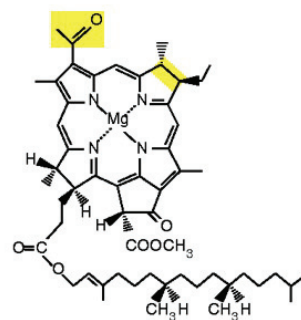
Chlorophyll a (Plants/Cyanobacteria)



Bacteriochlorophyll g (Heliobacteria)



Bacteriochlorophyll c (Green bacteria)

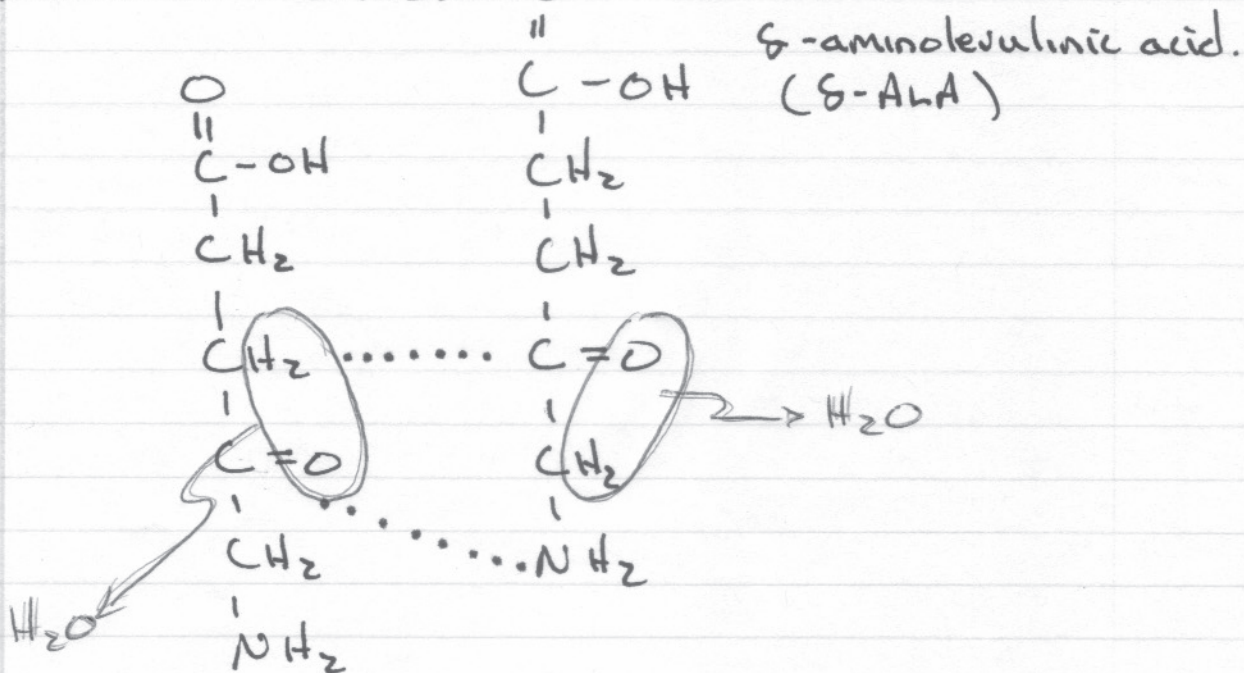


Bacteriochlorophyll a (Purple bacteria/green bacteria)

