David L. Nelson and Michael M. Cox

Lehninger Principles of Biochemistry

Fourth Edition

Chapter 20:

Carbohydrate Biosynthesis in Plants and Bacteria

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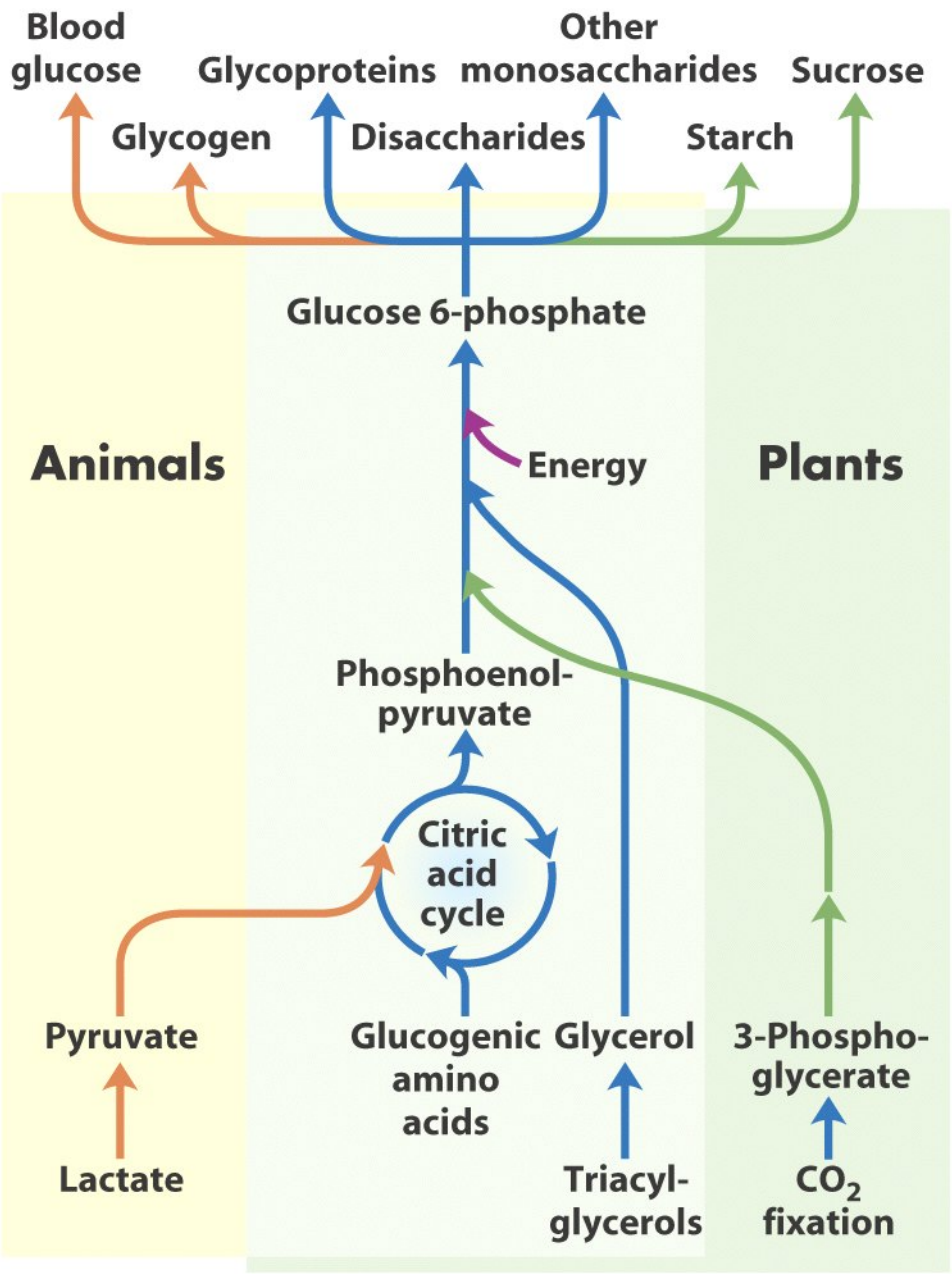
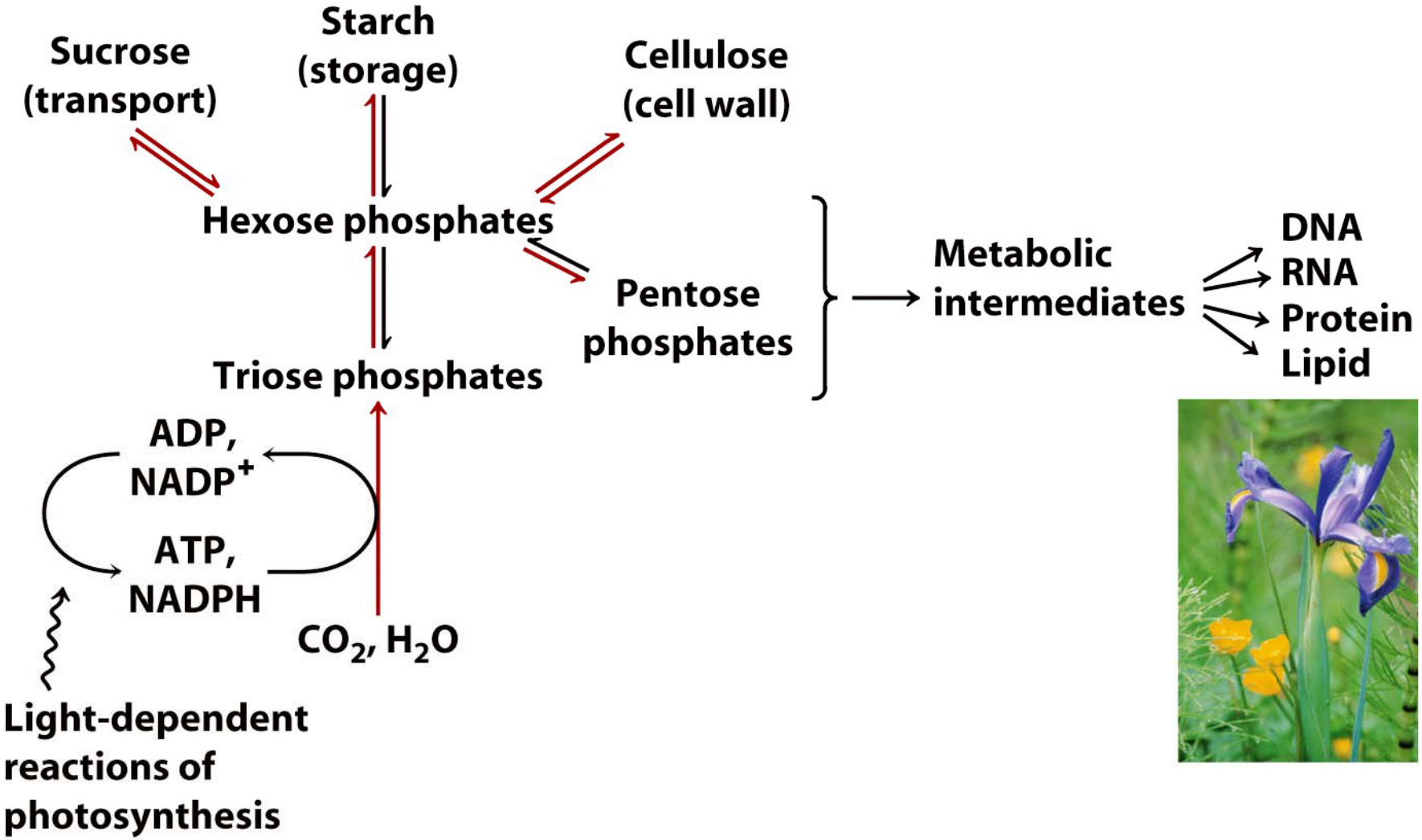
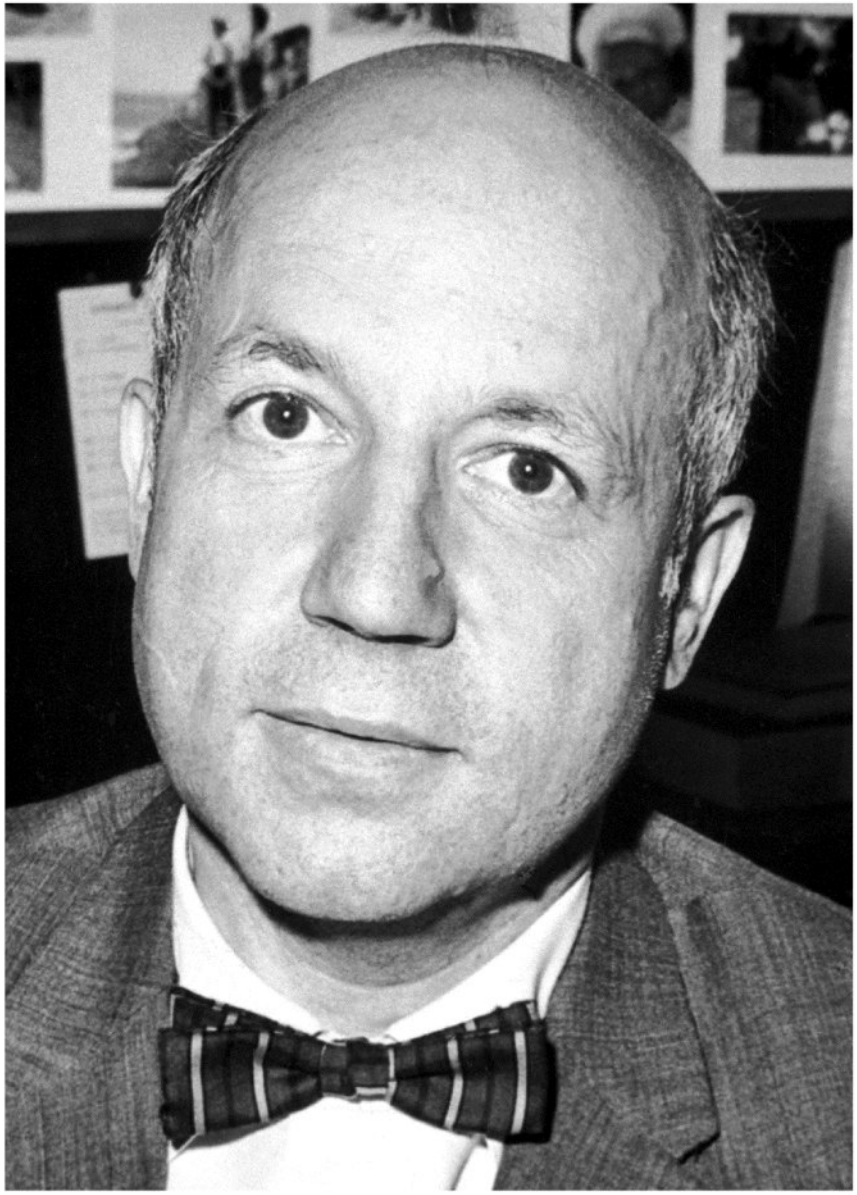
Metabolism

Catabolism
Anabolism

Carbohydrate Biosynthesis
CO_2 fixation (plant, bacteria)

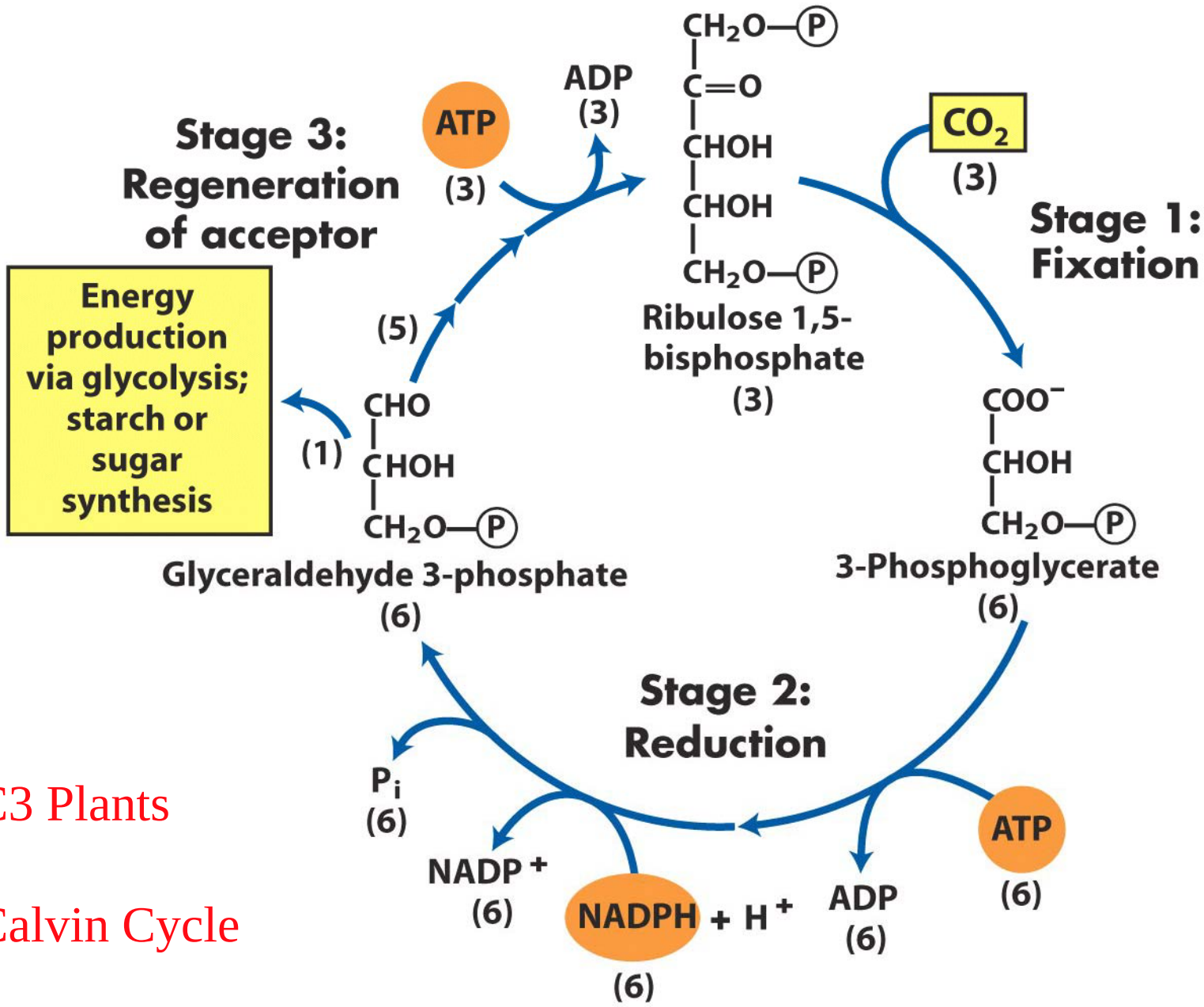

Blood glucose
Glycogen
Glycoproteins
Disaccharides
Other monosaccharides
Starch
Sucrose
Glucose 6-phosphate
Energy
Animals
Plants
Phosphoenol-pyruvate
Citric acid cycle
Pyruvate
Lactate
Glucogenic amino acids
Glycerol
Triacyl-glycerols
3-Phospho-glycerate
CO_2 fixation


Sucrose
(transport)
Starch
(storage)
Cellulose
(cell wall)
Hexose phosphates
Pentose
phosphates
Metabolic
intermediates
DNA
RNA
Protein
Lipid
Triose phosphates
ADP,
NADP+
ATP,
NADPH
CO2, H2O
Light-dependent
reactions of
photosynthesis



