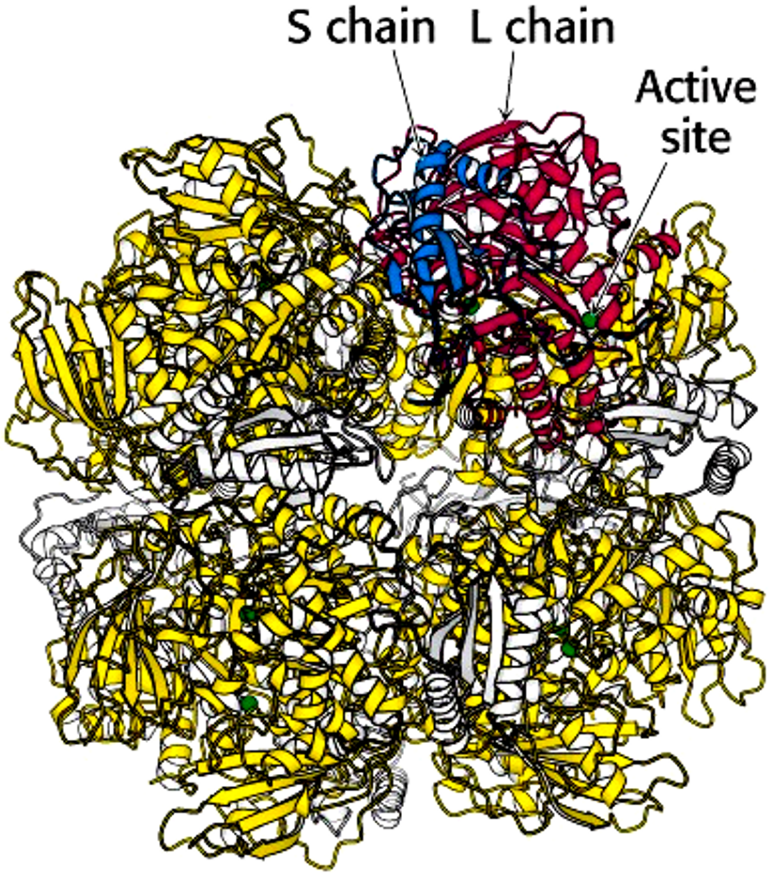
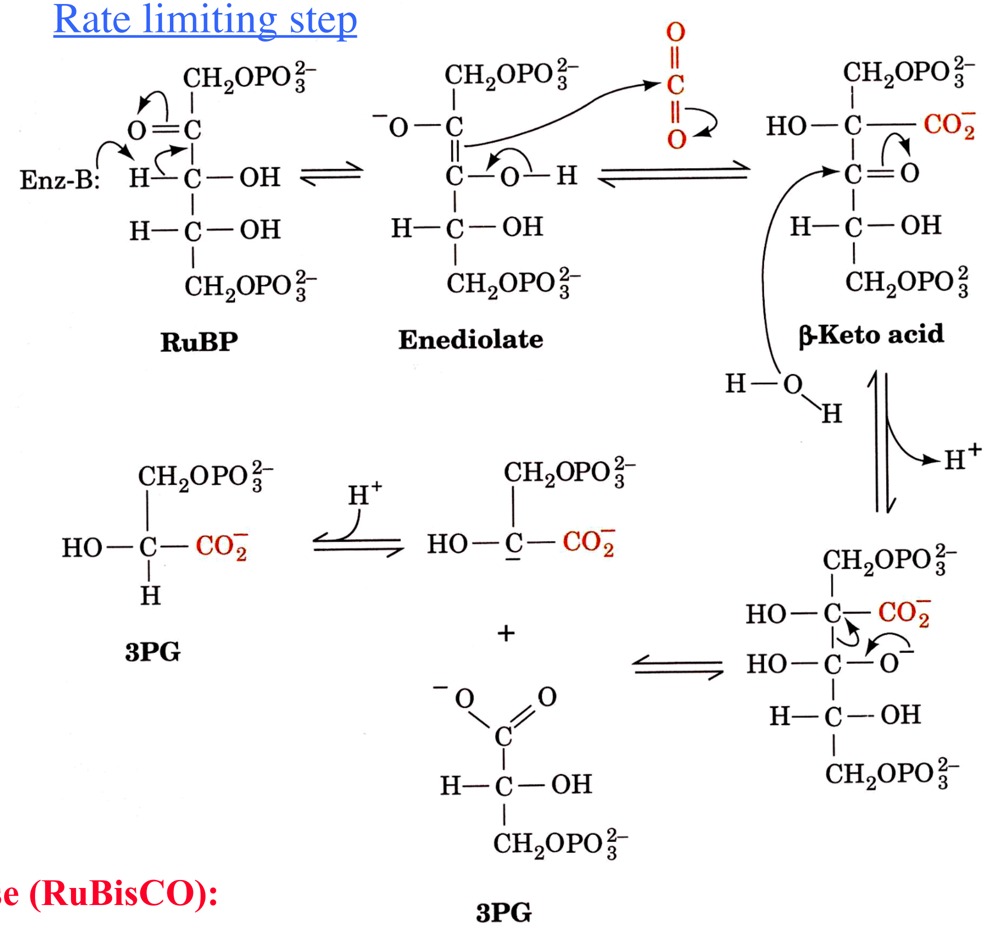
Meet the Most Abundant Protein on Earth