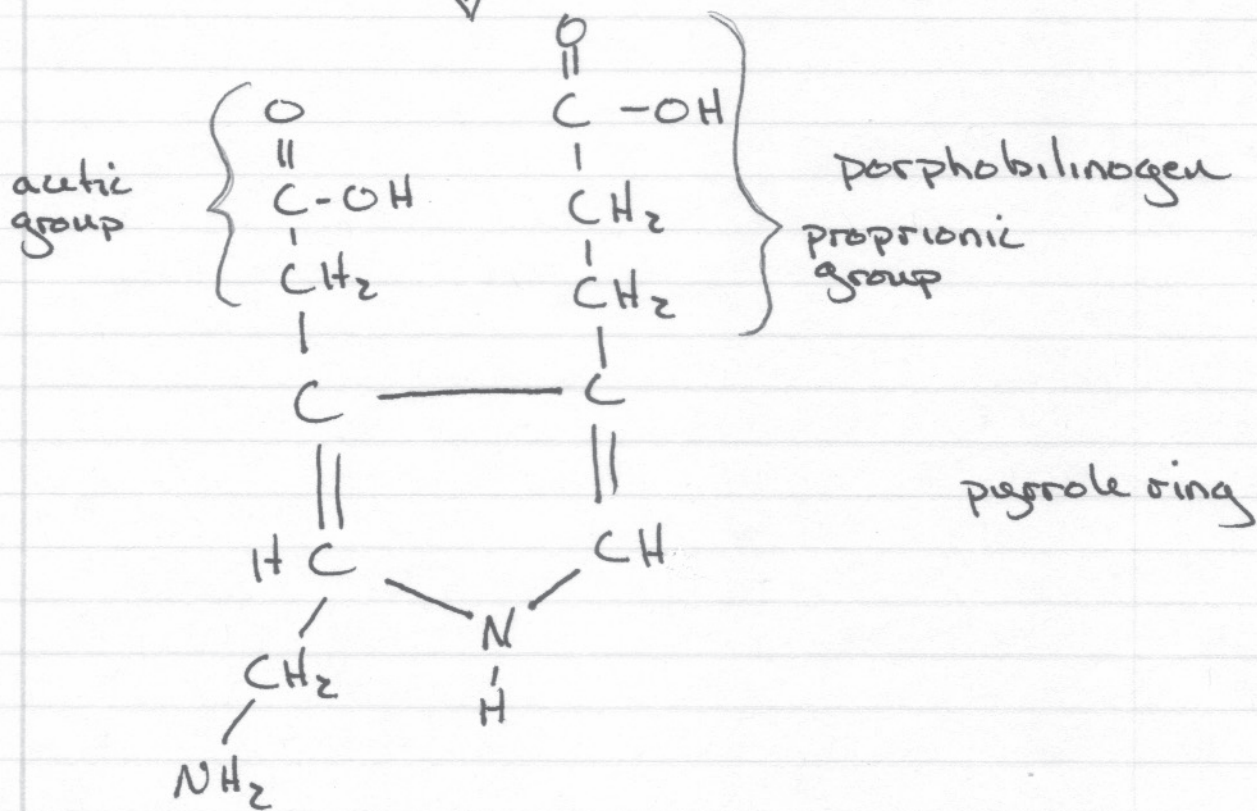
Photosynthesis
SC/BIOL 4160

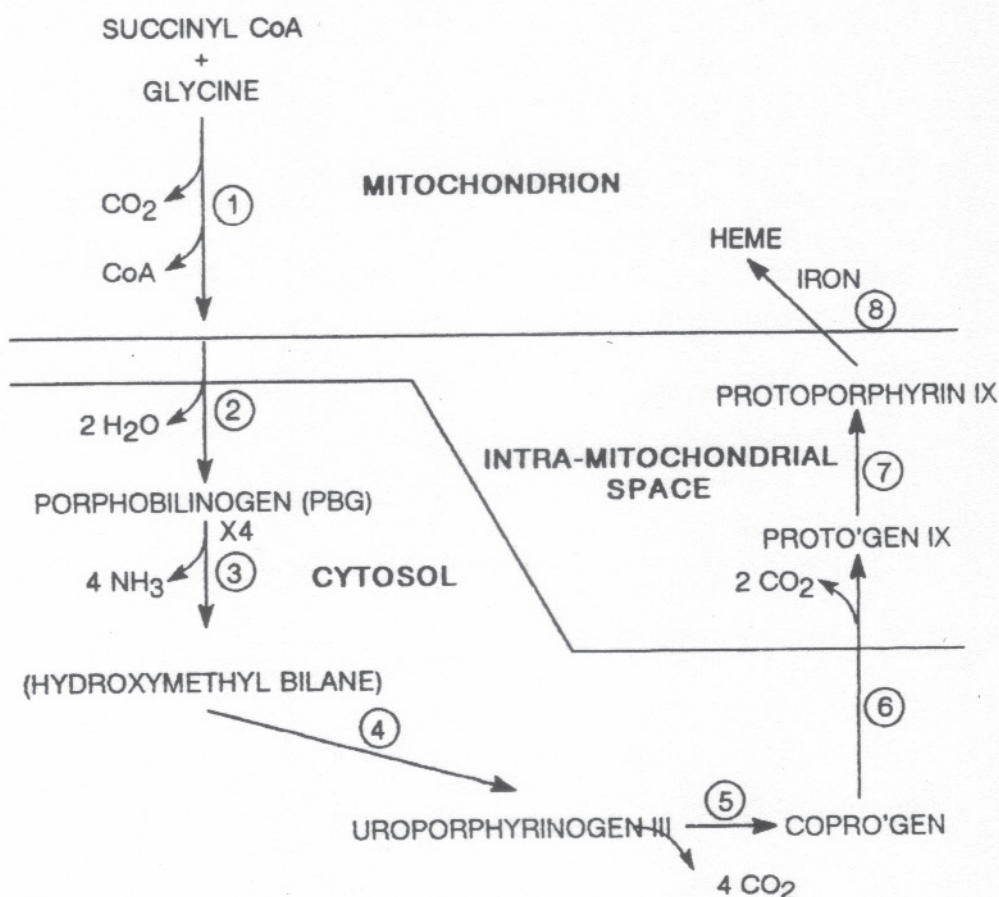
LIGHT and
CHLOROPHYLL

CHLOROPHYLL SYNTHESIS. 0



δ-ALA dehydratase $\rightarrow 2 \text{H}_2\text{O}$





- Key to Enzymes: ① ALA synthase; ② ALA dehydrase;
 ③ PBG deaminase; ④ uro'gen III synthase;
 ⑤ uro'gen III decarboxylase; ⑥ copro'gen III oxidase;
 ⑦ proto'gen IX oxidase; ⑧ ferrochelatase

Fig. 2.6 Overview of heme biosynthesis and where it occurs.

Where porphyrins come from

(NOTE. The citric acid cycle is also known as the Krebs cycle, after its discoverer Hans Krebs. It is a cyclical series of biochemical reactions which is fundamental to the metabolism of aerobic organisms. The enzymes for the Krebs cycle are located in the mitochondria and are in close association with the enzymes involved in the electron-transport chain, making the Krebs cycle a kind of biochemical switching station in the complex system of cellular metabolic pathways. It links together degradation, energy production, and biosynthesis.) The fact that glycine was the start of heme biosynthesis in animals was discovered by David Shemin who, in 1945, swallowed 66 g of ¹⁵N-labelled glycine over a three-day period. He took regular blood samples from himself, isolated the heme, and found that the ¹⁵N atoms ended up in the porphyrin.⁸ Shemin also found that the radiolabel was rapidly incorporated and then remained at a constant level for about 120 days (the approximate lifetime for a red blood cell), after which time it started to decline.