Melvin Calvin, 1911–1997

Nobel Laureate
Chemistry
1961

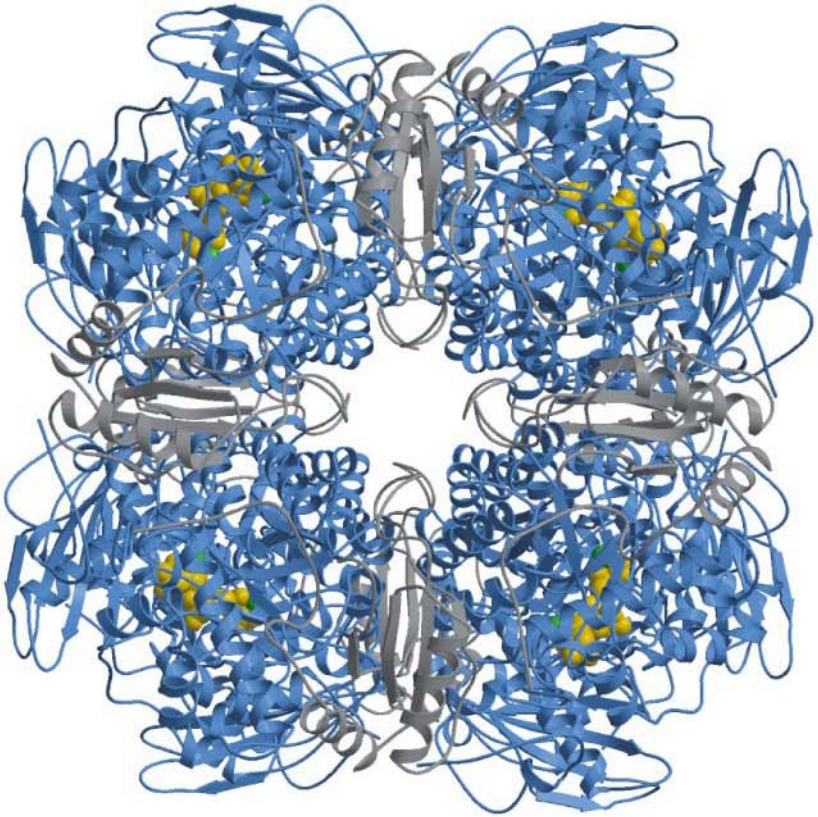


C3 Plants

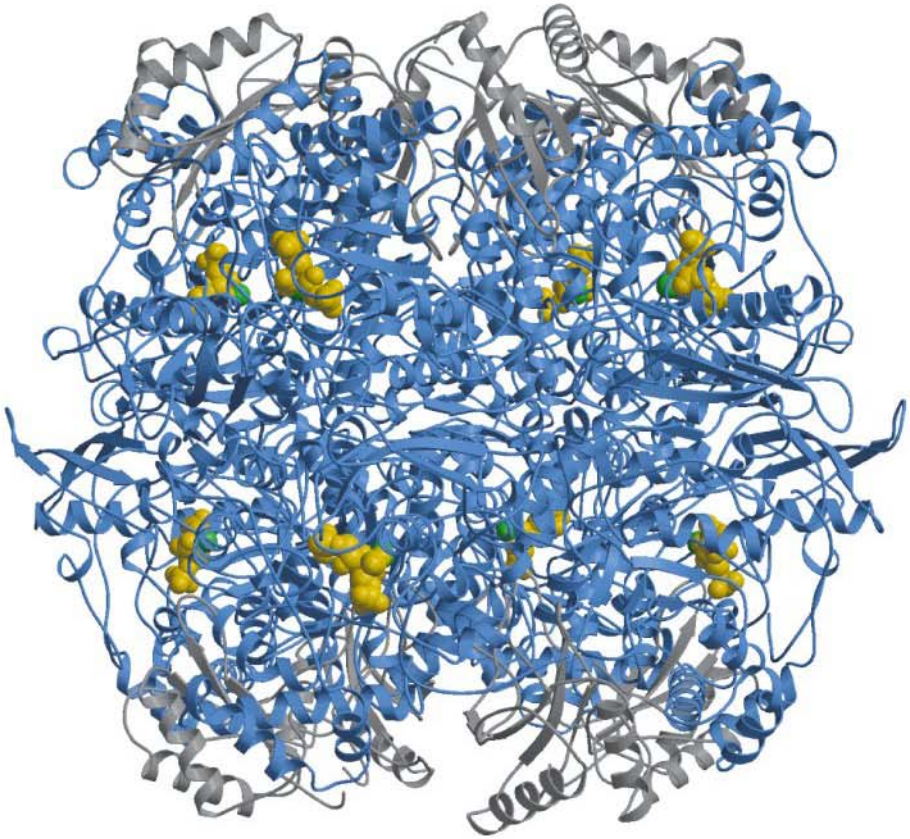
Calvin Cycle

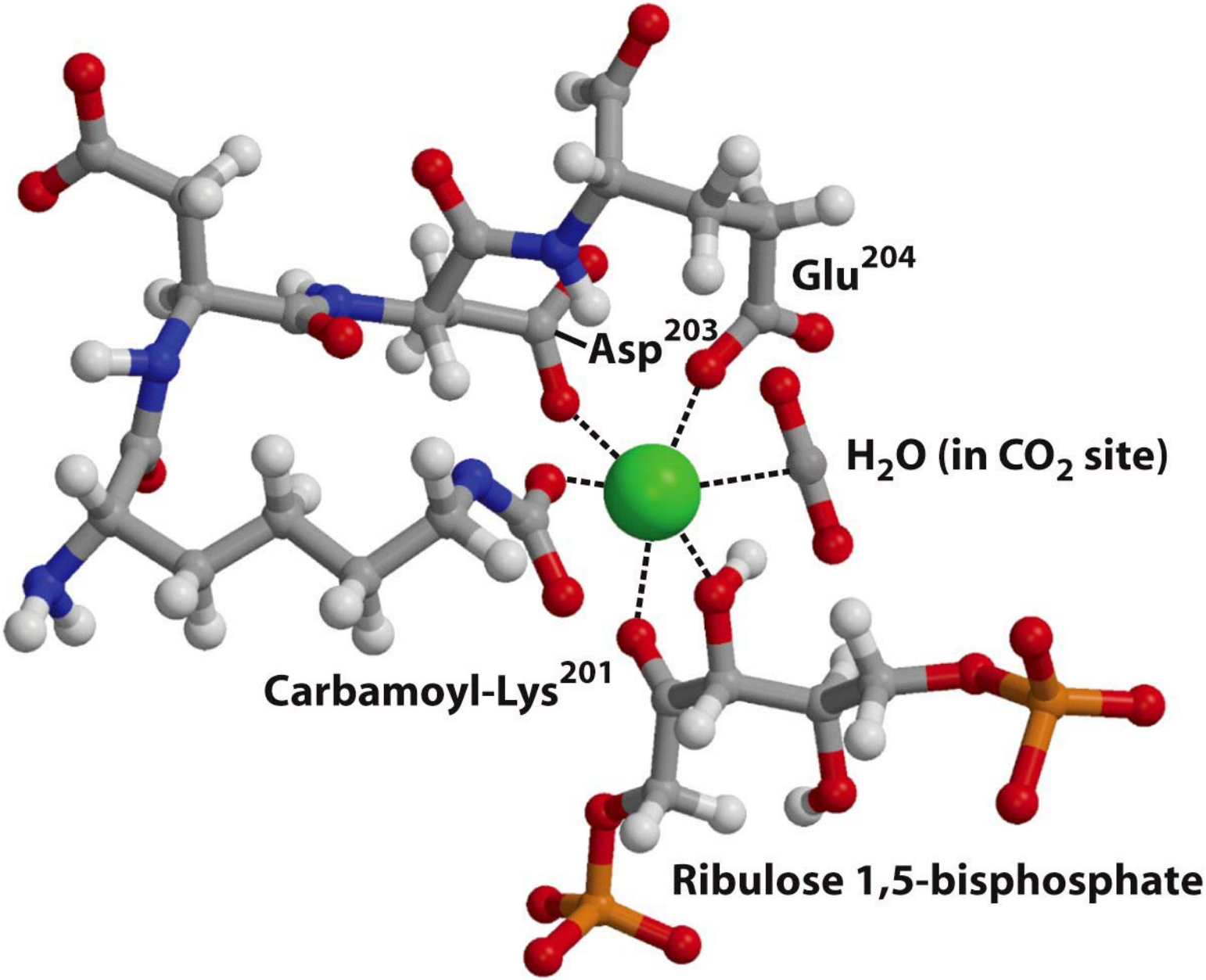
Ribulose 1,5-bisphosphate carboxylase/oxygenase (Rubisco) (from spinach)

