Lecture 7 - The Calvin Cycle and the Pentose Phosphate Pathway

Chem 454: Regulatory Mechanisms in Biochemistry
University of Wisconsin-Eau Claire

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Introduction

The Calvin cycle

- The dark reactions of photosynthesis in green plants
- Reduces carbon from CO2 to hexose (C6H12O6)
- Requires ATP for free energy and NADPH as a reducing agent.

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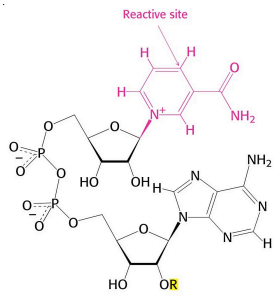
Introduction

NADH versus NADPH



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Introduction

The Pentose Phosphate Pathway

- Used in all organisms
- Glucose is oxidized and decarboxylated to produce reduced NADPH
- Used for the synthesis and degradation of pentoses
- Shares reactions with the Calvin cycle

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1. The Calvin Cycle

Source of carbon is CO2

Takes place in the stroma of the chloroplasts

Comprises three stages

- Fixation of CO2 by ribulose 1,5-bisphosphate to form two 3-phosphoglycerate molecules
- Reduction of 3-phosphoglycerate to produce hexose sugars
- Regeneration of ribulose 1,5-bisphosphate

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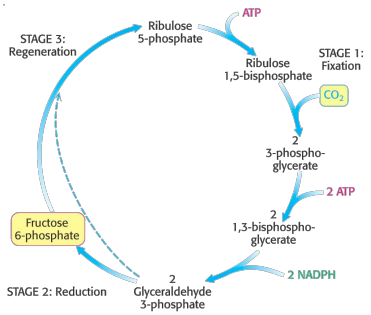
1. Calvin Cycle

Three stages



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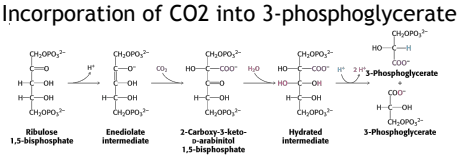
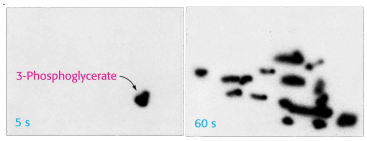
1.1 Stage I: Fixation

Incorporation of CO2 into 3-phosphoglycerate





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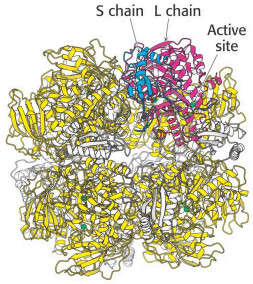
1.1 Stage I: Fixation

Rubisco: Ribulose 1,5-bisphosphate carboxylase/ oxygenase



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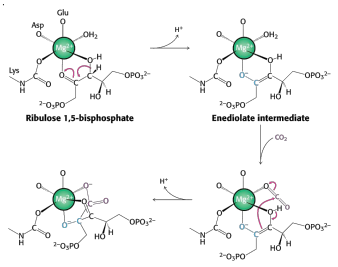
1.1 Stage I: Fixation

Active site contains a divalent metal ion



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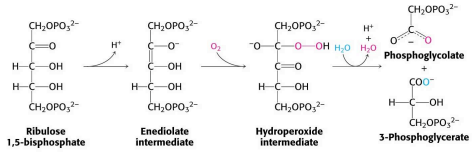
1.2 Rubisco Oxygenase Activity

Rubisco also catalyzes a wasteful oxygenase reaction:



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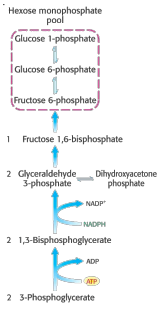
1.3 State II: Formation of Hexoses

Reactions similar to those of gluconeogenesis

- But they take place in the chloroplasts
- And use NADPH instead of NADH



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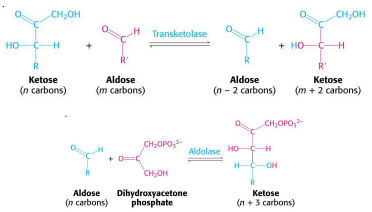
1.3 State III: Regeneration of Ribulose 1,5-Bisphosphosphate

Involves a sequence of transketolase and aldolase reactions.