Rate limiting step



➢ **Ribulose bis-phosphate carboxylase/oxygenase (RuBisCO):**

♣ **8 large (L), 477-amino acid catalytic subunits + 8 small (S), 123-amino acid subunit (regulatory???) in square prism symmetry**

♣ **$k_{cat} \approx 3\ s^{-1}$ (slow!);**

♣ **comprises up to 50% of leaf proteins ⇒ most abundant in biosphere!;**

♣ **fixes ~10^{11} tons of CO_2 per year;**

♣ **has peculiar side reaction in which O_2 gets fixed instead of CO_2 (oxygenase activity!)**

♣ **reason possibly protection from O_2 at low $[CO_2]$?**

Reminiscent of pyruvate carboxylase, but no biotin!

But wait – how does this all work together? Regulation needed!

➢ Chloroplast stroma contain the enzymes of the Calvin cycles as well as those of glycolysis and the pentose phosphate pathway, which are used to generate ATP and NADPH
⇒ **At night**, the **Calvin cycle** has to be **downregulated (through absence of activation)** so that ATP and NADPH from the catabolic pathways do not get consumed in a futile cycle

Table 24-1 Standard and Physiological Free Energy Changes for the Reactions of the Calvin Cycle

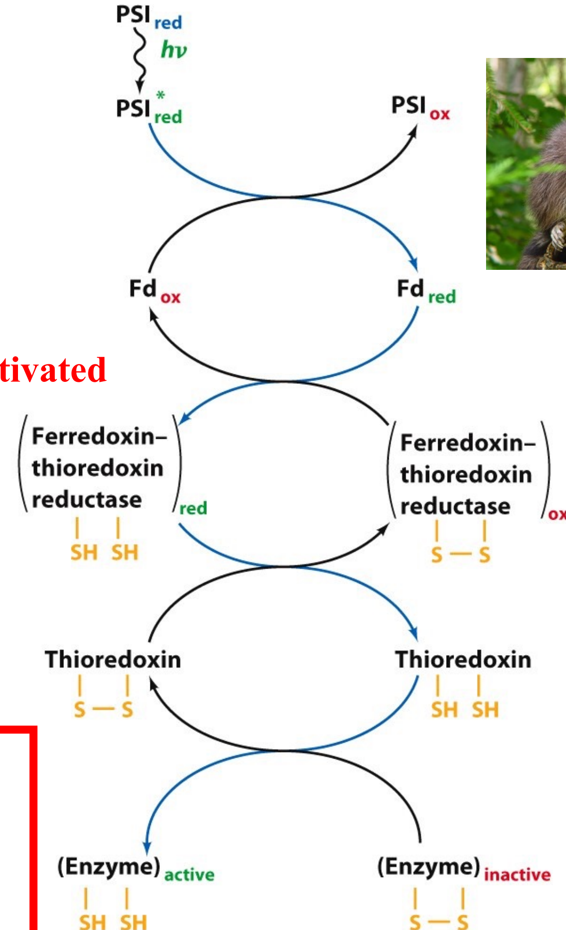
Step[a]	Enzyme	$\Delta G^{\circ\prime}$ (kJ · mol^{-1})	ΔG (kJ · mol^{-1})
1	Phosphoribulokinase	−21.8	−15.9
2	Ribulose bisphosphate carboxylase	−35.1	−41.0 ←
3 + 4	Phosphoglycerate kinase + glyceraldehyde-3-phosphate dehydrogenase	+18.0	−6.7
5	Triose phosphate isomerase	−7.5	−0.8
6	Aldolase	−21.8	−1.7
7	Fructose bisphosphatase	−14.2	−27.2 ←
8	Transketolase	+6.3	−3.8
9	Aldolase	−23.4	−0.8
10	Sedoheptulose bisphosphatase	−14.2	−29.7 ←
11	Transketolase	+0.4	−5.9
12	Phosphopentose epimerase	+0.8	−0.4
13	Ribose phosphate isomerase	+2.1	−0.4

[a]Refer to Fig. 24-31.