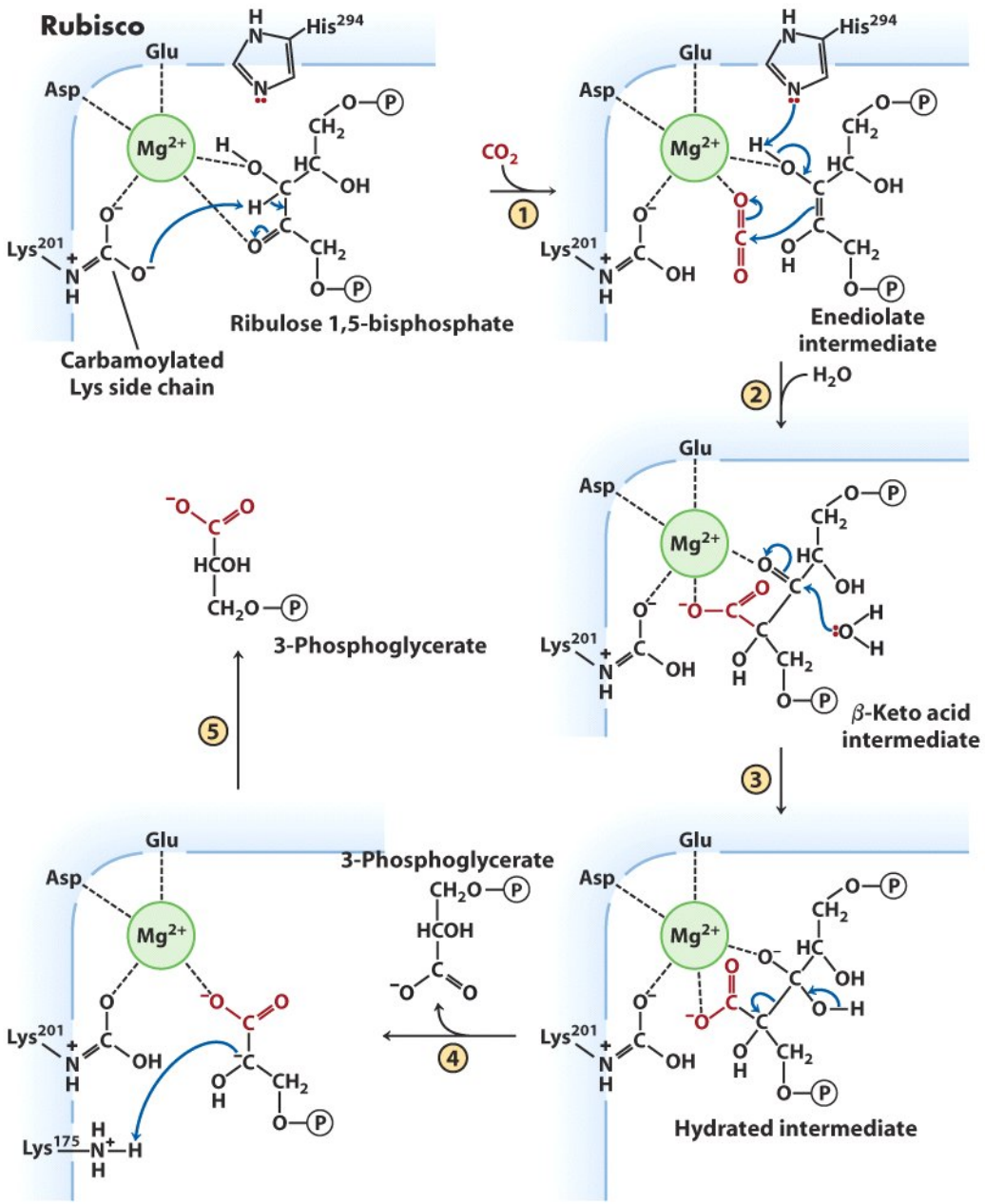
Top view

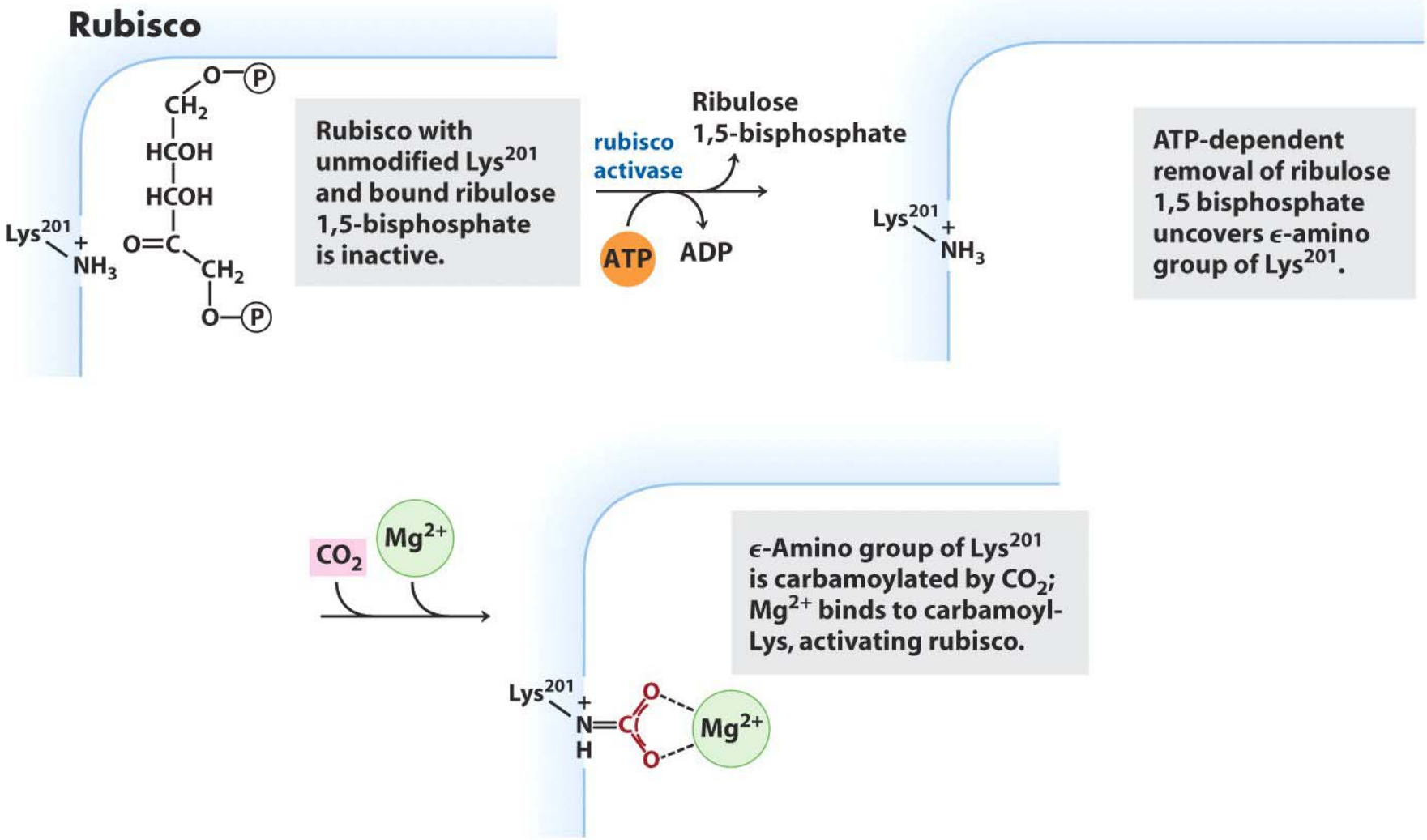


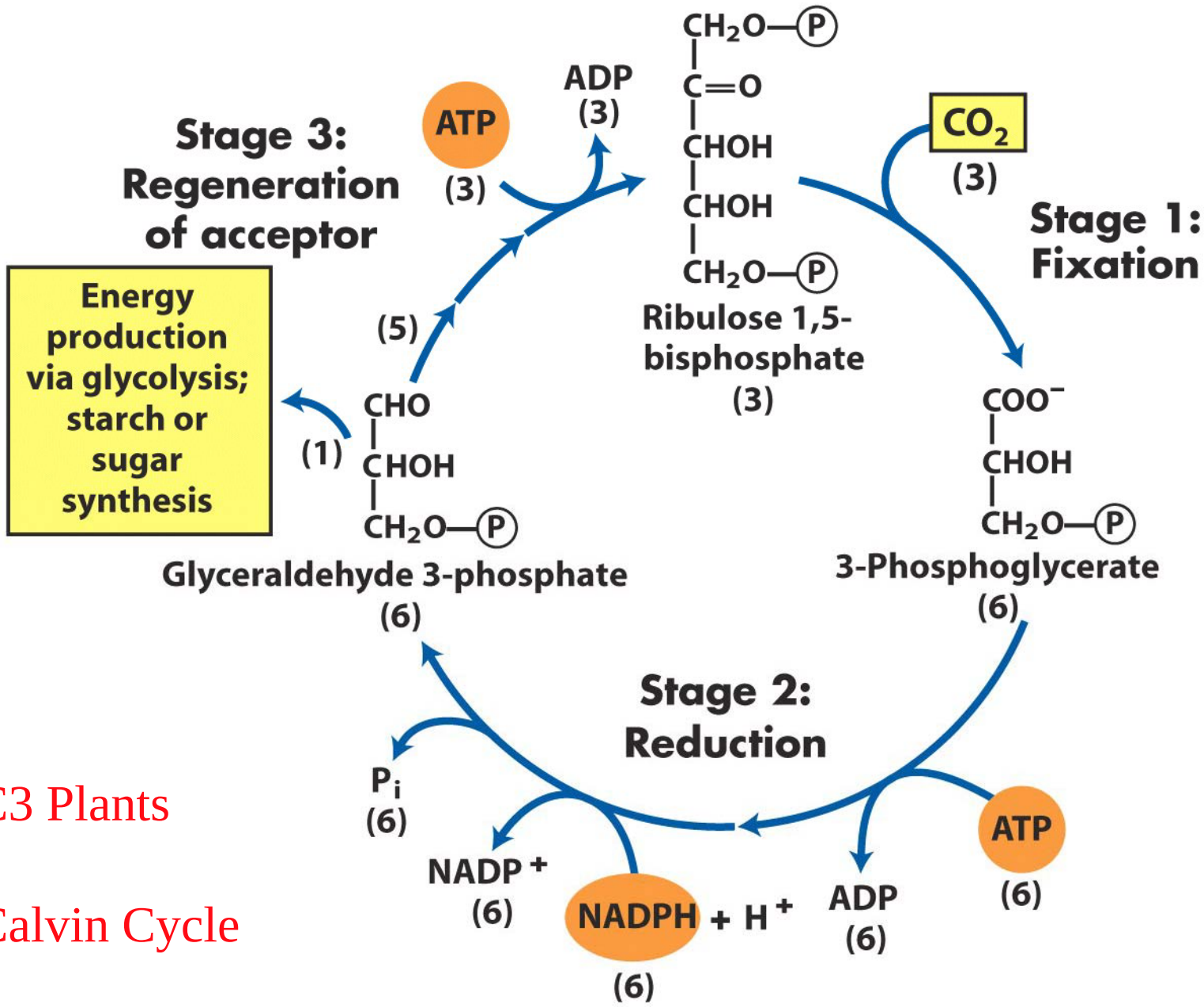
Side view




Glu204
Asp203
H2O (in CO2 site)
Carbamoyl-Lys201
Ribulose 1,5-bisphosphate

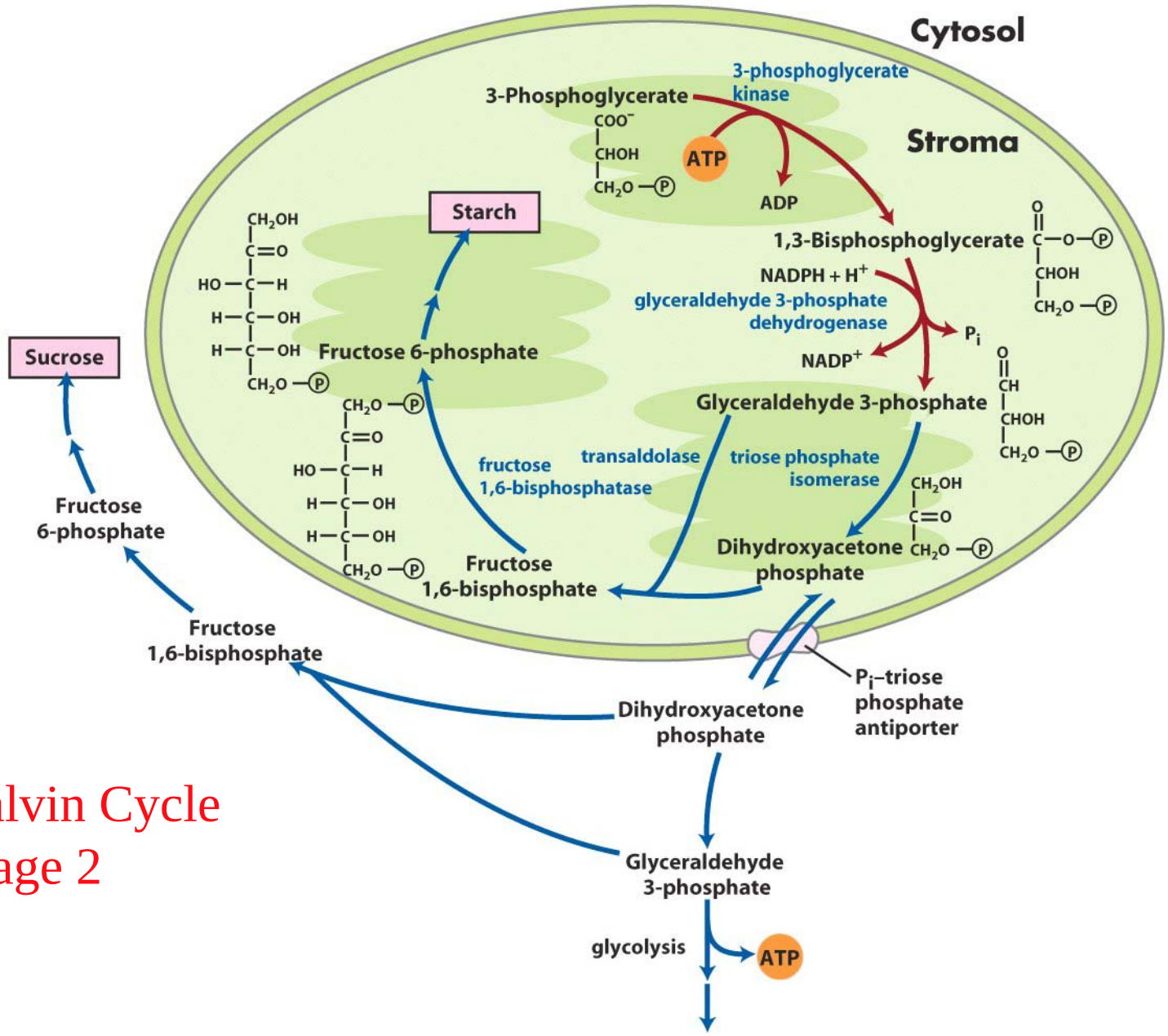

Rubisco
Glu
His294
Asp
Mg2+
Lys201
Ribulose 1,5-bisphosphate
Carbamoylated
Lys side chain
CO2
1
Enediolate
intermediate
H2O
2
β-Keto acid
intermediate
3
Hydrated intermediate
4
3-Phosphoglycerate
5
Lys175


Rubisco
Rubisco with unmodified Lys201 and bound ribulose 1,5-bisphosphate is inactive.
rubisco activase
Ribulose 1,5-bisphosphate
ATP
ADP
ATP-dependent removal of ribulose 1,5 bisphosphate uncovers ϵ-amino group of Lys201.
CO2
Mg2+
ϵ-Amino group of Lys201 is carbamoylated by CO2; Mg2+ binds to carbamoyl-Lys, activating rubisco.