"ALA formation from glutamate

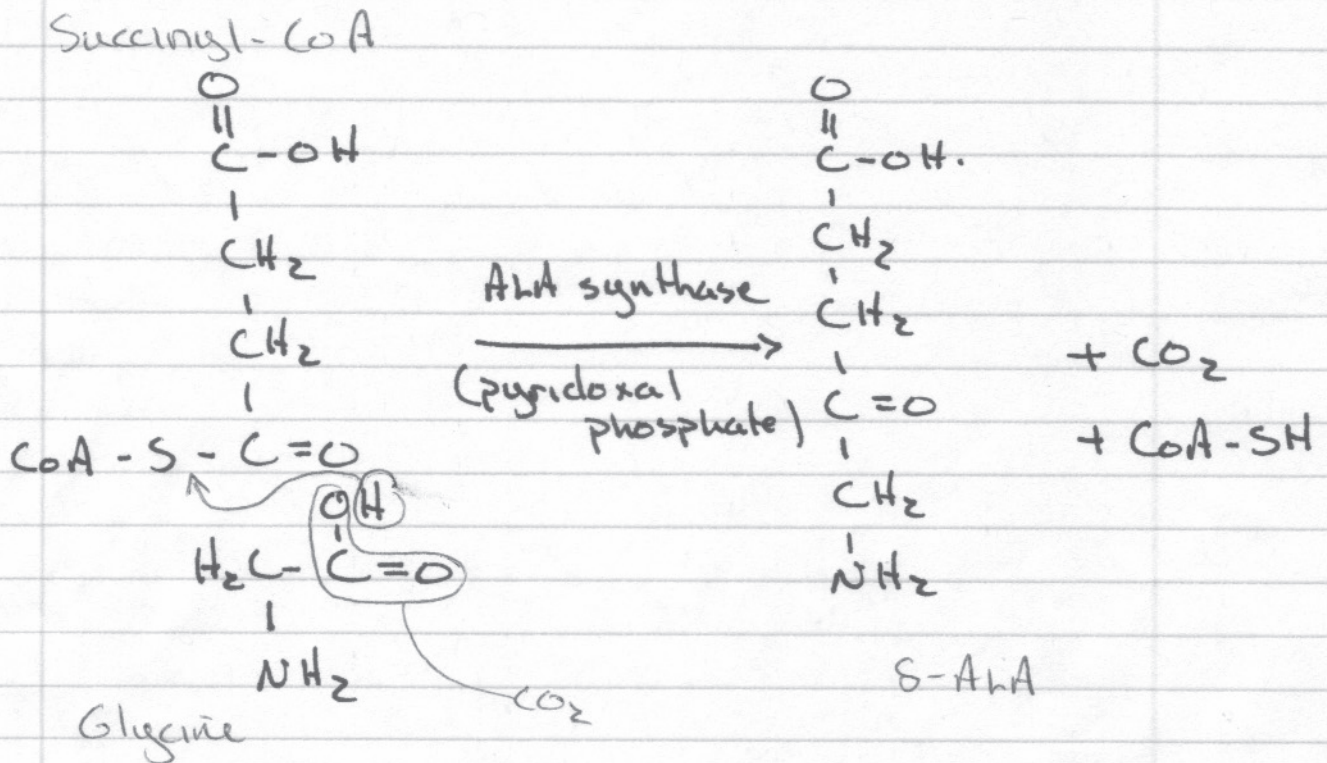
Delta-Aminolevulinic acid (ALA), the first universal tetrapyrrole precursor, can be formed by two different pathways. Members of the alpha proteobacterial group (which includes photosynthetic bacteria of the Rhodobacter and Rhodospirillum genera as well as the nonphotosynthetic genera Agrobacterium, Rhizobium and Bradyrhizobium), and all eukaryotic organisms that do not contain chloroplasts (animals, yeasts, fungi), form ALA by condensation of succinyl-coenzyme A with glycine in a reaction catalyzed by the pyridoxal-P-containing enzyme ALA synthase (EC 2.3.1.37) (Gibson et al. 1958; Kikuchi et al. 1958). In contrast, all plants and algae, and all bacteria that are not in the alpha proteobacterial group, including cyanobacteria, many photosynthetic bacteria, and archaea, form ALA by a different route that begins with the five-carbon precursor, glutamate (Beale and Castelfranco 1974; Beale et al. 1975; Meller et al. 1975), which is activated by ligation to tRNA-Glu (Kannangara et al. 1984), followed by reduction of the alpha carboxyl group of the activated glutamate to form glutamate 1-semialdehyde (GSA) (Pontoppidan and Kannangara 1994), and transamination of GSA to form ALA (Kannangara and Gough 1978). The fact that ALA biosynthesis in all plants and most bacteria differs from that in animals suggests that it may be possible to develop herbicides and antibiotics that specifically target steps in the five-carbon ALA biosynthetic pathway, and that are nontoxic to animals."