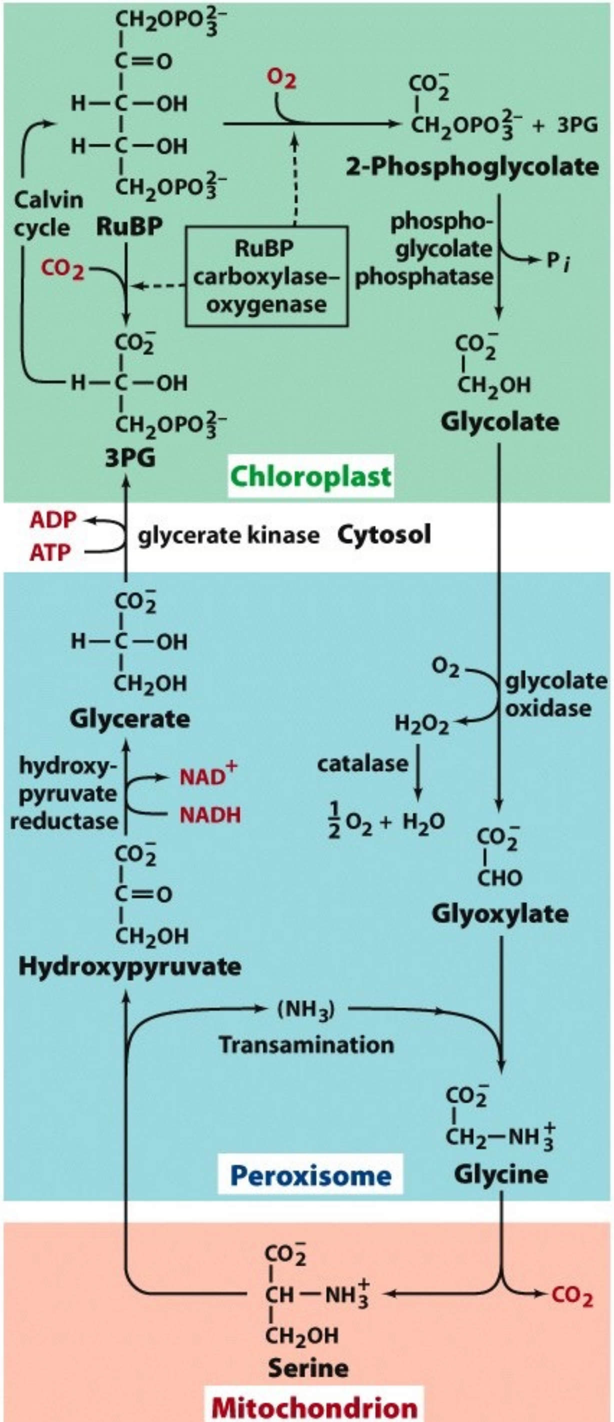
Source: Bassham, J.A. and Buchanan, B.B., *in* Govindjee (Ed.), *Photosynthesis,* Vol. II, p. 155, Academic Press (1982).

most likely to be regulated

Light activated through redox sensing:

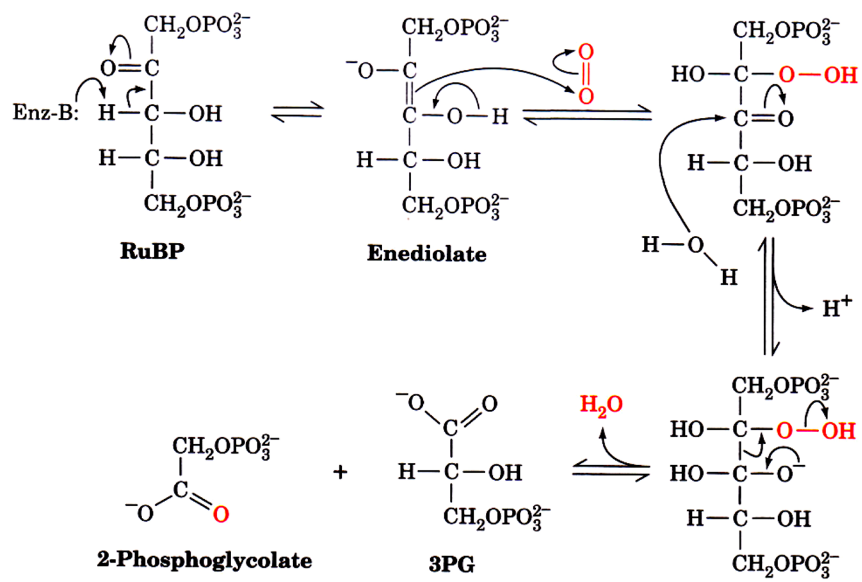


RuBisCO controlled by:
➢ pH (sharply optimal is 8.0, which is reached as protons are pumped from stroma to thylakoid lumen upon illumination)
➢ Mg^{2+} stimulation (as cofactor; proton influx into the lumen leads to Mg^{2+} efflux)
➢2-carboxyarabinitol-1-phosphate inhibition (produced only in the dark)