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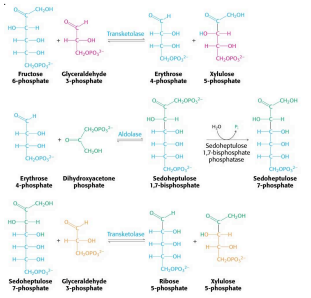
1.3 State III: Regeneration of Ribulose 1,5-Bisphosphophosphate



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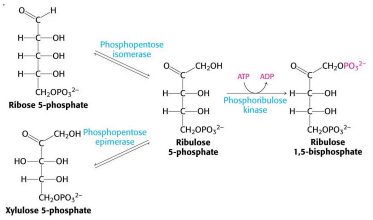
1.3 State III: Regeneration of Ribulose 1,5-Bisphosphophosphate

The resulting ribose 5-phosphate and xylulose 5-phosphate are converted to ribulose 5-phosphate by an *isomerase* and an *epimerase*



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1.3 State III: Regeneration of Ribulose 1,5-Bisphosphophosphate

The net reaction for stage III

Fructose 6-phosphate + 2 glyceraldehyde 3-phosphate
+ dihydroxyacetone phosphate + 3ATP + H_2O ⟶
3 ribulose 1,5-bisphosphate + 3 ADP + Pi

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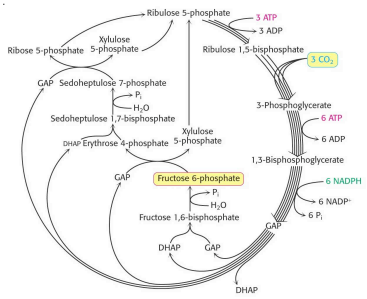
1.3 The Calvin Cycle



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1.4 Balance Reaction for Calvin Cycle

Net Balanced Reaction

$$6\ CO_2 + 18\ ATP + 12\ NADPH + 12\ H_2O \longrightarrow$$
$$C_6H_{12}O_6 + 18\ ADP + 18\ Pi + 12\ NADP^+ + 6\ H^+$$

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3. The Pentose Phosphate Pathway

Pathway is used to serve the NADPH needs of all organisms

$$Glucose + 2\ NADP^+ + H_2O \longrightarrow$$
$$ribose\ 5\text{-}phosphate + 2\ NADPH + 2\ H^+ + CO_2$$

It also provides a source of five carbon sugars

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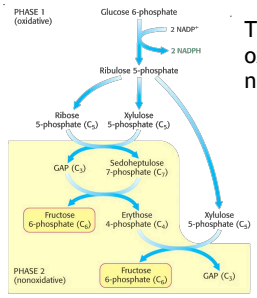
3. The Pentose Phosphate Pathway



There is an oxidative and nonoxidative phase.

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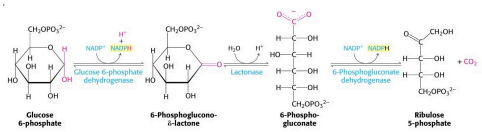
3. Phase 1 of The Pentose Phosphate Pathway

There oxidative phase



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3.2 Phase 2
The Pentose Phosphate Pathway

The pentose phosphate pathway and glycolysis are linked by transketolase and transaldolase

- When the need for NADPH is greater than the need for ribose 5-phosphate, the ribose 5-phosphate is converted into the glycolytic intermediates glyceraldehyde 3-phosphate and fructose 6-phosphate

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3.2 Phase 2
The Pentose Phosphate Pathway

The pentose phosphate pathway and glycolysis are linked by transketolase and transaldolase

$C_5 + C_5 \xrightarrow{\text{transketolase}} C_3 + C_7$

$C_3 + C_7 \xrightarrow{\text{transaldolase}} C_6 + C_4$

$C_4 + C_5 \xrightarrow{\text{transketolase}} C_6 + C_3$

$C_5 + C_5 + C_5 \longrightarrow C_6 + C_6 + C_3$

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3.2 Phase 2
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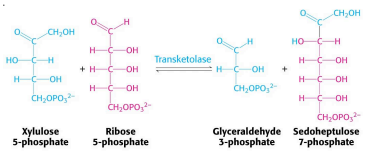