Samuel I. Beale 1999. Enzymes of chlorophyll biosynthesis. Photosynthesis Research 60: 43-73.

S-AMINOLEVULINIC ACID SYNTHESIS.

There are two known pathways for the synthesis of S-aminolevulinic acid.

One, known to occur in heme synthesis* uses succinate & glycine substrates.



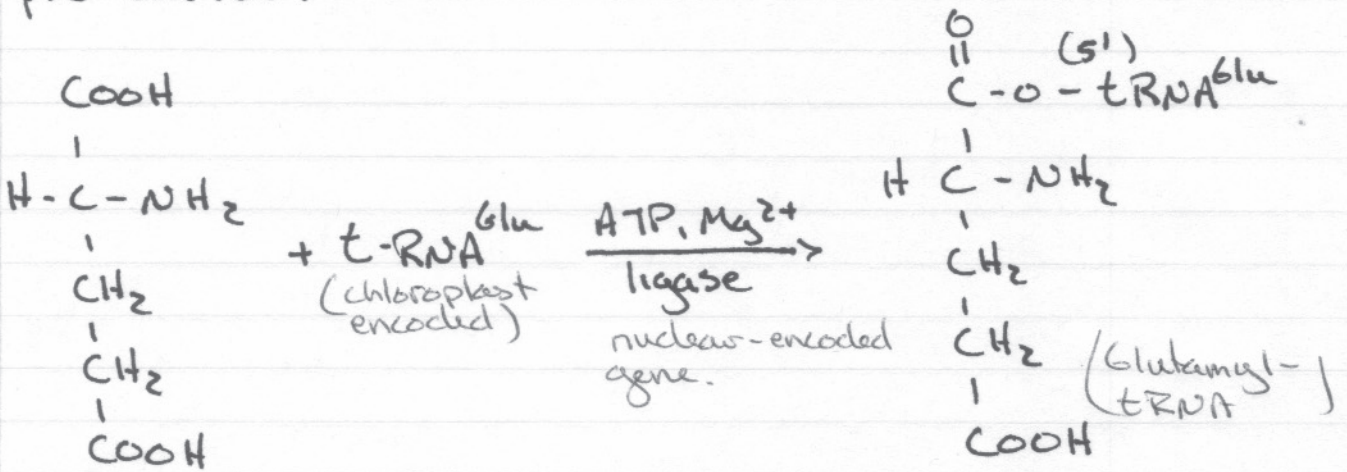
* In leaf tissue: chlorophyll: 2.7-3.7
heme: 0.041-0.052

nmoles per
gm fresh weight.

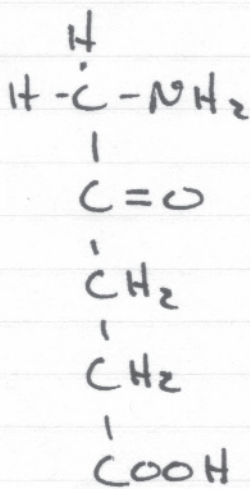
NB. This pathway occurs in α -proteobacterial groups such as *Rhodobacter*, *Rhodospseudomonas* & *Rhodospirillum* and in eukaryotic groups that do not contain chloroplasts (animals, yeasts & fungi).

(Beale, SI 1999. Enzymes of chlorophyll biosynthesis. *Photosynthesis Research* 60: 43-73.)

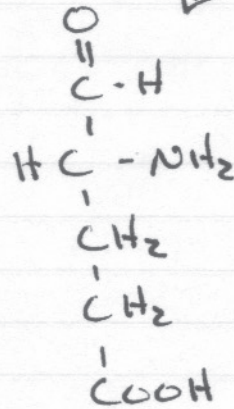
Other groups (from cyanobacteria, algae and plants) use a different biosynthetic pathway using the 5-carbon glutamate as the pre-cursor.



glutamate



δ -aminolevulinic acid



glutamyl-tRNA reductase
NADPH dependent.
270 kDa oligomer

amino transferase (mutase)
45 kDa, nuclear encoded. Gene expression may be light-regulated.