But another problem is less well controlled: Photorespiration

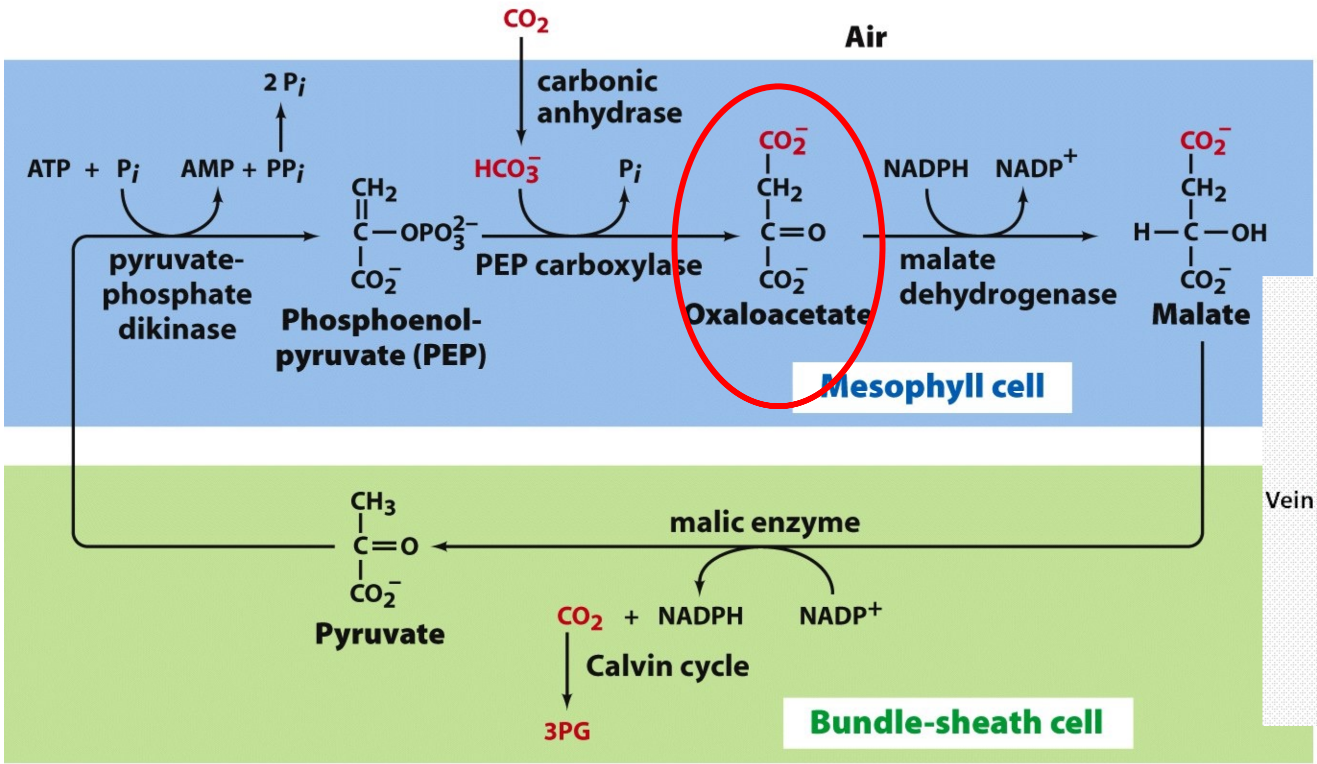
➤ A nasty side reaction of RuBisCO:

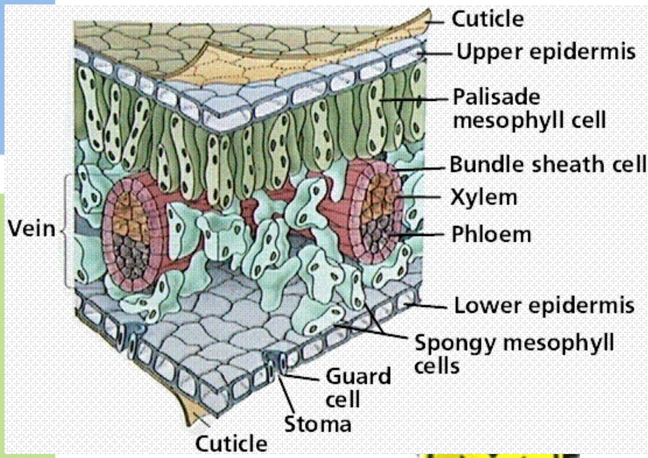


➤ Leads to consumption of O_2 (and ATP) and evolution of CO_2, independent of oxidative phosphorylation

How so-called C4 plants deal with it

- The CO_2 compensation point of ~40-70 ppm CO_2 (the normal atmospheric concentration is 330 ppm) saves many plants the trouble
- But the CO_2 compensation point increases with temperature (as O2 becomes a better substrate) so that tropical plants under hot and sunny conditions (i.e., ~5% of all plants, including corn) utilize the C_4 pathway below to increase their local concentration of CO_2 for the Calvin cycle





Chapter 24: What have we learned?