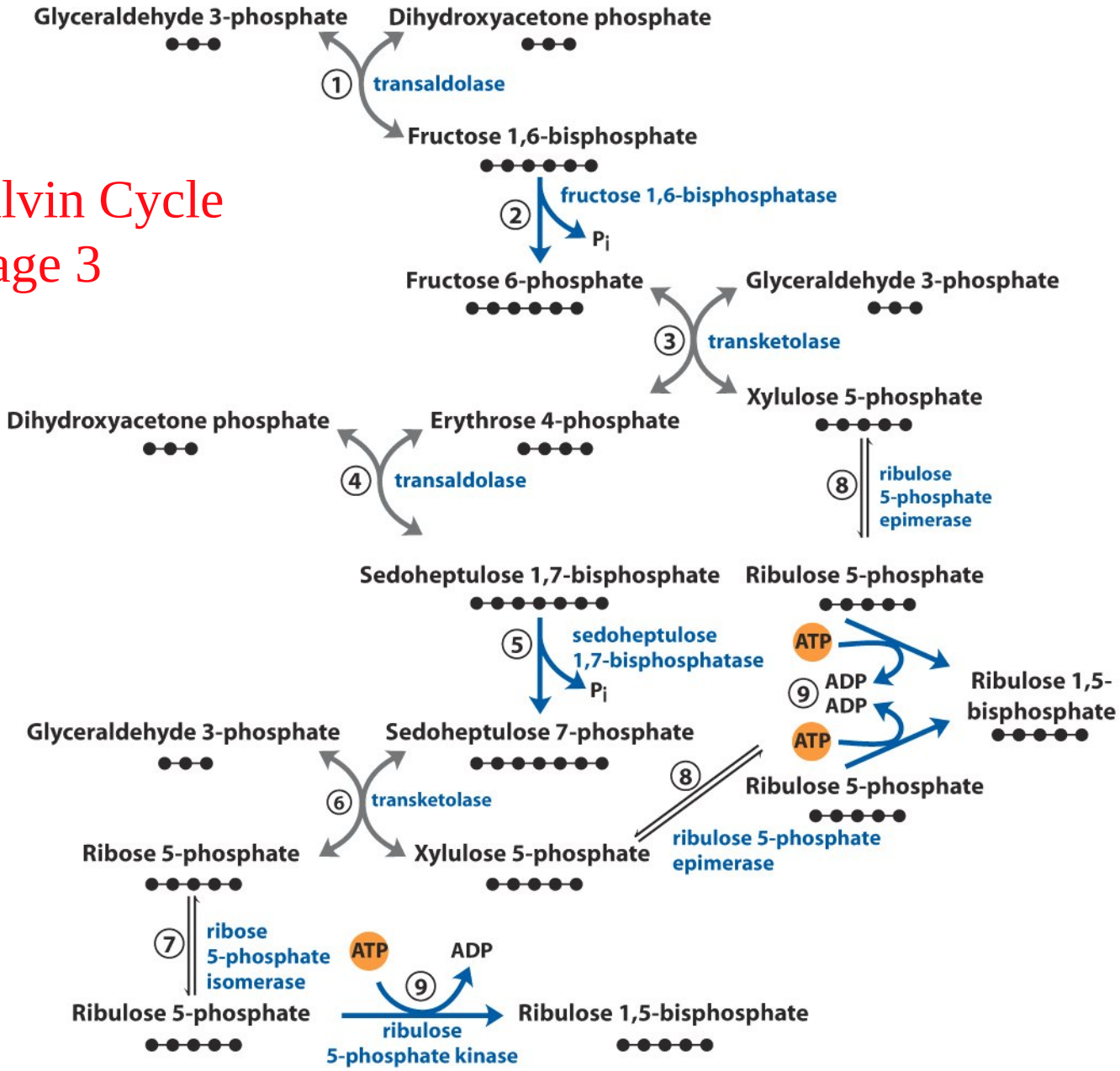
C3 Plants

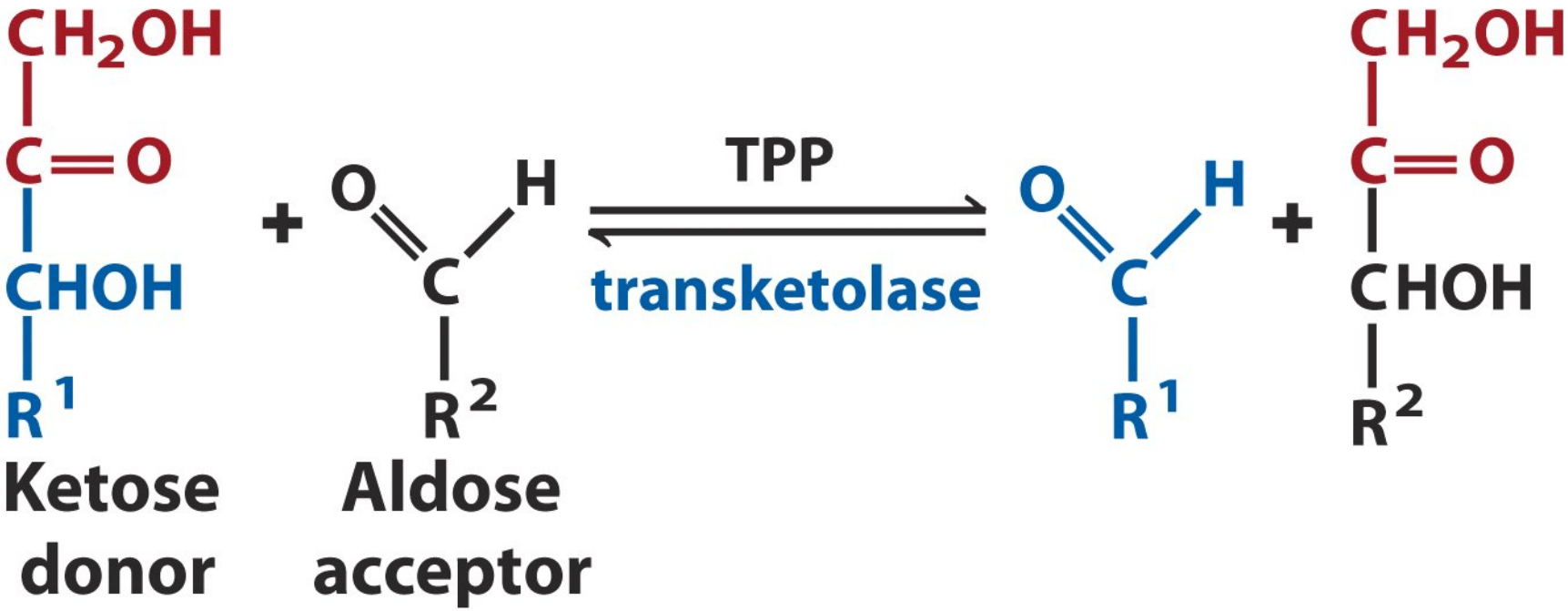
Calvin Cycle

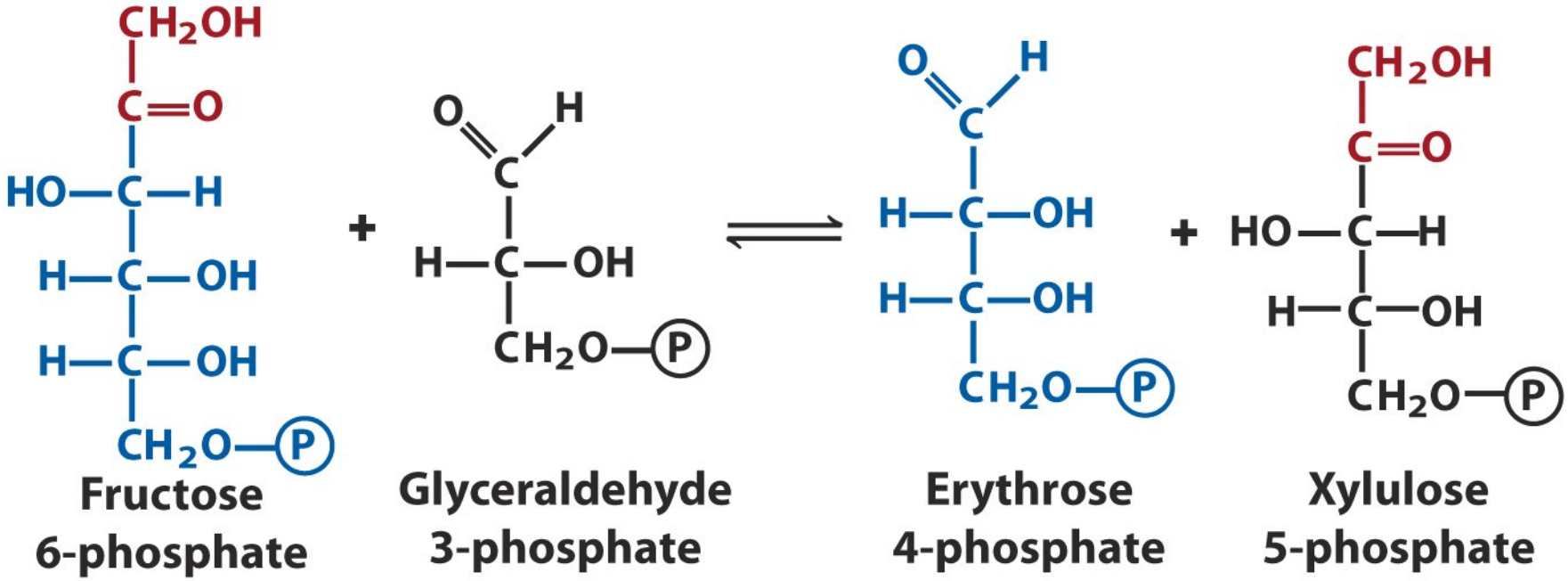


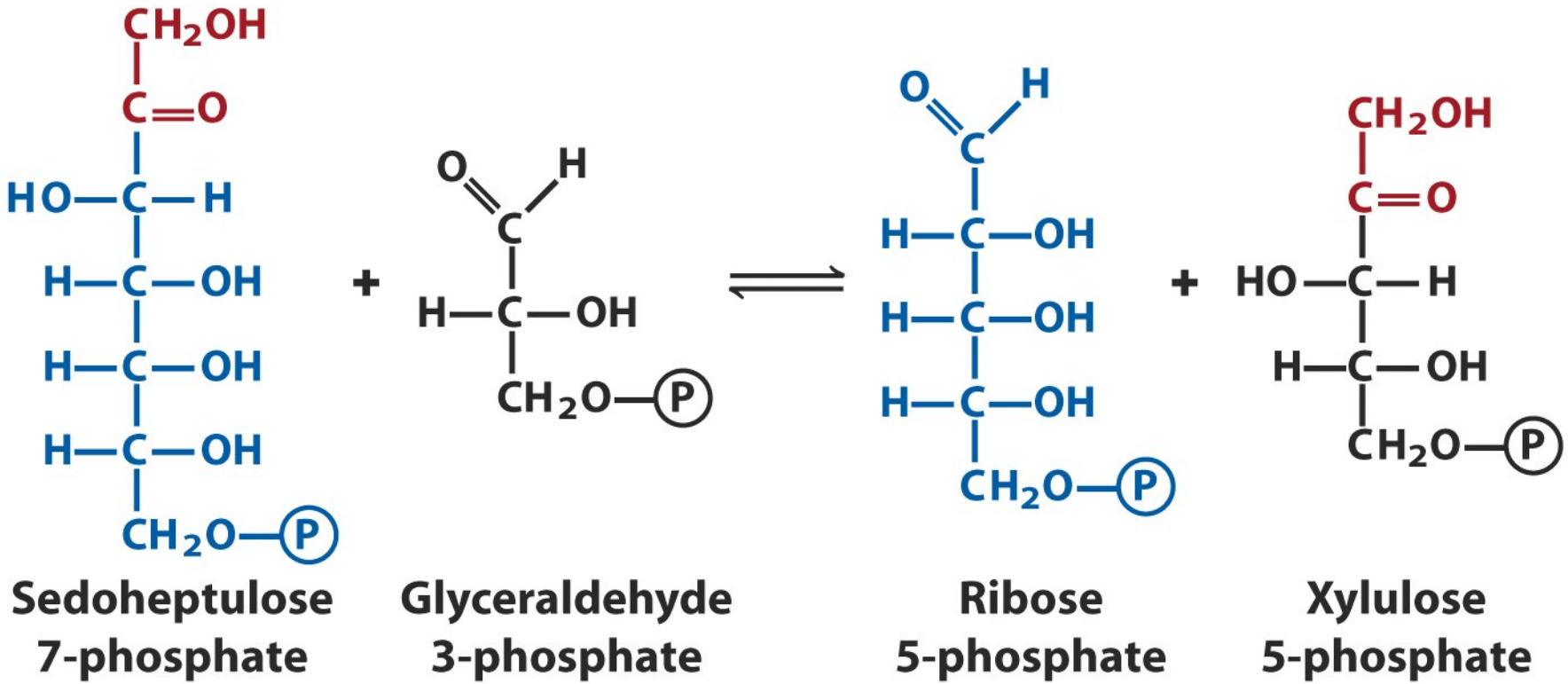
Calvin Cycle
Stage 2

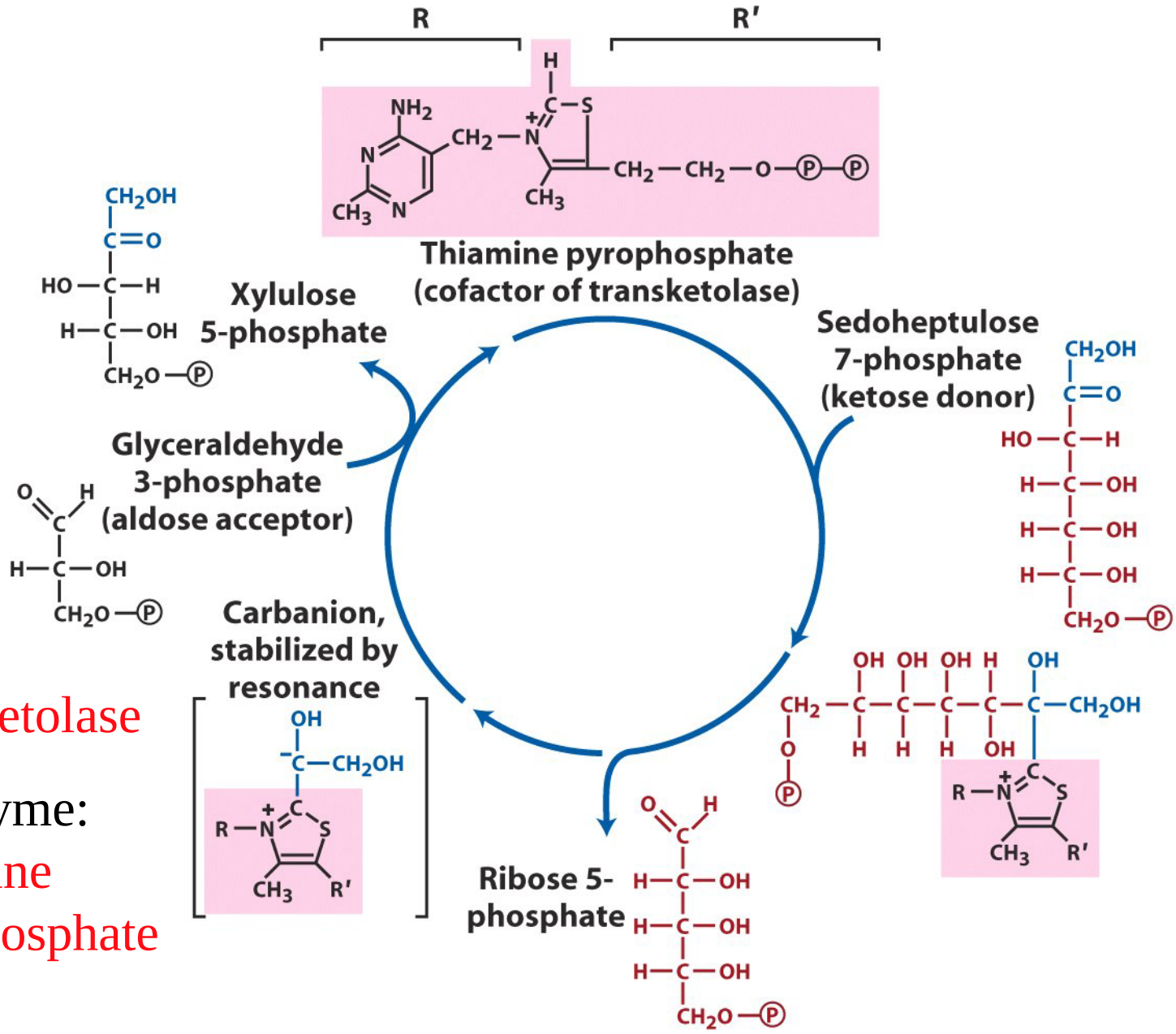
Calvin Cycle
Stage 3




CH2OH
C=O
CHOH
R1
Ketose donor
O
H
C
R2
Aldose acceptor
TPP
transketolase
O
H
C
R1
CH2OH
C=O
CHOH
R2


Fructose
6-phosphate
Glyceraldehyde
3-phosphate
Erythrose
4-phosphate
Xylulose
5-phosphate

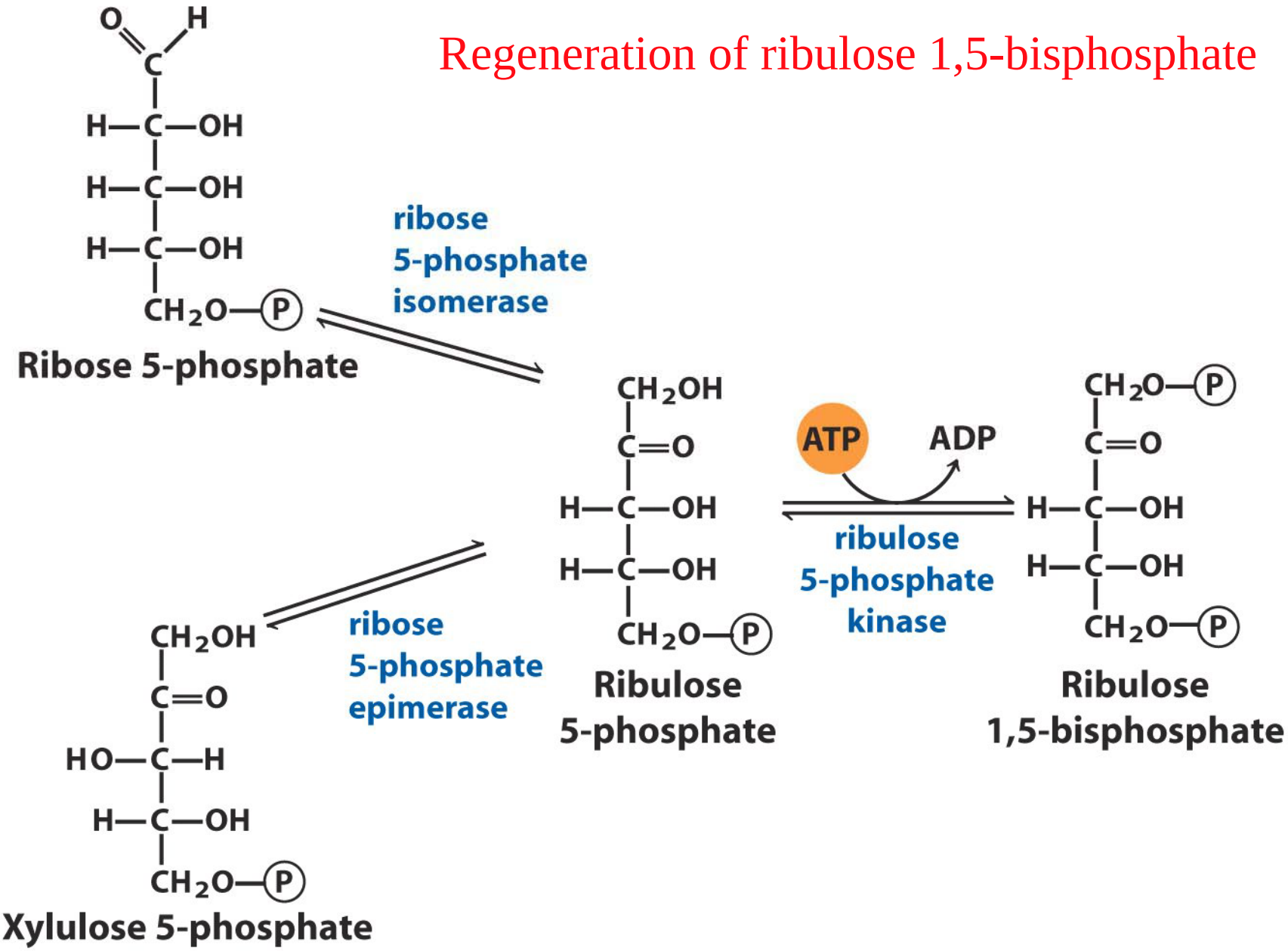

Sedoheptulose 7-phosphate
Glyceraldehyde 3-phosphate
Ribose 5-phosphate
Xylulose 5-phosphate



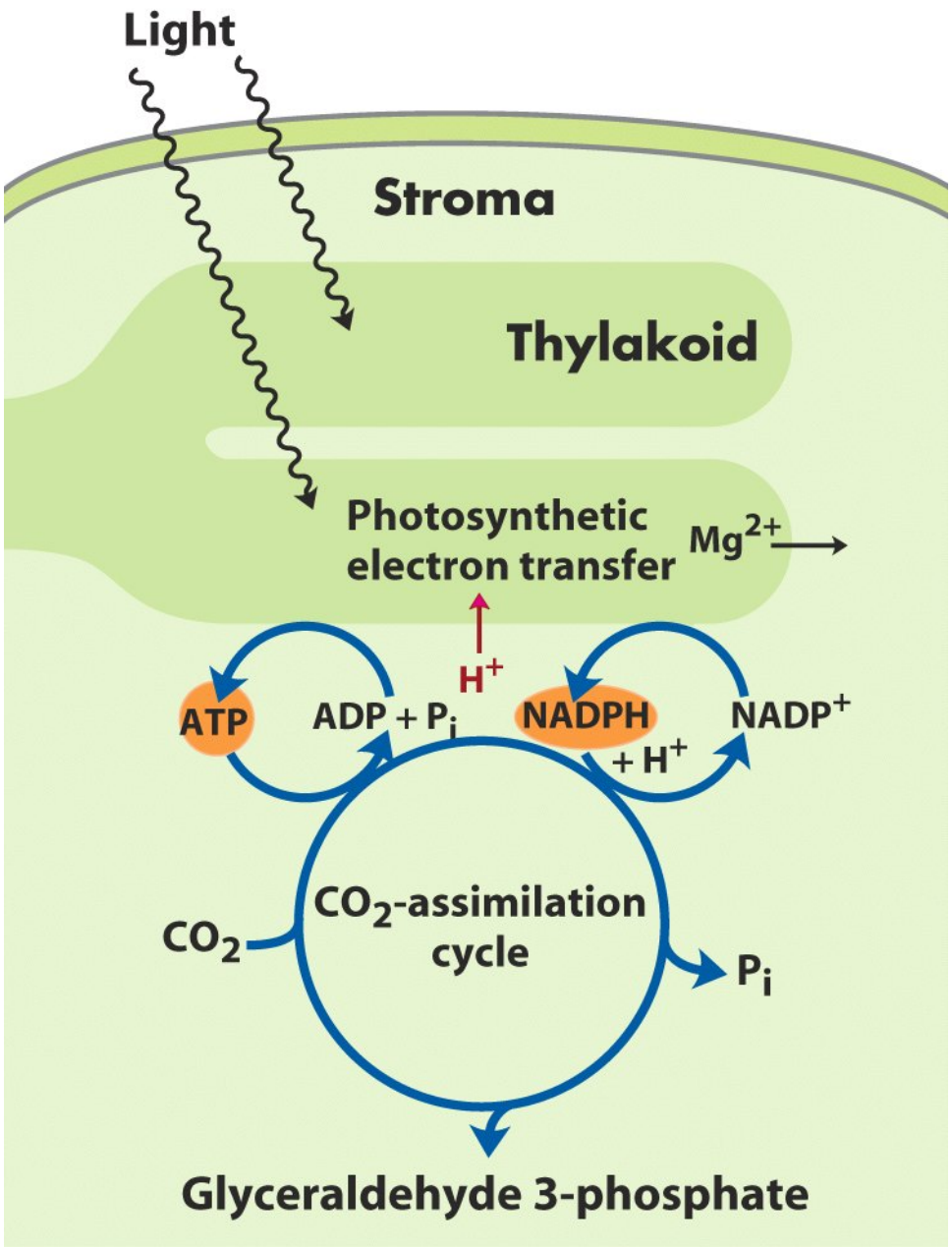
Transketolase

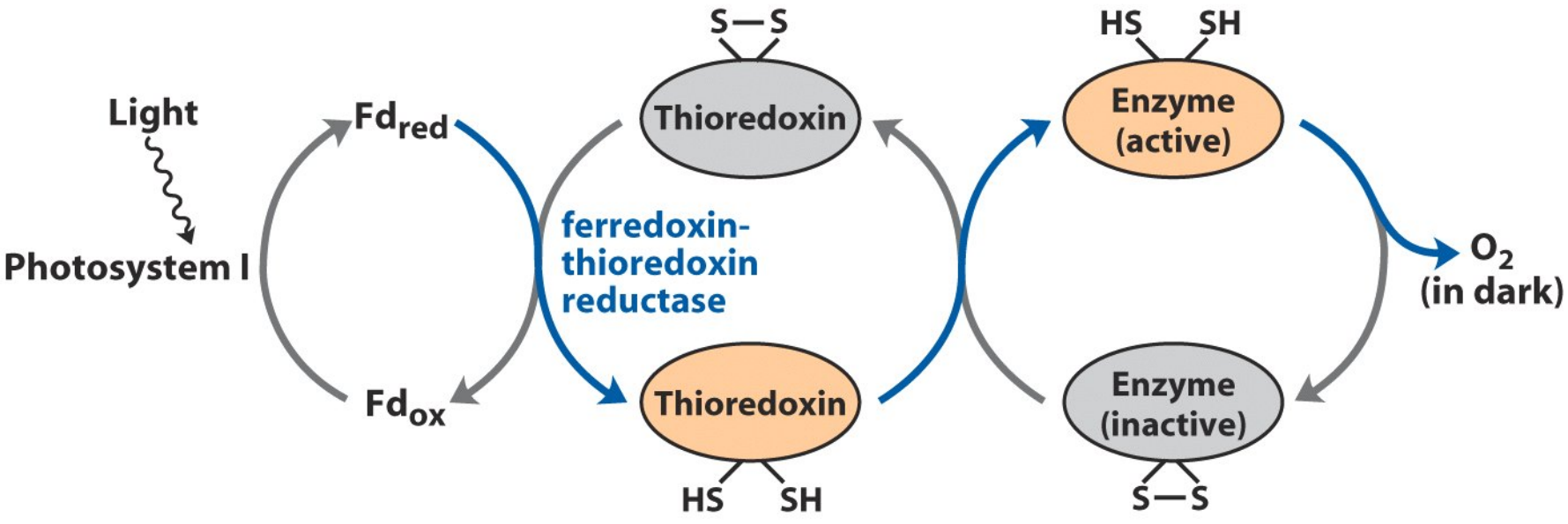
Coenzyme:
Thiamine pyrophosphate
(TPP)

Regeneration of ribulose 1,5-bisphosphate



Source of ATP and NADPH





Enzymes activated by light in Calvin cycles

Sedoheptulose 1,7-bisphosphatase

Fructose 1,6-bisphosphatase

Ribulose 1-phosphate kinase

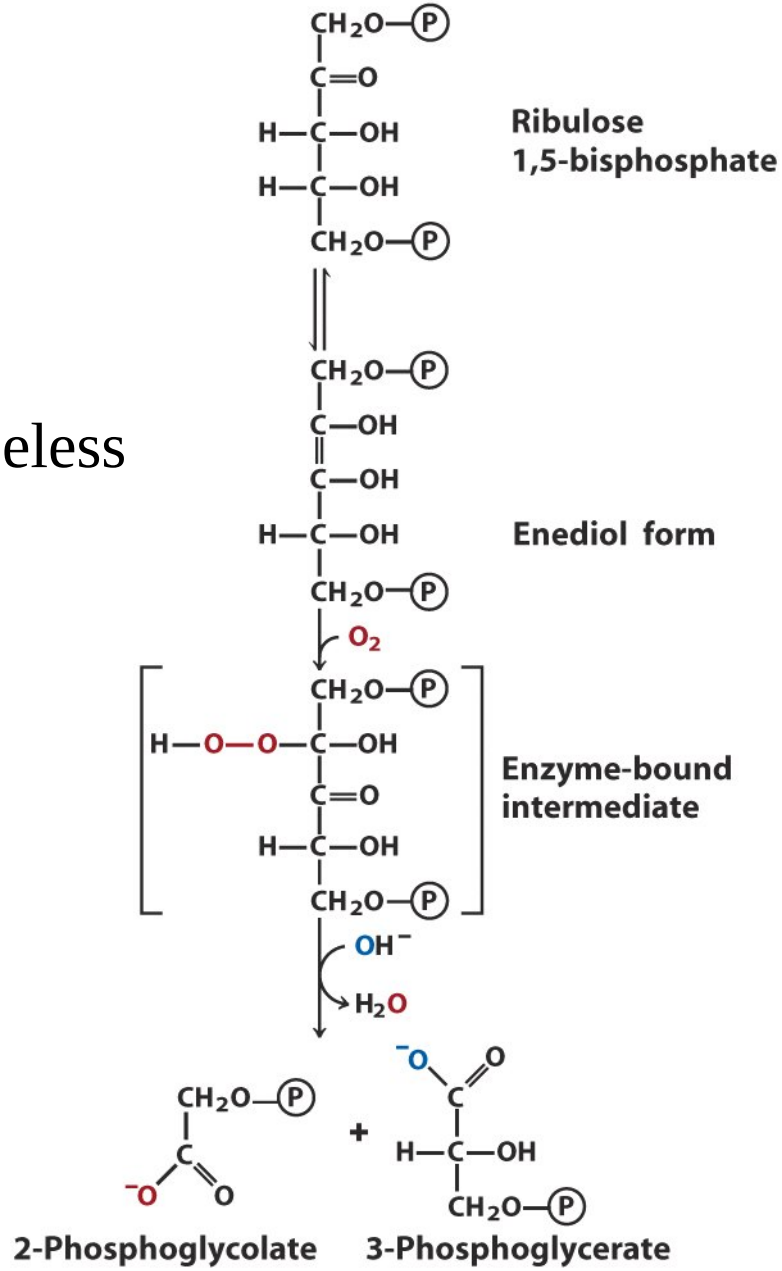
Glyceraldehyde 3-phosphate dehydrogenase