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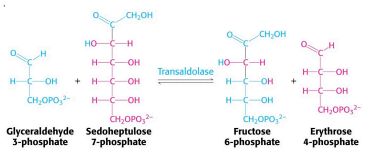

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3.2 Phase 2
The Pentose Phosphate Pathway

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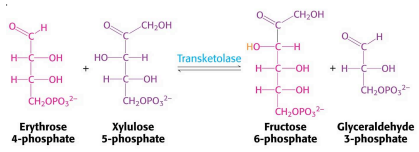

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3.2 The Pentose Phosphate Pathway

TABLE 20.3 Pentose phosphate pathway

Reaction	Enzyme
Oxidative phase	
Glucose 6-phosphate + $NADP^+$ ⟶ 6-phosphoglucono-δ-lactone + NADPH + H^+	Glucose 6-phosphate dehydrogenase
6-Phosphoglucono-δ-lactone + H_2O ⟶ 6-phosphogluconate + H^+	Lactonase
6-Phosphogluconate + $NADP^+$ ⟶ ribulose 5-phosphate + CO_2 + NADPH	6-Phosphogluconate dehydrogenase
Nonoxidative Phase	
Ribulose 5-phosphate ⟺ ribose 5-phosphate	Phosphopentose isomerase
Ribulose 5-phosphate ⟺ xylulose 5-phosphate	Phosphopentose epimerase
Xylulose 5-phosphate + ribose 5-phosphate ⟺ sedoheptulose 7-phosphate + glyceraldehyde 3-phosphate	Transketolase
Sedoheptulose 7-phosphate + glyceraldehyde 3-phosphate ⟺ fructose 6-phosphate + erythrose 4-phosphate	Transaldolase
Xylulose 5-phosphate + erythrose 4-phosphate ⟺ fructose 6-phosphate + glyceraldehyde 3-phosphate	Transketolase

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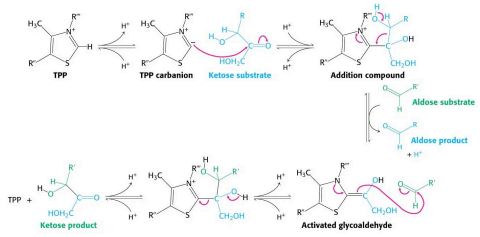
3.3 Transketolase Mechanism



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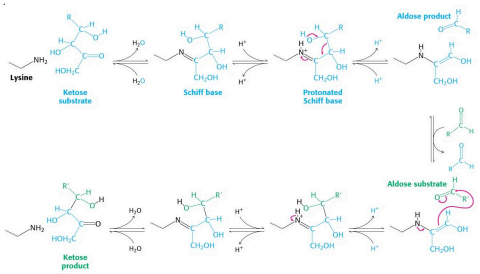
3.3 Transaldolase Mechanism



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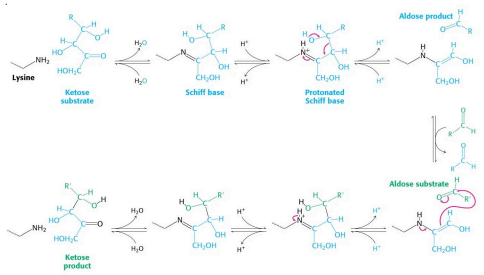
3.3 Transaldolase Mechanism



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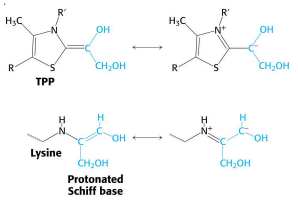
3.3 Transketoase and Transaldolase Mechanisms

Both mechanisms stabilize the carbanion intermediate



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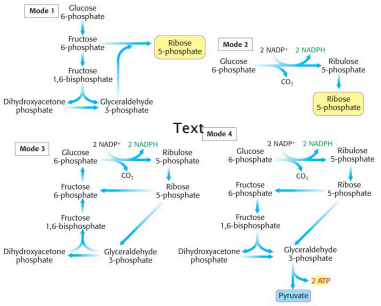
4. Coordination with Glycolysis



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