- Anatomy of chloroplasts, analogies to mitochondria
- Chlorophylls
- Absorption processes
- The bacterial photosynthetic reaction center and how it works
- Photosystems II and I and how they work
- The Z-scheme
- Making NADPH and ATP in photosynthesis
- Q cycles in Electron Transport Systems
- Light harvesting, segregation, regulation
- The Calvin cycle
- The RuBisCO mechanism, regulation, and what can go wrong
- The C4 pathway

Lipid Metabolism

Voet & Voet, Chapter 25

Major roles of lipids in cell structure and metabolism:

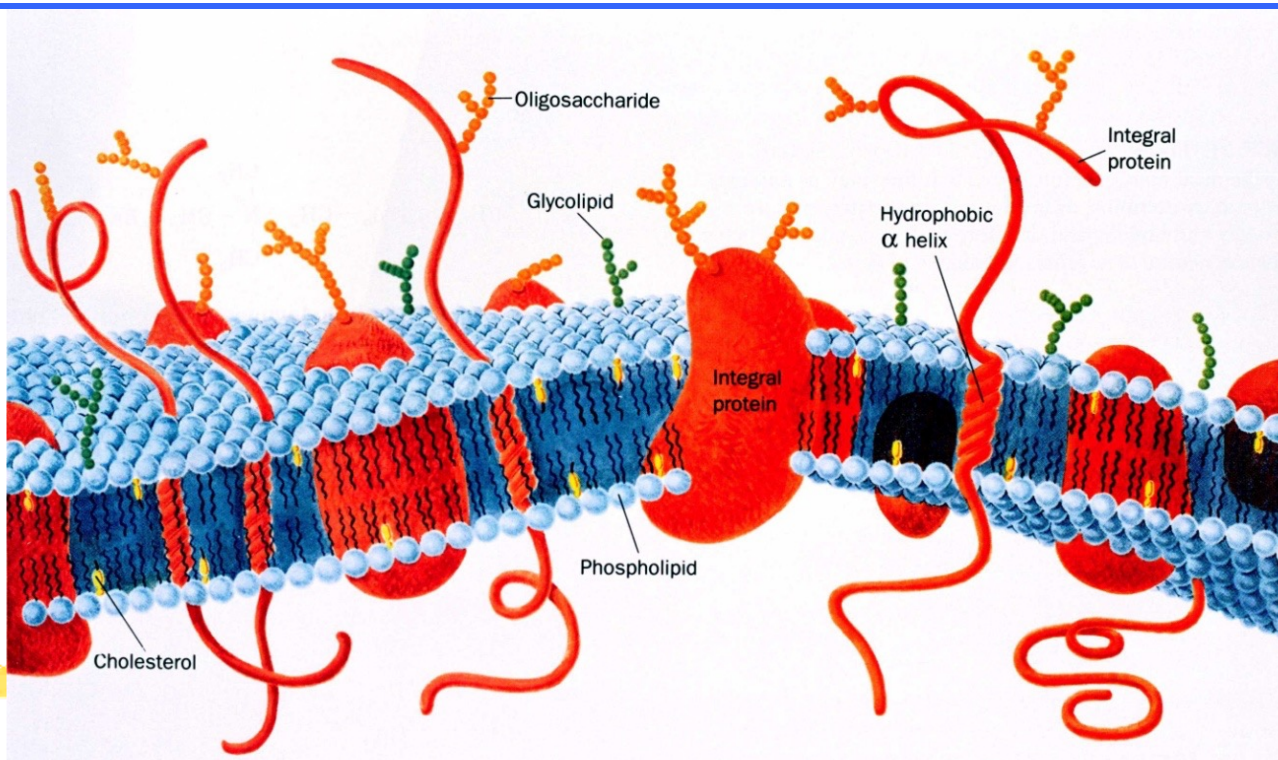
triacylglycerols: major form of stored energy in mammals

phospholipids, glycolipids, cholesterol: components of cell membranes

cholesterol: precursor of steroid hormones and bile salts

prostaglandins, prostacyclins, thromboxanes, leucotrienes, lipoxins: hormones and intracellular messengers