Oxygenase Activity of Rubisco

Ribulose 1,5-bisphosphate carboxylase/oxygenase

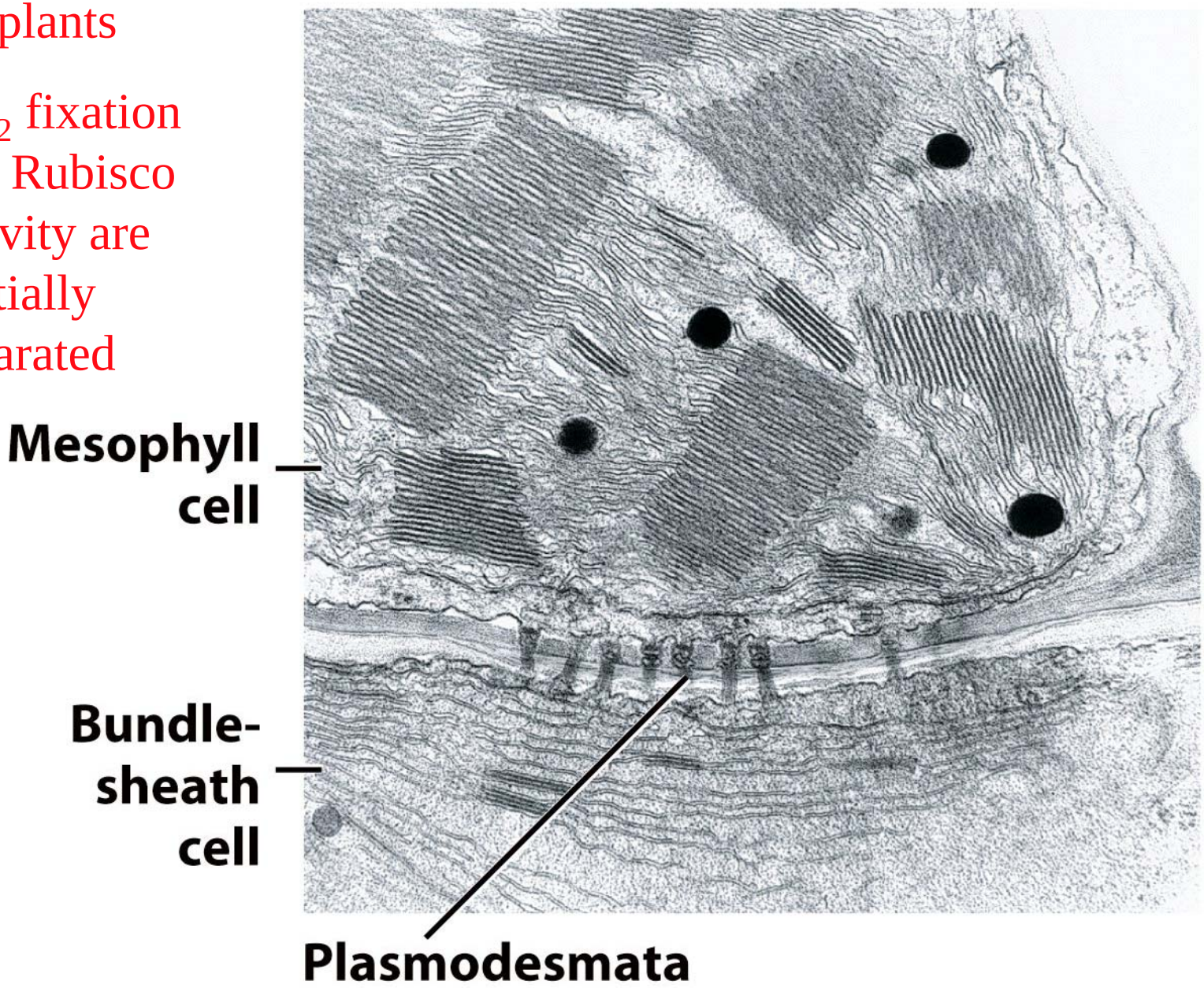
Photorespiration

2-phosphoglycerate: metabolic useless



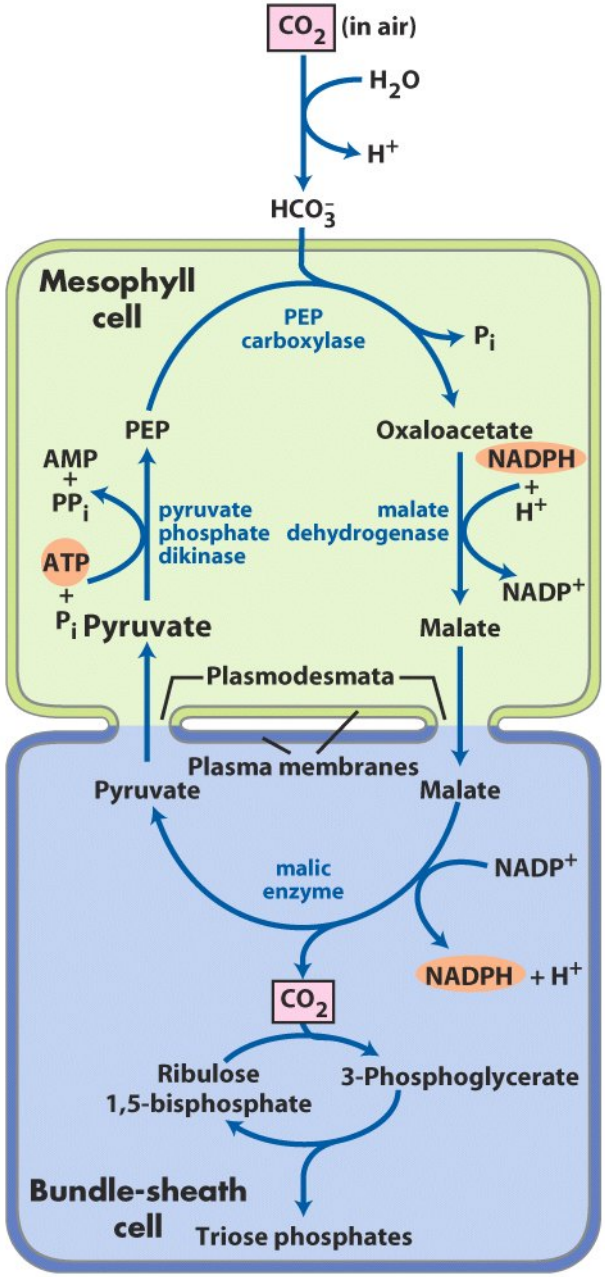
C4 plants

CO_2 fixation and Rubisco activity are spatially separated



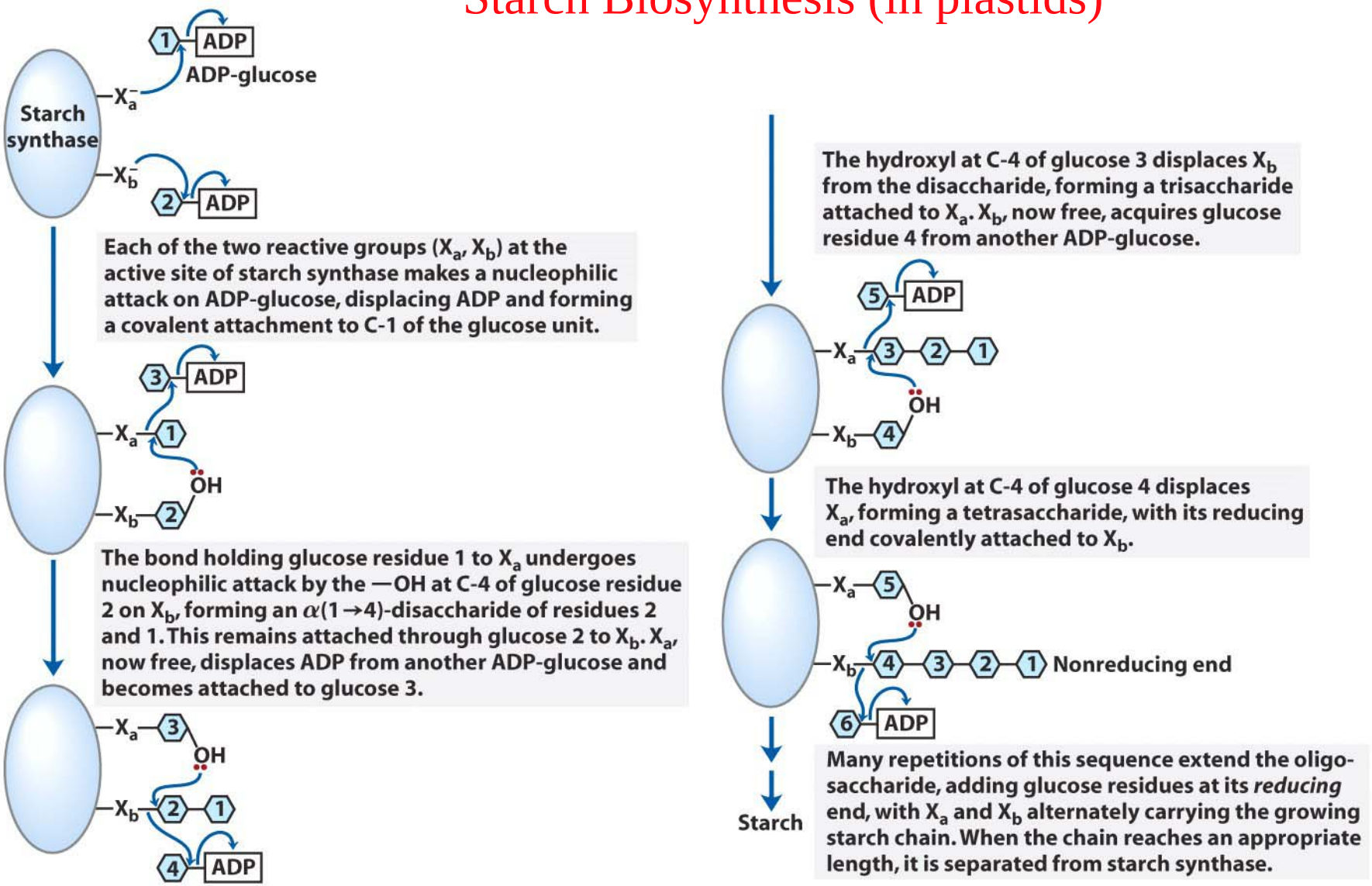
Carbon assimilation in C4 plants

PEP carboxylase does not use O_2 as an alternate substrate

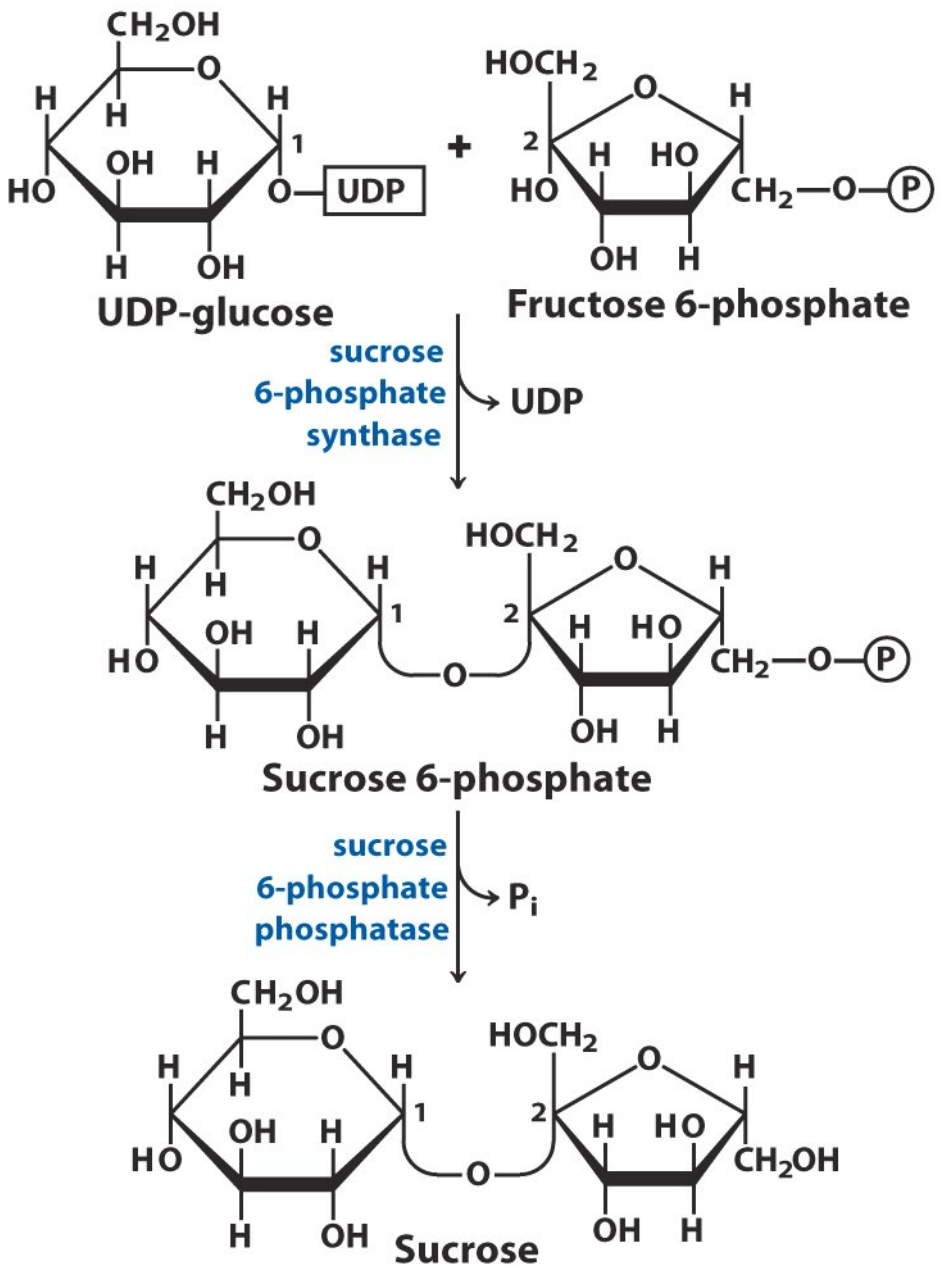


No O_2 available for Rubisco thus no photorespiration side reaction

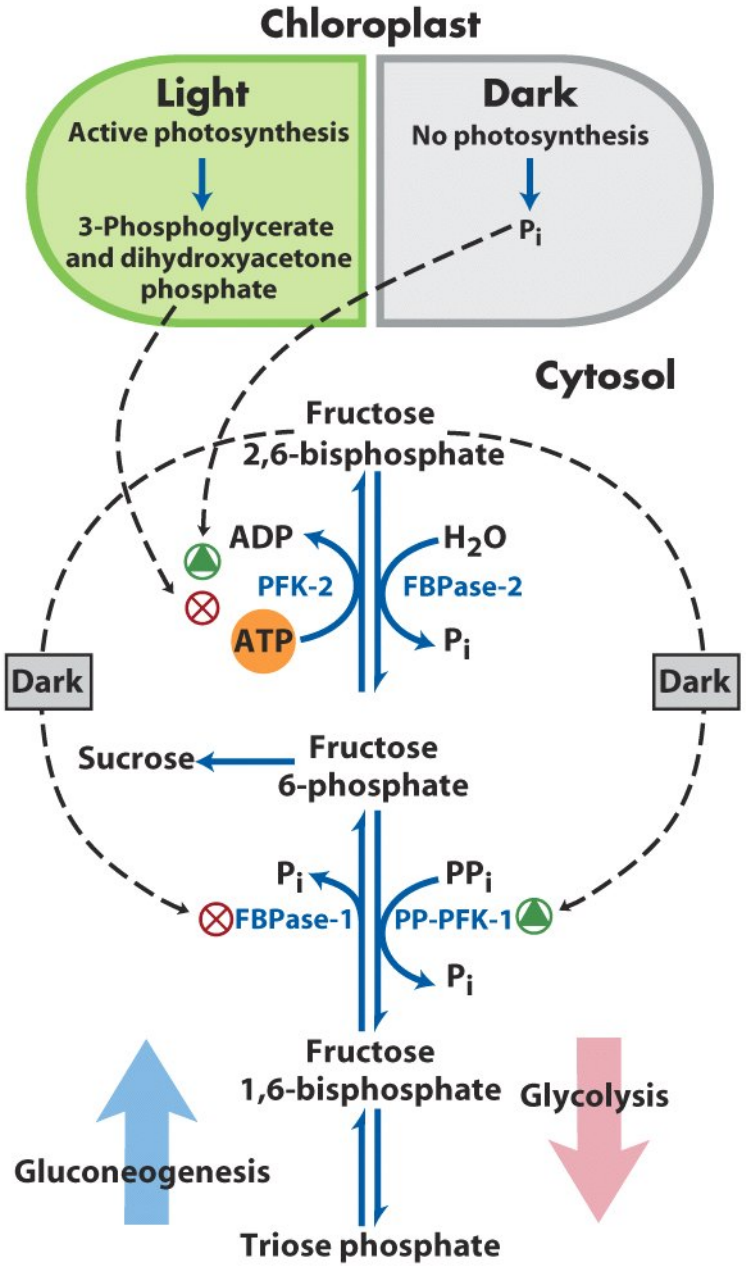
Starch Biosynthesis (in plastids)