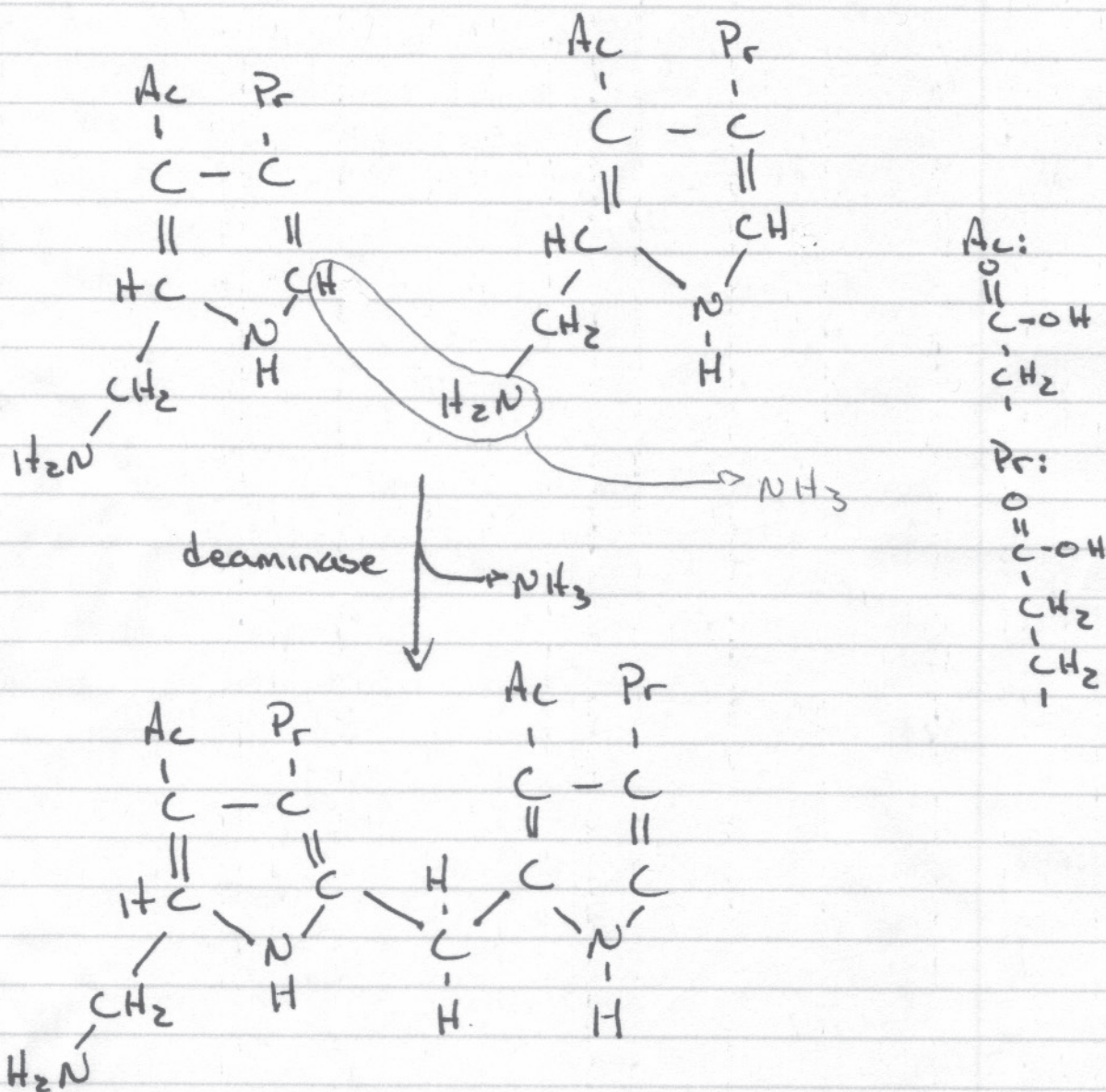
glutamate 1-semialdehyde

notabene: In eukaryotic cells, δ -ALA synthesis occurs in the chloroplast stroma. Evidence that supports cyanobacteria as the progenitor of the chloroplast.