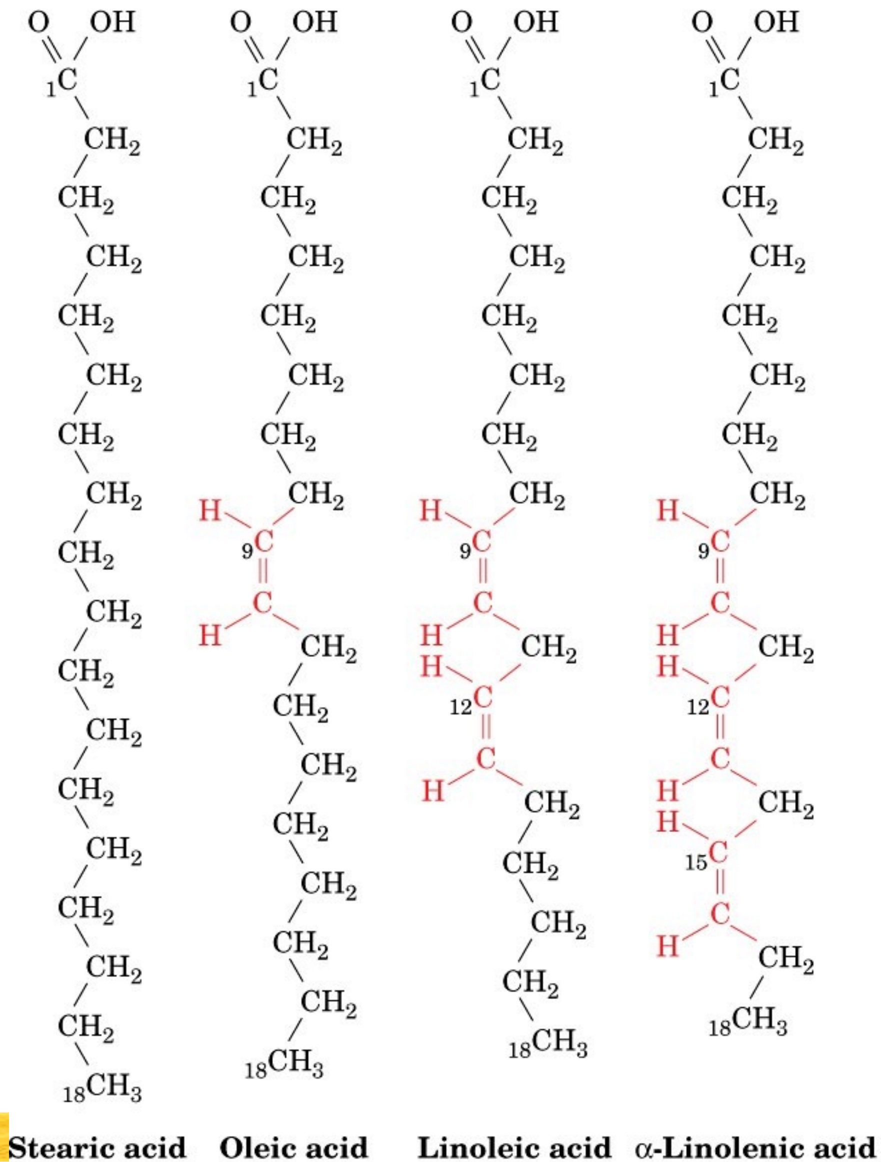
Fatty acid side chains: protein targeting to membranes



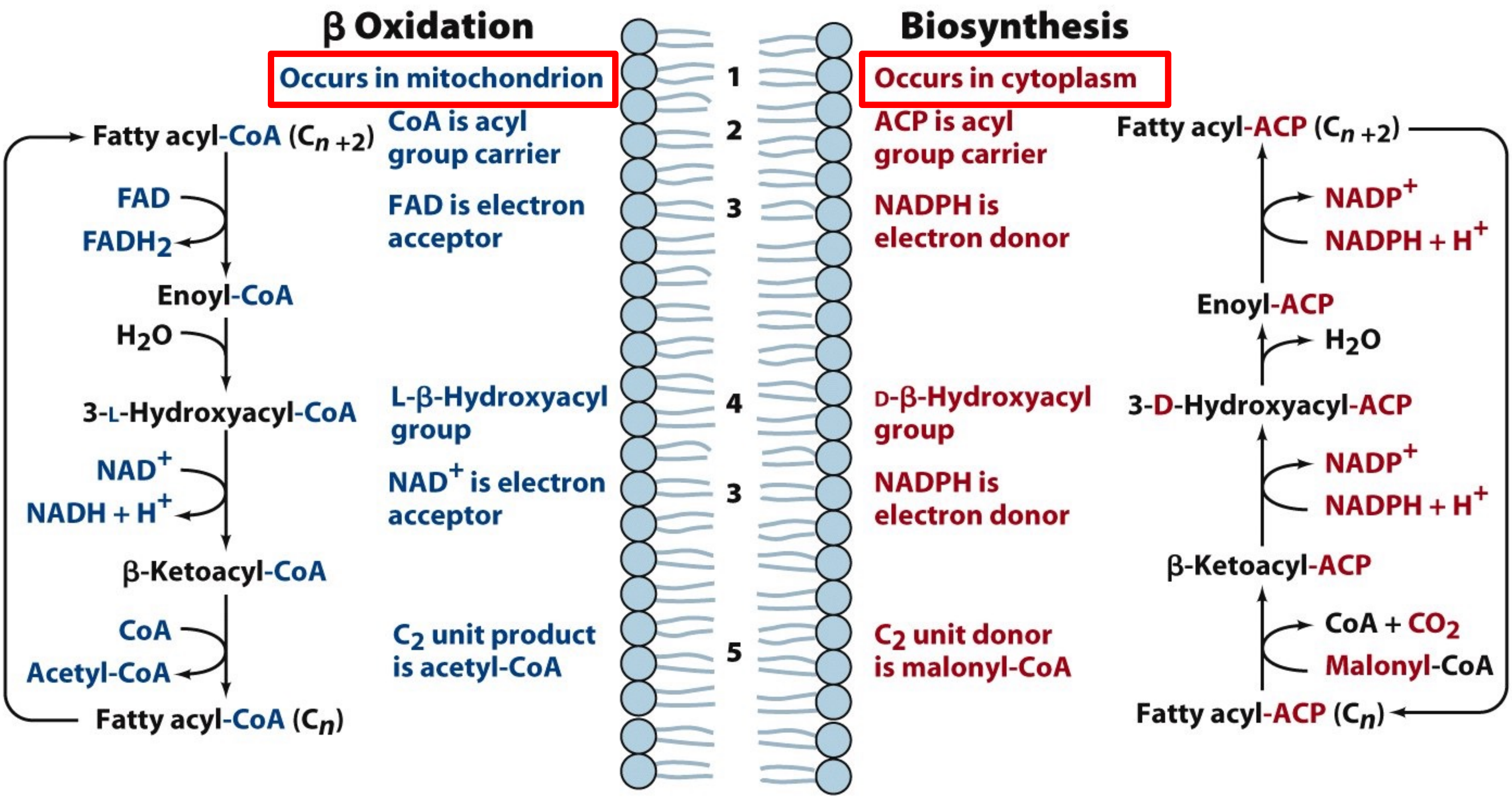
Fatty acids have 4 major physiological roles