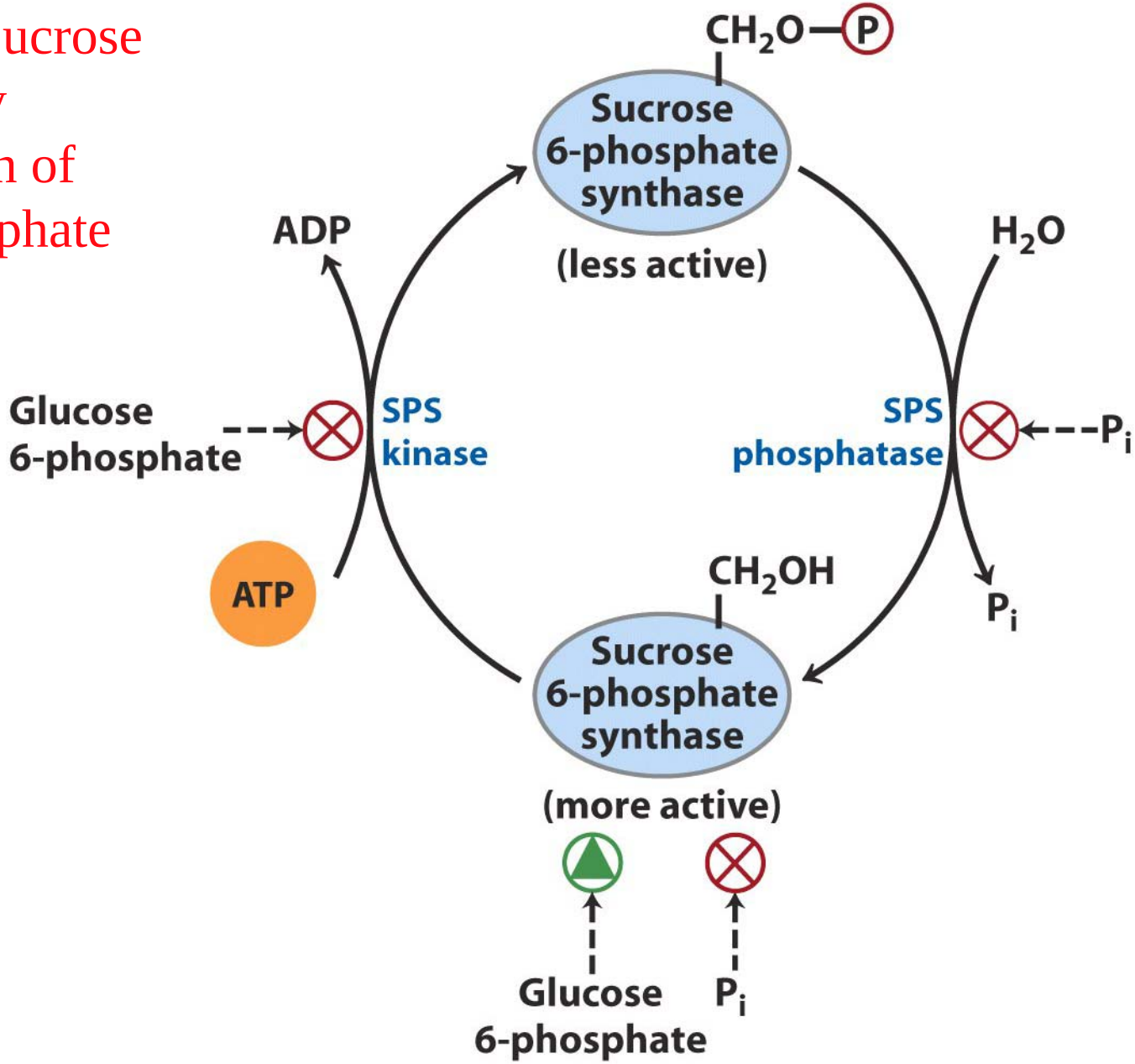
Sucrose Biosynthesis (in cytosol)



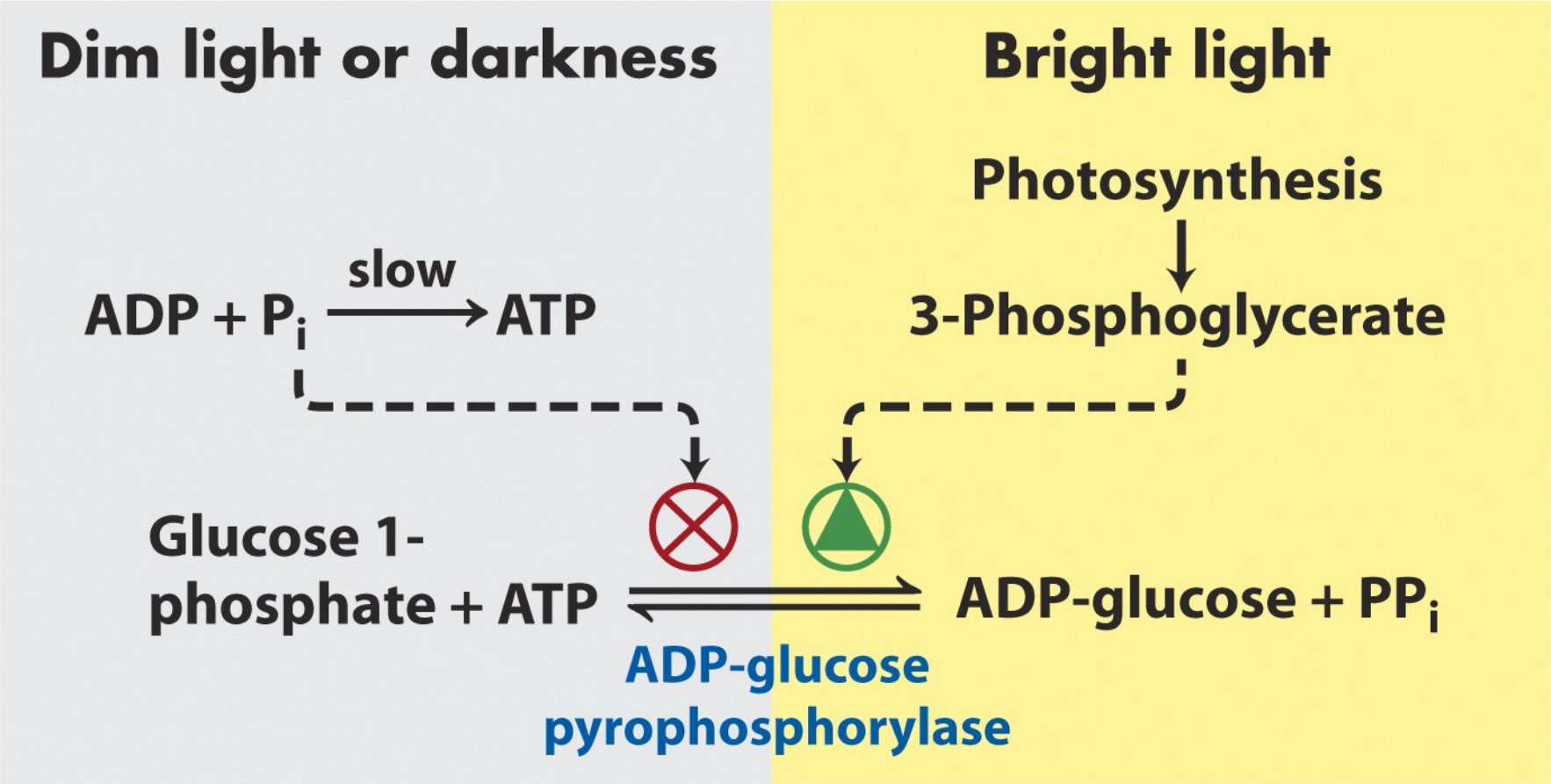
Regulation of Sucrose Biosynthesis by Fructose 2,6-bisphosphate



Regulation of Sucrose Biosynthesis by Phosphorylation of Sucrose 6-phosphate Synthase

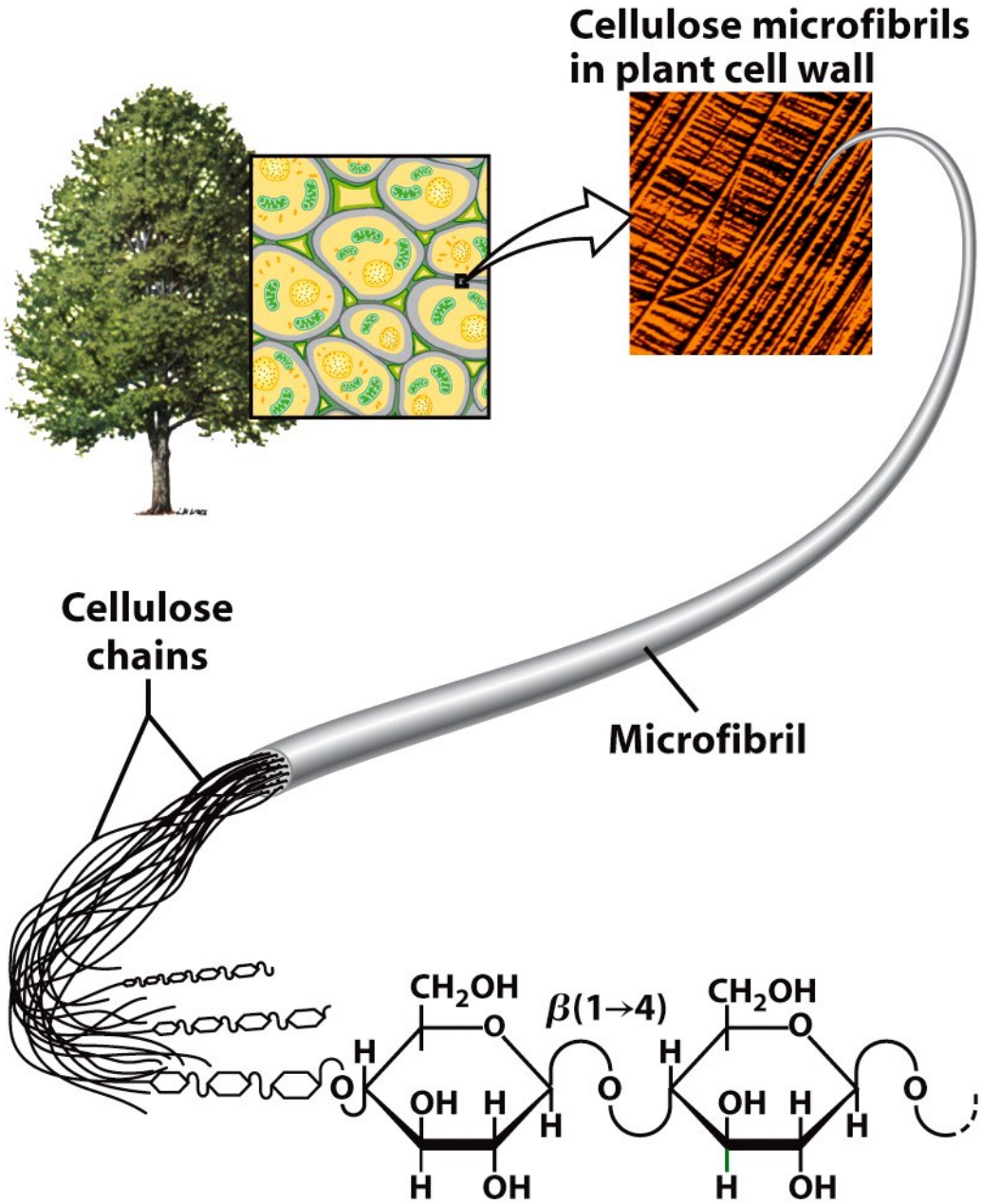


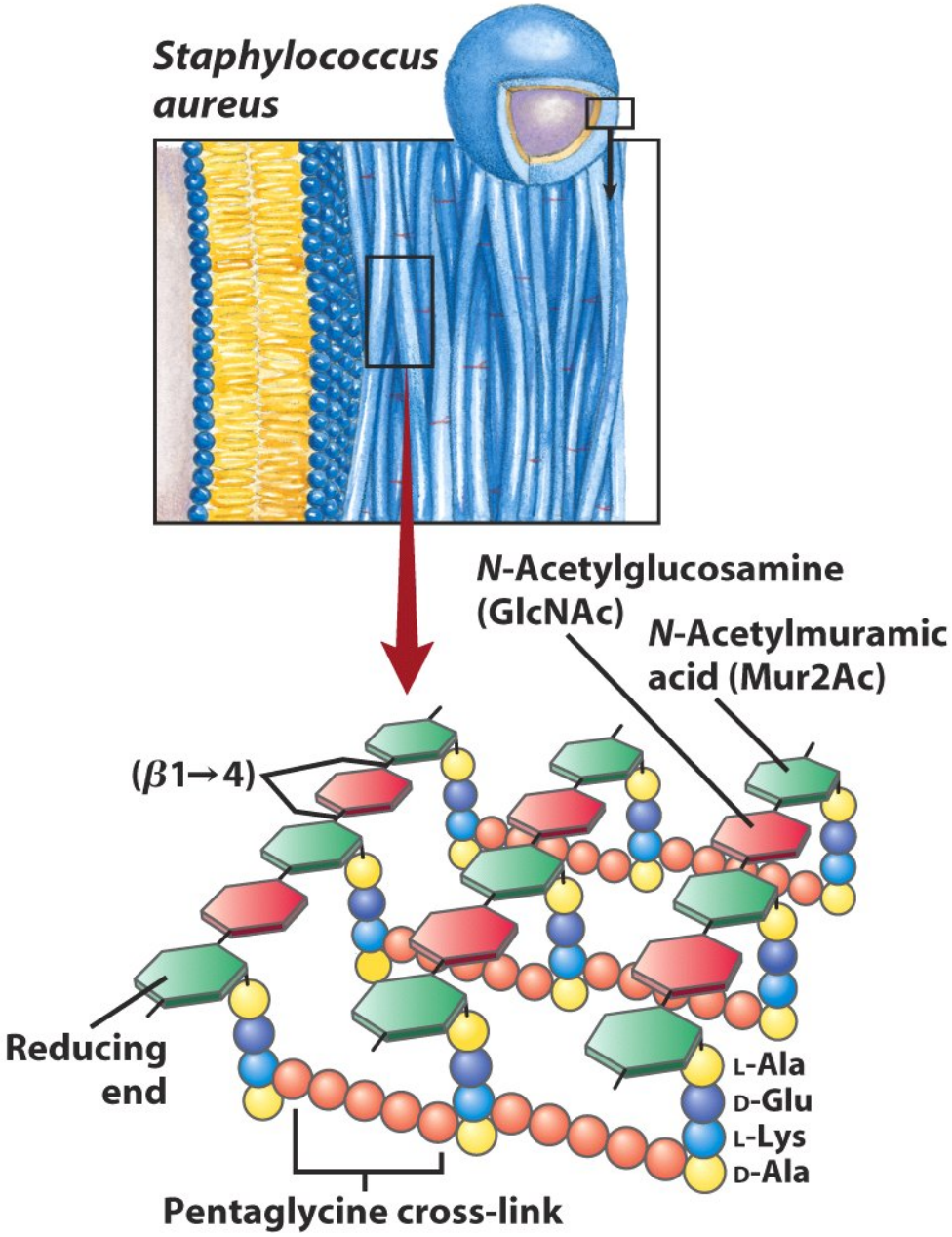
Regulation of Starch Biosynthesis



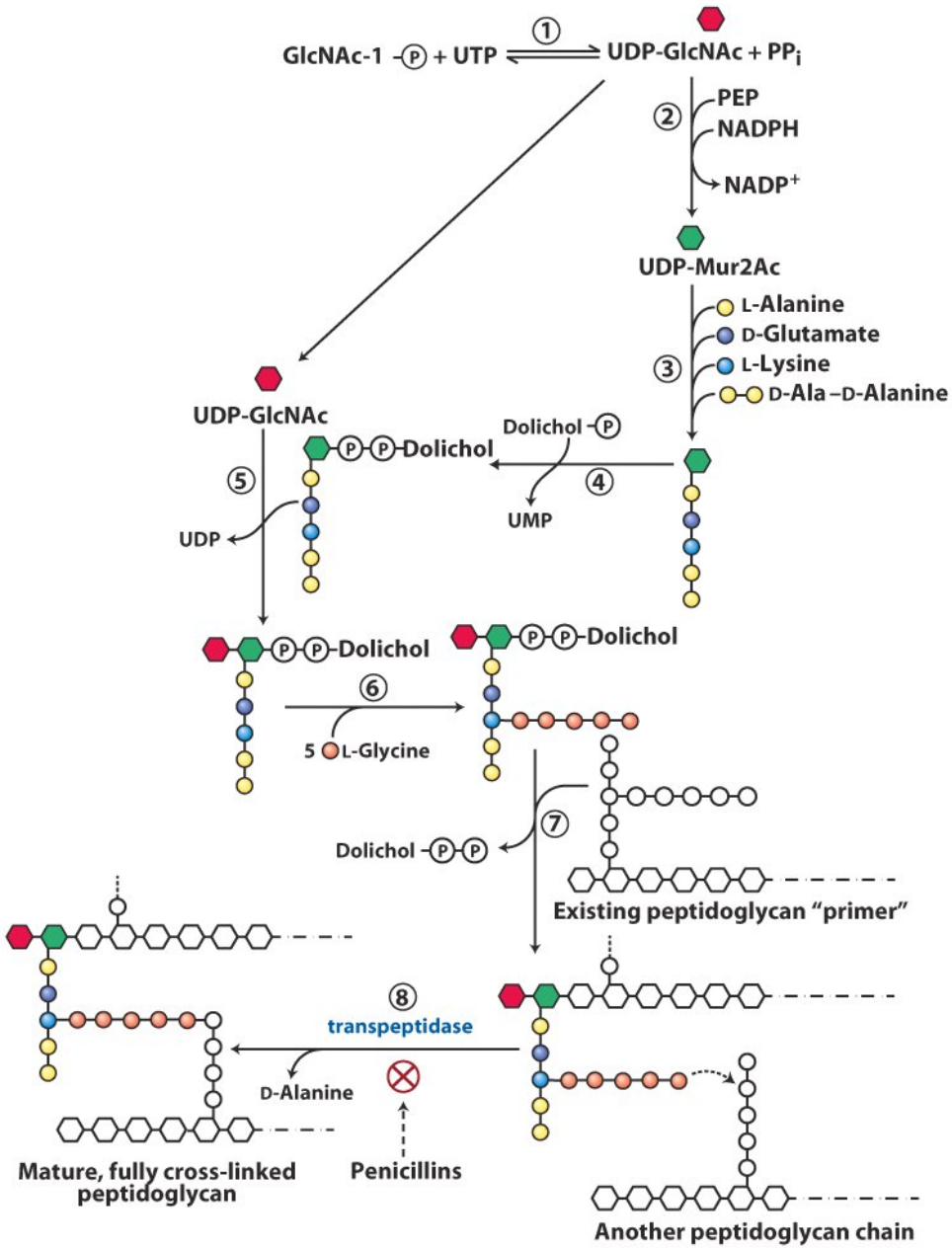
Plant Cell Wall

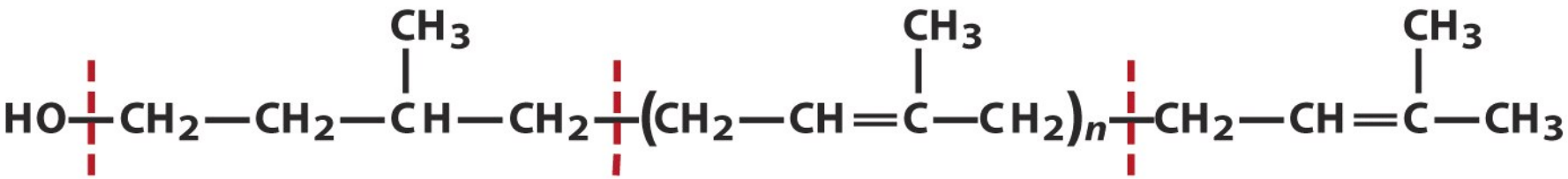
Cellulose




Staphylococcus aureus
N-Acetylglucosamine (GlcNAc)
N-Acetylmuramic acid (Mur2Ac)
(β1→4)
Reducing end
L-Ala
D-Glu
L-Lys
D-Ala
Pentaglycine cross-link