The amount of t-RNA^{Glu} maybe regulated, and its stromal concentration may be an important control point for chlorophyll biosynthesis.

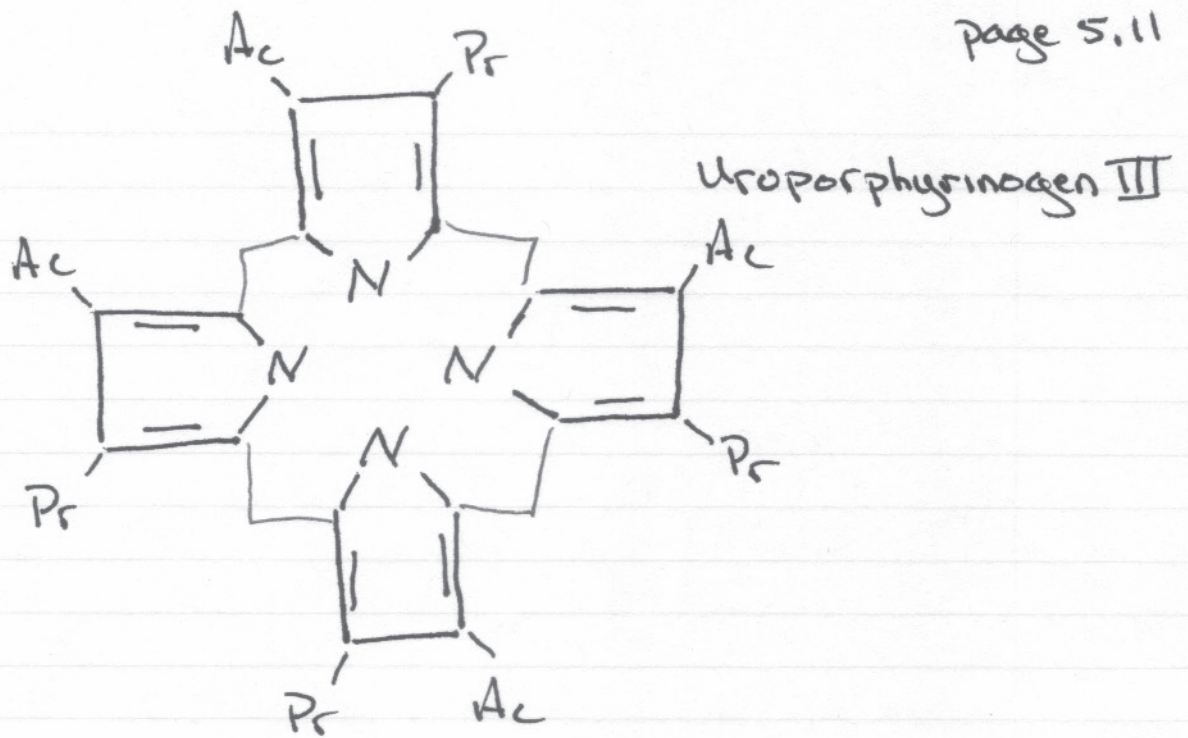
PORPHOBILINOGEN AND BEYOND.....

The polymerization of the individual pyrroles to yield the tetrapyrrole requires de-amination of the porphobilinogens (4):



yielding hydroxymethylbilane.

followed by dehydration to yield ring closure via uroporphyrinogen III synthase.



Decarboxylation of the Ac (acetic) and Pr (propionic) groups, followed by Mg complexation

then reduction yield protochlorophyllide, then chlorophyllide.

Finally, phytol tail addition yields chlorophyll.

The complexity of chlorophyll biosynthesis is great, from initial pyrrole to the photo-synthetically active final product.