- ➢ **components of phospholipids and glycolipids**
- ➢ **covalent attachment to proteins, protein targeting**
- ➢ **fuel and storage (triglycerides)**
- ➢ **hormones and intracellular messengers**

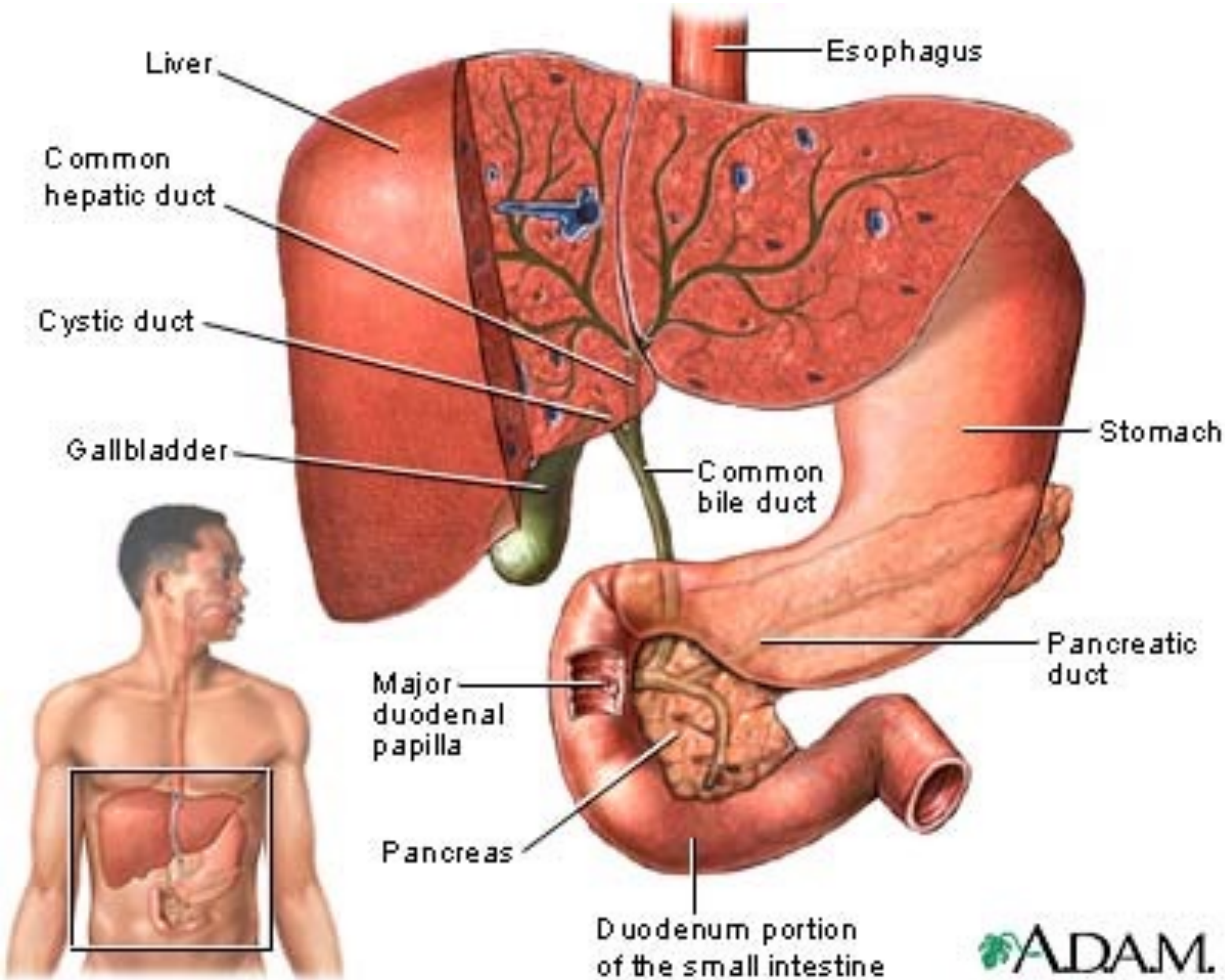
Please note: double bonds (when present) are *cis* and unconjugated