??? QuickTime?和 唯TIFF財　縛｜ 貢乾?縛｜ ? ?螃粟??畫蚓

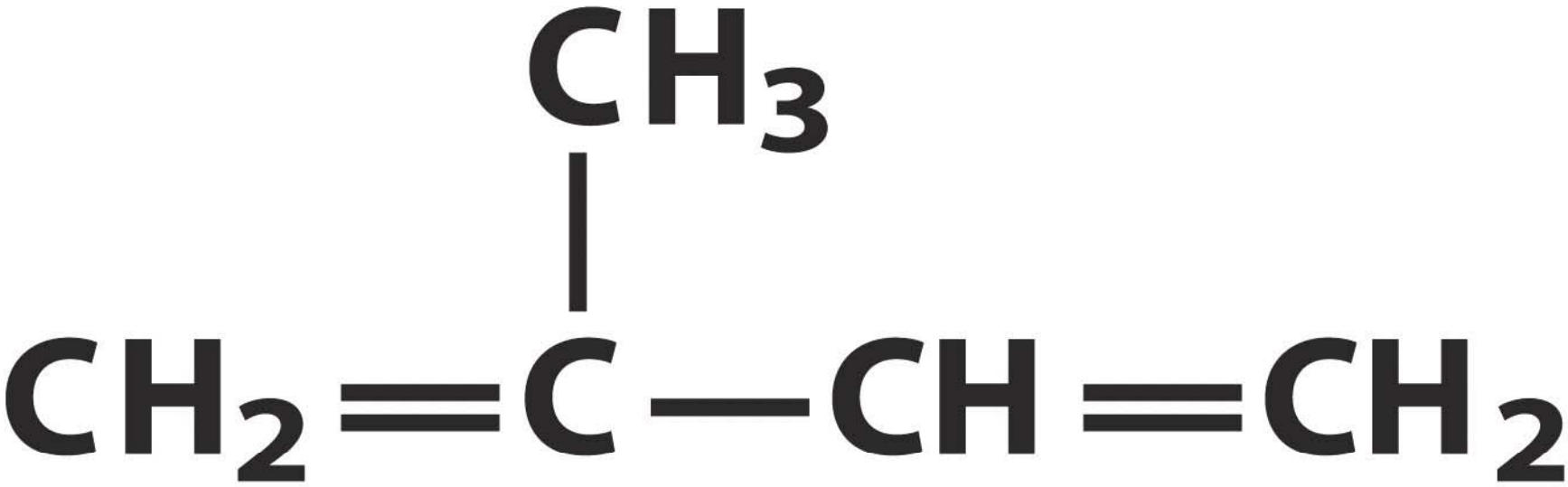

GlcNAc-1 -P + UTP
1
UDP-GlcNAc + PPi
2
PEP
NADPH
NADP+
UDP-Mur2Ac
3
L-Alanine
D-Glutamate
L-Lysine
D-Ala –D-Alanine
UDP-GlcNAc
Dolichol -P
P-P-Dolichol
4
UMP
5
UDP
P-P-Dolichol
P-P-Dolichol
6
5 L-Glycine
7
Dolichol -P-P
Existing peptidoglycan "primer"
8
transpeptidase
D-Alanine
Penicillins
Mature, fully cross-linked peptidoglycan
Another peptidoglycan chain



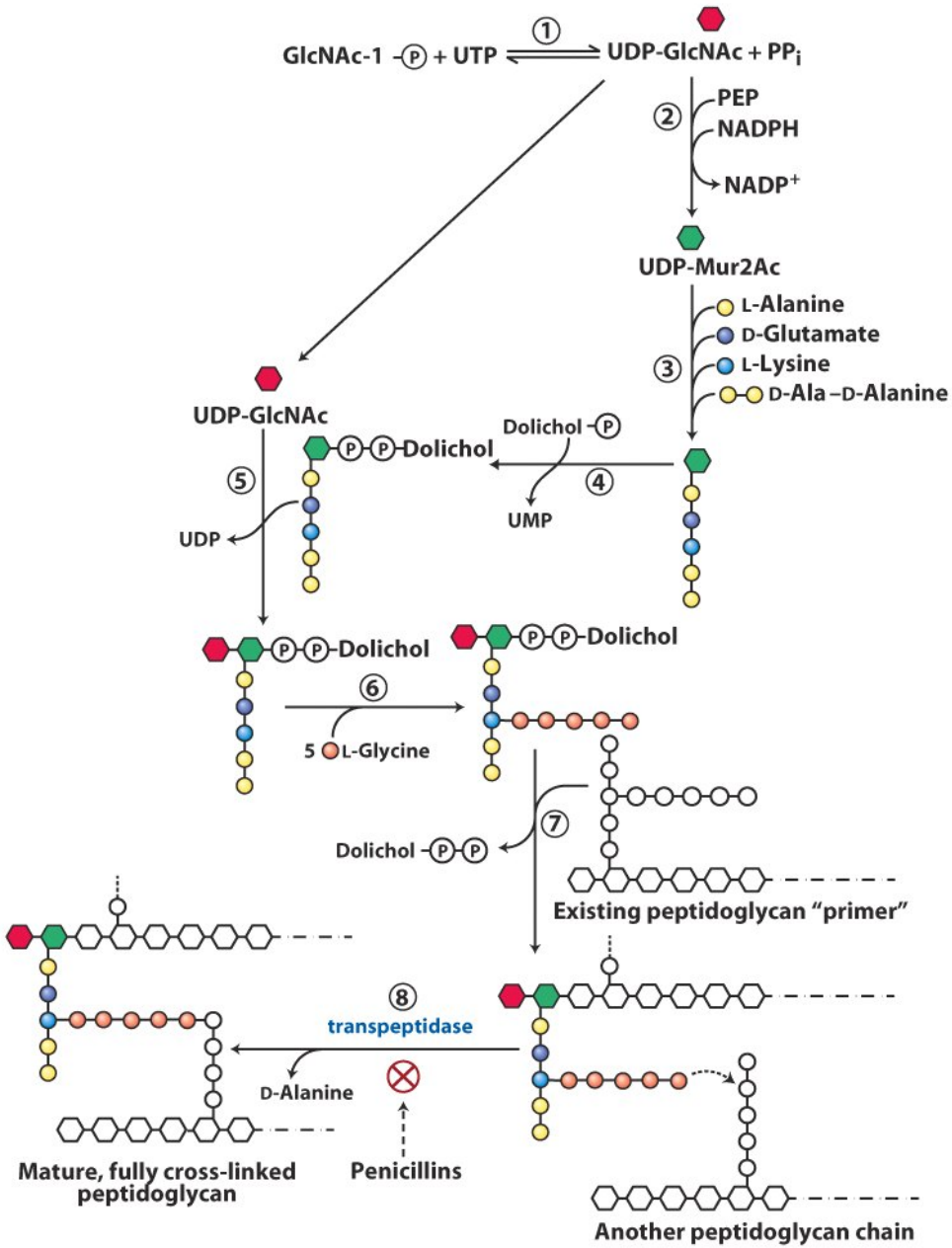
(f)

Dolichol: a sugar carrier

(n = 9 to 22)



Isoprene


GlcNAc-1 -P + UTP
1
UDP-GlcNAc + PPi
2
PEP
NADPH
NADP+
UDP-Mur2Ac
3
L-Alanine
D-Glutamate
L-Lysine
D-Ala –D-Alanine
UDP-GlcNAc
Dolichol -P
P-P-Dolichol
4
UMP
5
UDP
P-P-Dolichol
P-P-Dolichol
6
5 L-Glycine
7
Dolichol -P-P
Existing peptidoglycan "primer"
8
transpeptidase
D-Alanine
Penicillins
Mature, fully cross-linked peptidoglycan
Another peptidoglycan chain

The process that penicillins' action take places

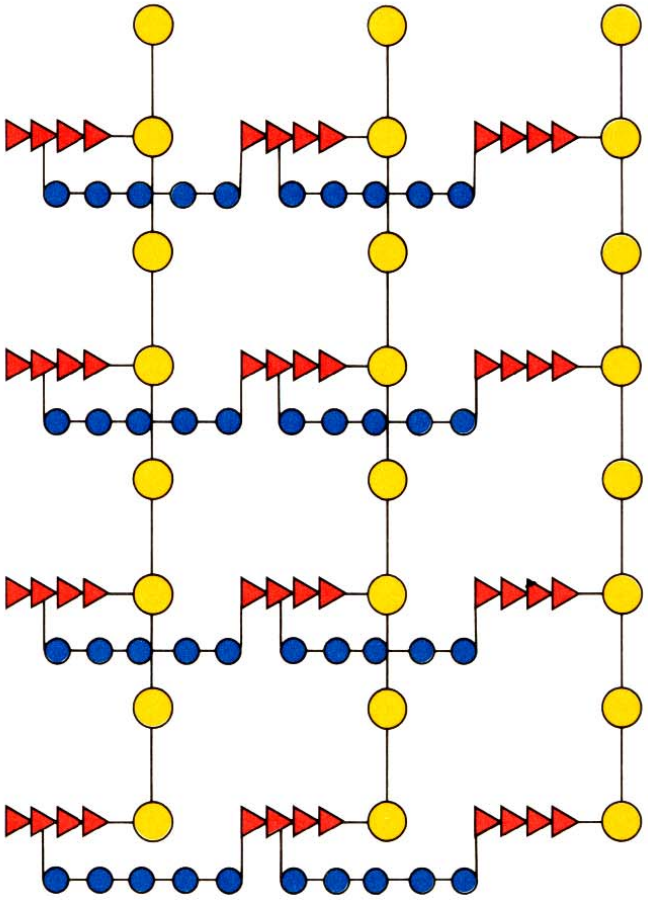
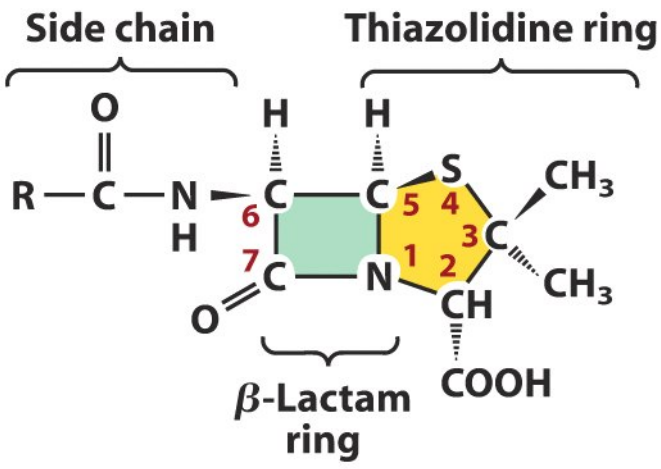
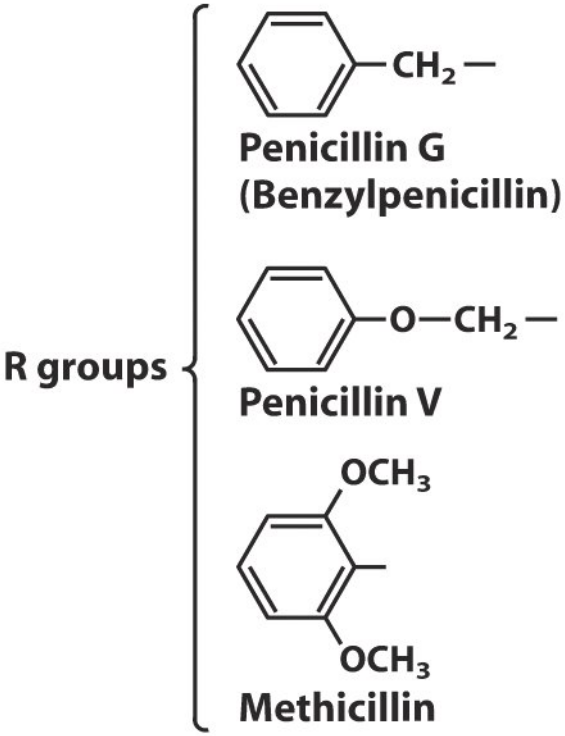


Figure 8-29
Schematic diagram of the peptidoglycan in *Staphylococcus aureus*. The sugars are shown in yellow, the tetrapeptides in red, and the pentaglycine bridges in blue. The cell wall is a single, enormous bag-shaped macromolecule because of extensive cross-linking.



General structure of penicillins



The Natural Affinity Label: Penicillins
Mechanism-base (Suicide) Enzyme Inhibitor