Sneak preview: Symmetry between fatty acid degradation and biosynthesis

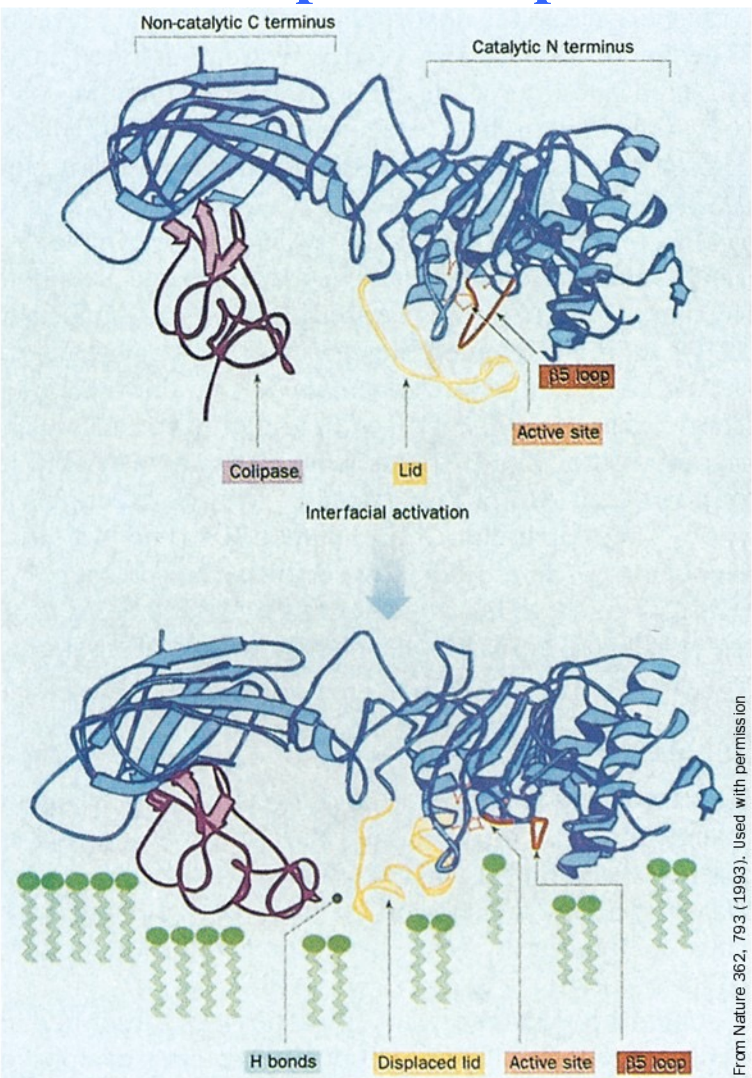


Digestion : Where It All Happens

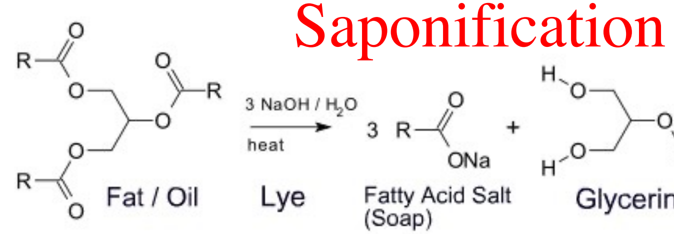


Dietary Lipids are Digested by Pancreatic Lipases at the Lipid-Water Interface

pancreatic lipase-colipase complex



Saponification



- ➢ **Catalyzes stepwise hydrolysis to form additional "soap": triacylglycerol → 1,2-diacylglycerol → 2-acylglycerol**

- ➢ **"Interfacial activation": The enzyme is only active in complex with micelles that open its lid (with the help of hydrogen bonding to the colipase)**