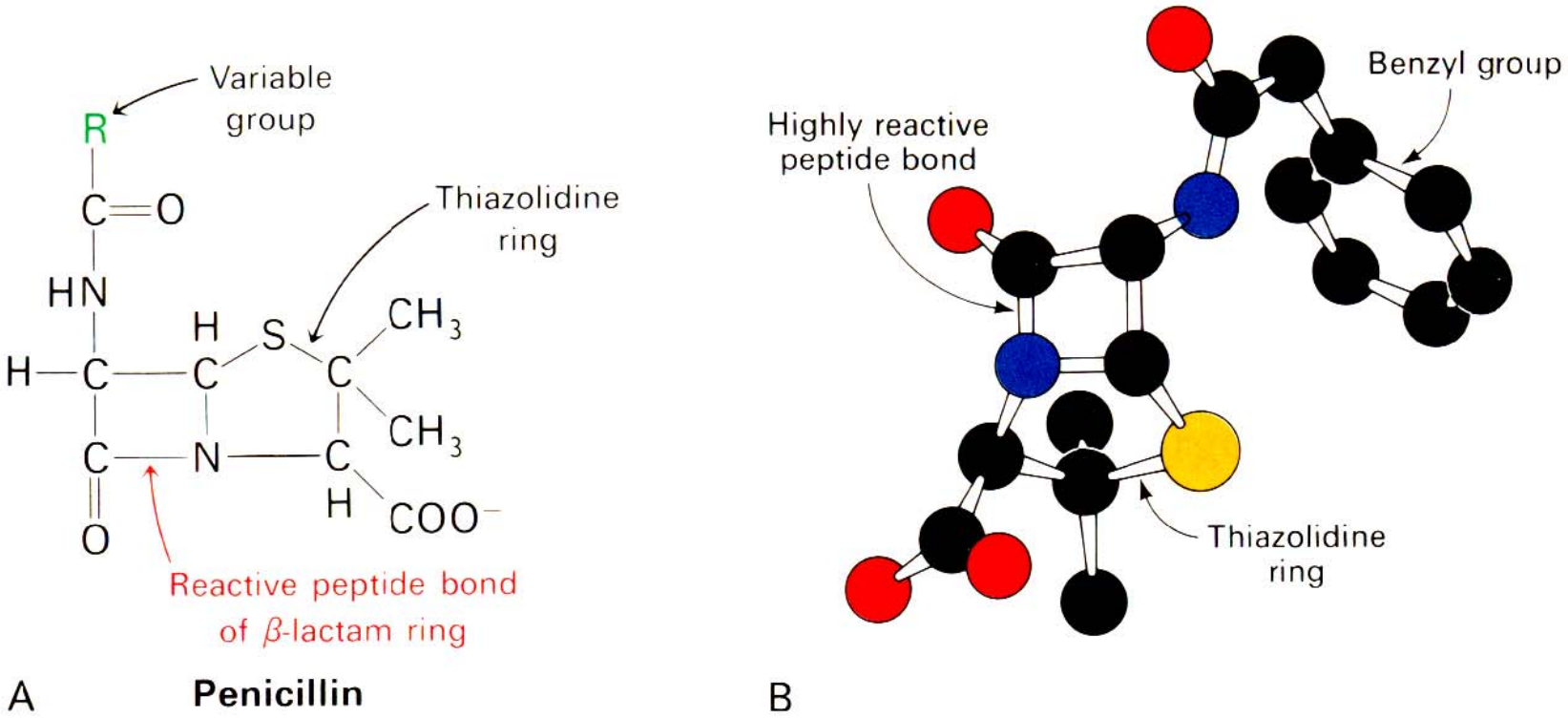
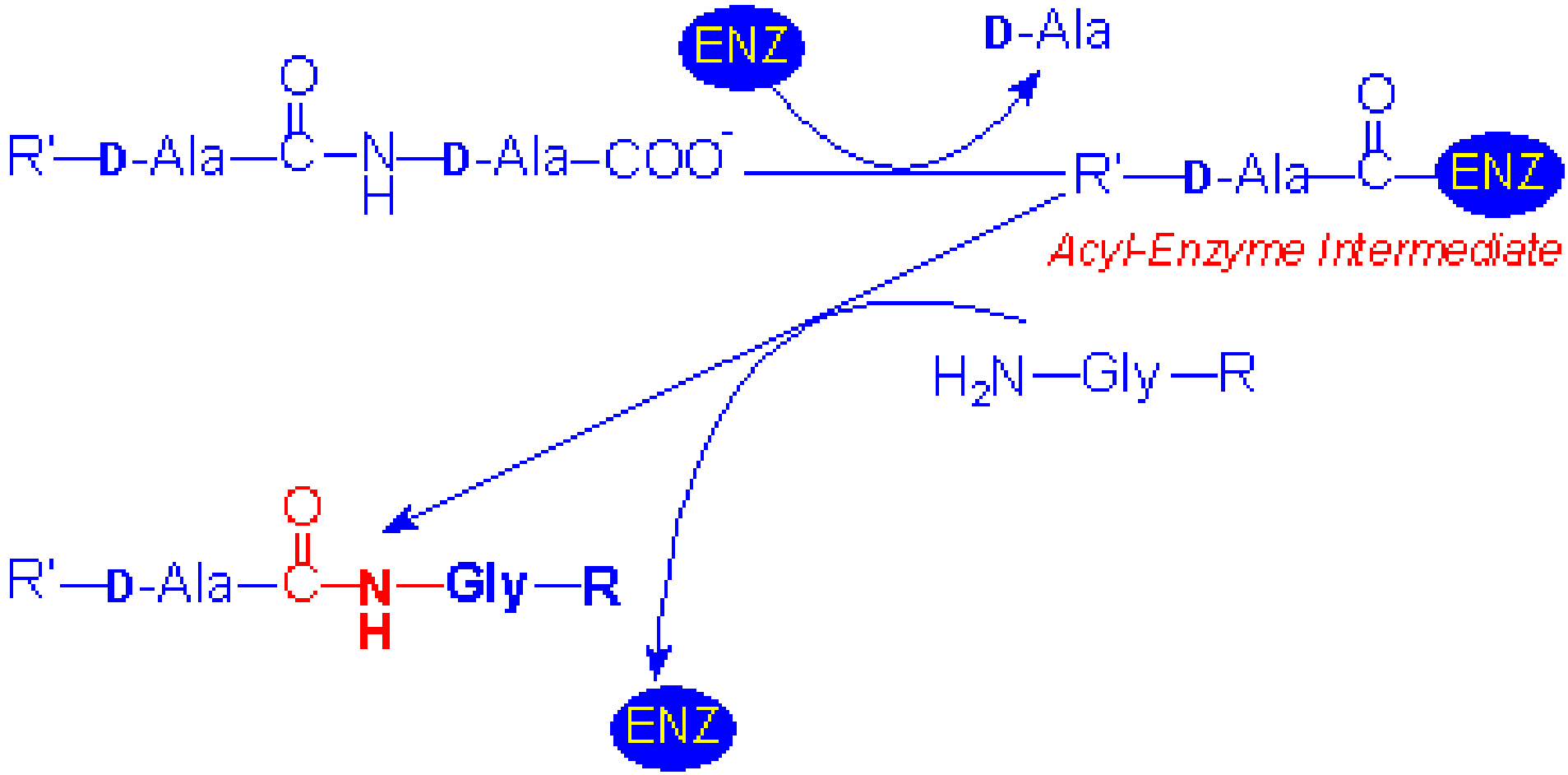
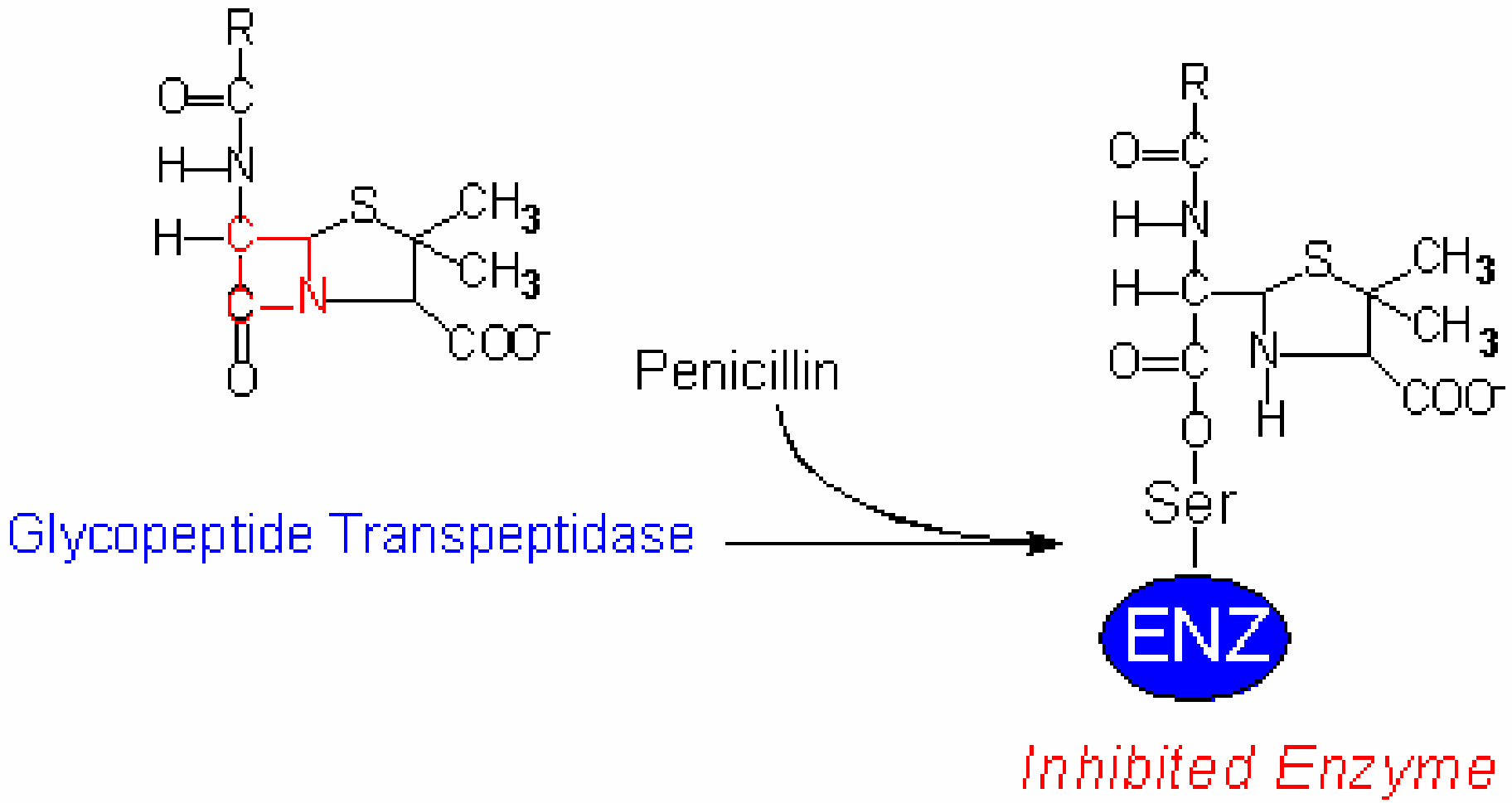


Figure 8-28
(A) Structural formula of penicillin and (B) model of benzyl penicillin. The reactive site of penicillin is the peptide bond of its β-lactam ring.

Penicillin Inhibits Bacterial Peptidoglycan Synthesis



Penicillin mimics the D-Ala D-Ala structure. Penicillin has a four-membered lactam ring which is strained, making it highly reactive. The conformation of this part of Penicillin is similar to that of the transition state of the substrate, a species that interacts with the enzyme strongly.



Similarity of Penicillin with the Transition-State of the Substrate of Glycopeptide Transpeptidase

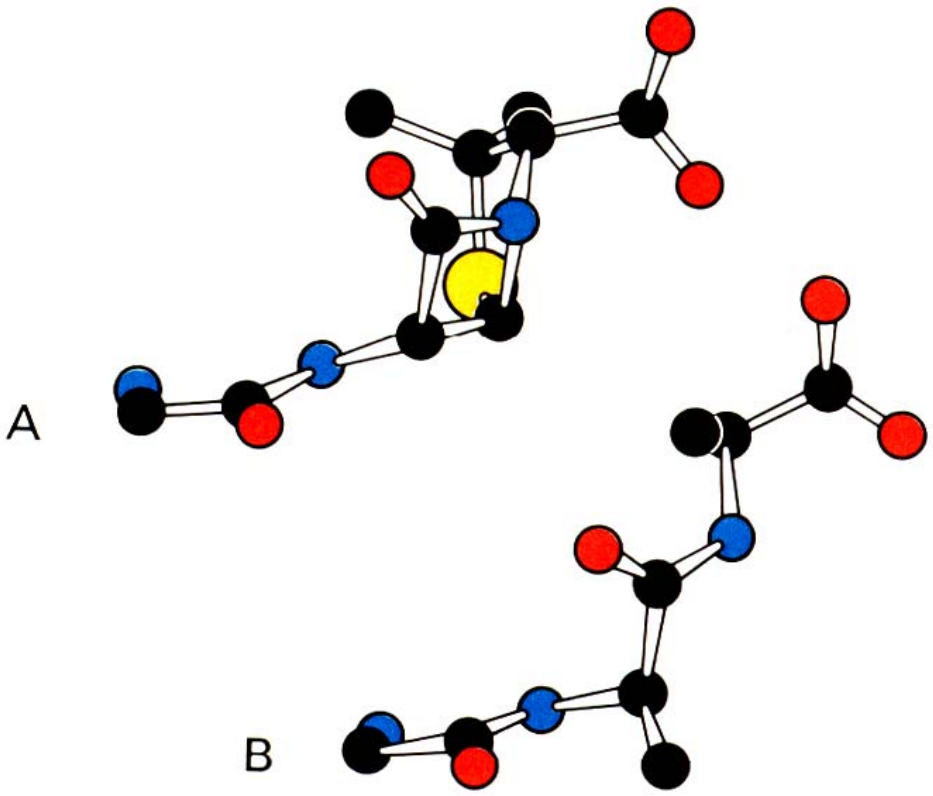
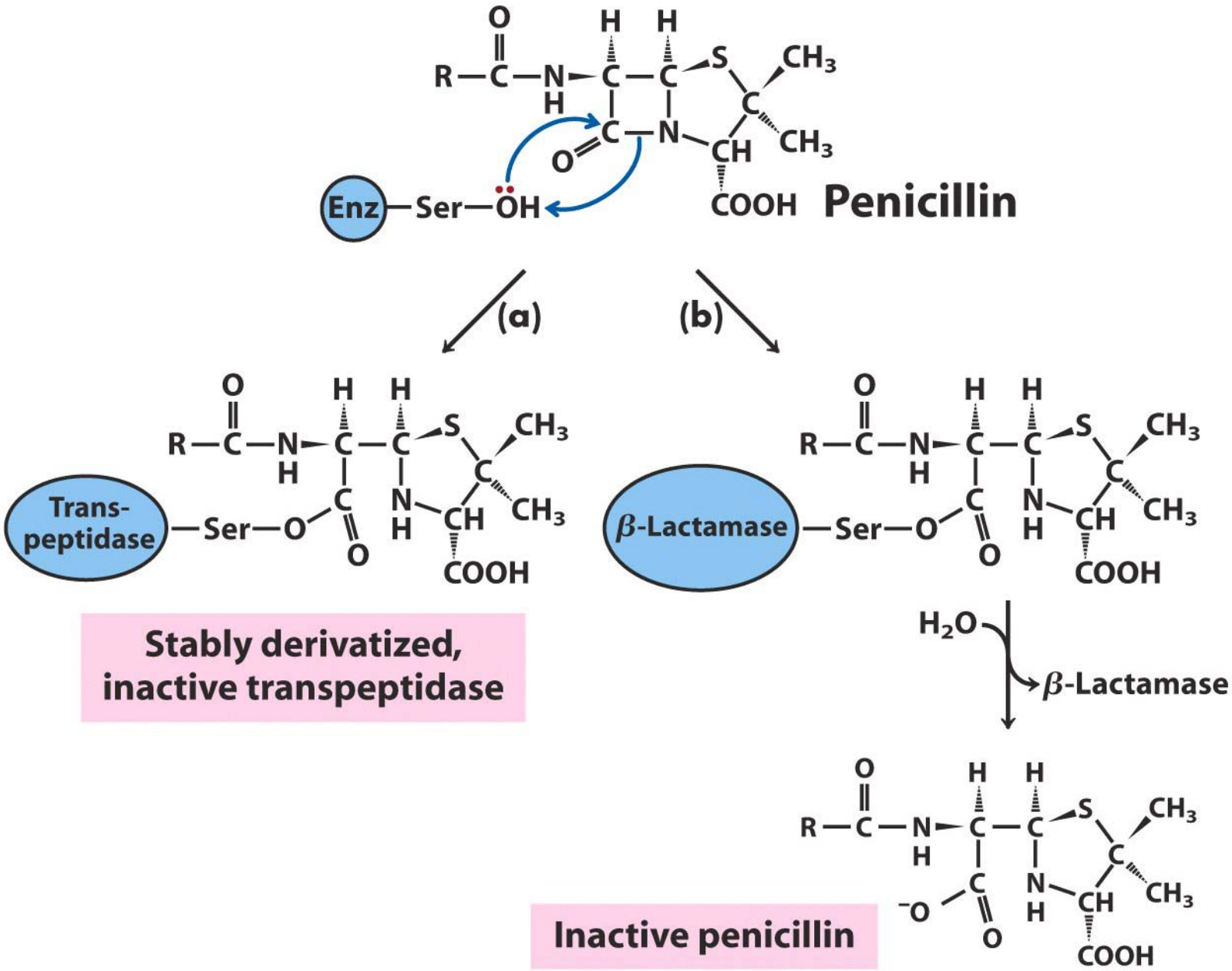
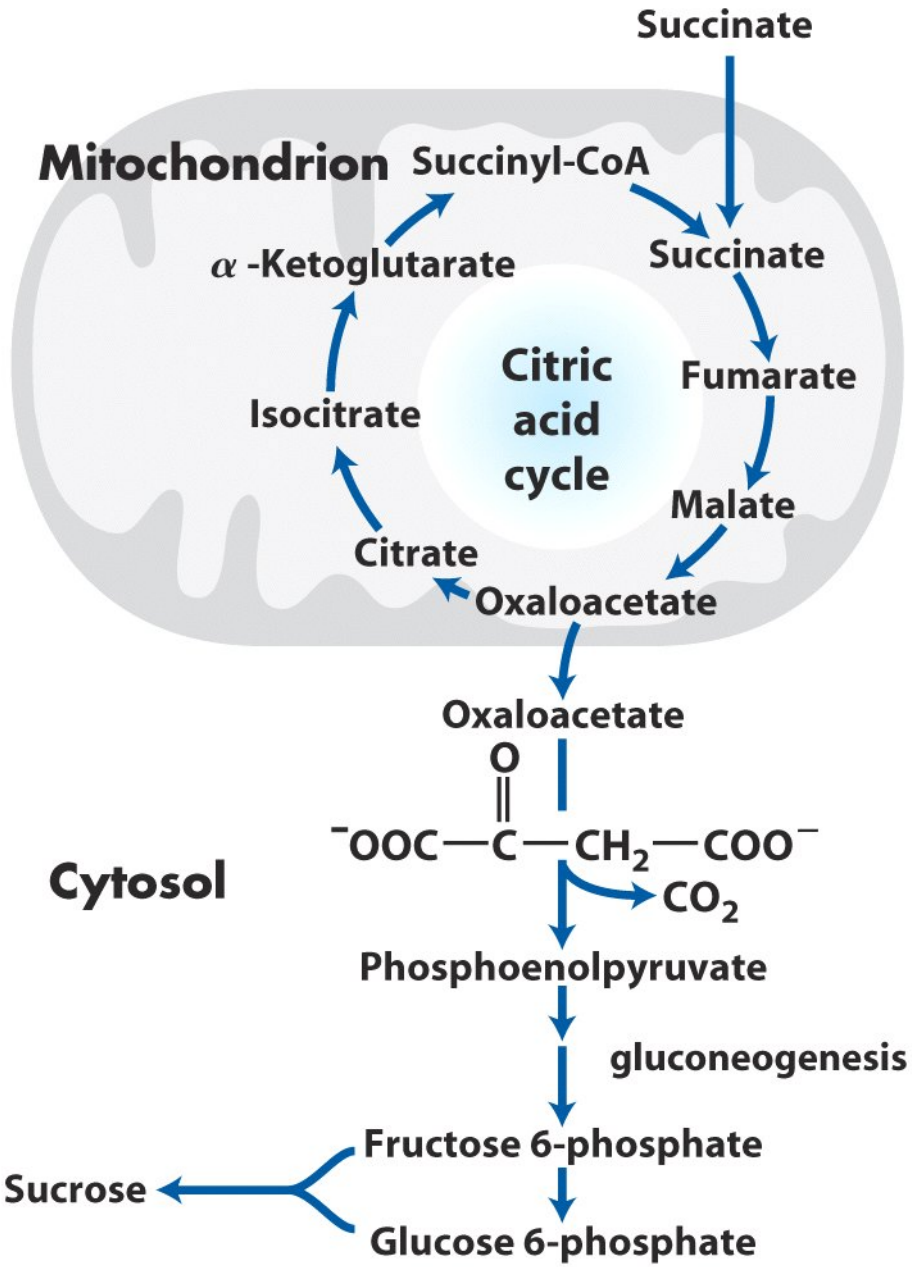


Figure 8-33
The conformation of penicillin in the vicinity of its reactive peptide bond (A) resembles the postulated conformation of the transition state of R–D-Ala–D-Ala (B) in the transpeptidation reaction. [After B. Lee. *J. Mol. Biol.* 61(1971):464.]


Penicillin
Enz
Ser
OH
(a)
(b)
Trans-
peptidase
β-Lactamase
Stably derivatized,
inactive transpeptidase
H2O
β-Lactamase
Inactive penicillin


Succinate
Mitochondrion
Succinyl-CoA
α -Ketoglutarate
Succinate
Citric acid cycle
Fumarate
Isocitrate
Malate
Citrate
Oxaloacetate
Oxaloacetate
O
⁻OOC—C—CH₂—COO⁻
Cytosol
CO₂
Phosphoenolpyruvate
gluconeogenesis
Fructose 6-phosphate
Sucrose
Glucose 6-phosphate