Respiration and Lipid Metabolism

Chapter 11

OrR

PHOTOSYNTHESIS PROVIDES the organic building blocks that plants depend on.

Respiration, with its associated carbon metabolism, releases the energy stored in carbon compounds in a controlled manner for cellular use.

At the same time it generates many carbon precursors for biosynthesis.

Aerobic respiration is the biological process by which reduced organic compounds are mobilized and subsequently oxidized in a controlled manner.

During respiration, free energy is released and transiently stored in a compound, ATP, which can be readily utilized for the maintenance and development of the plant.

Though aerobic respiration is similar for all eukaryotic organisms, **some specific aspects of plant respiration distinguish it from its animal counterpart**.

Glucose is most commonly cited as the substrate for respiration.

However, in a functioning **plant cell** the reduced carbon is derived from sources such as the disaccharide sucrose, hexose phosphates and triose phosphates from starch degradation and photosynthesis, fructose-containing polymers (fructans), and other sugars, **as well as lipids (primarily triacylglycerols), organic acids**, and on occasion, proteins
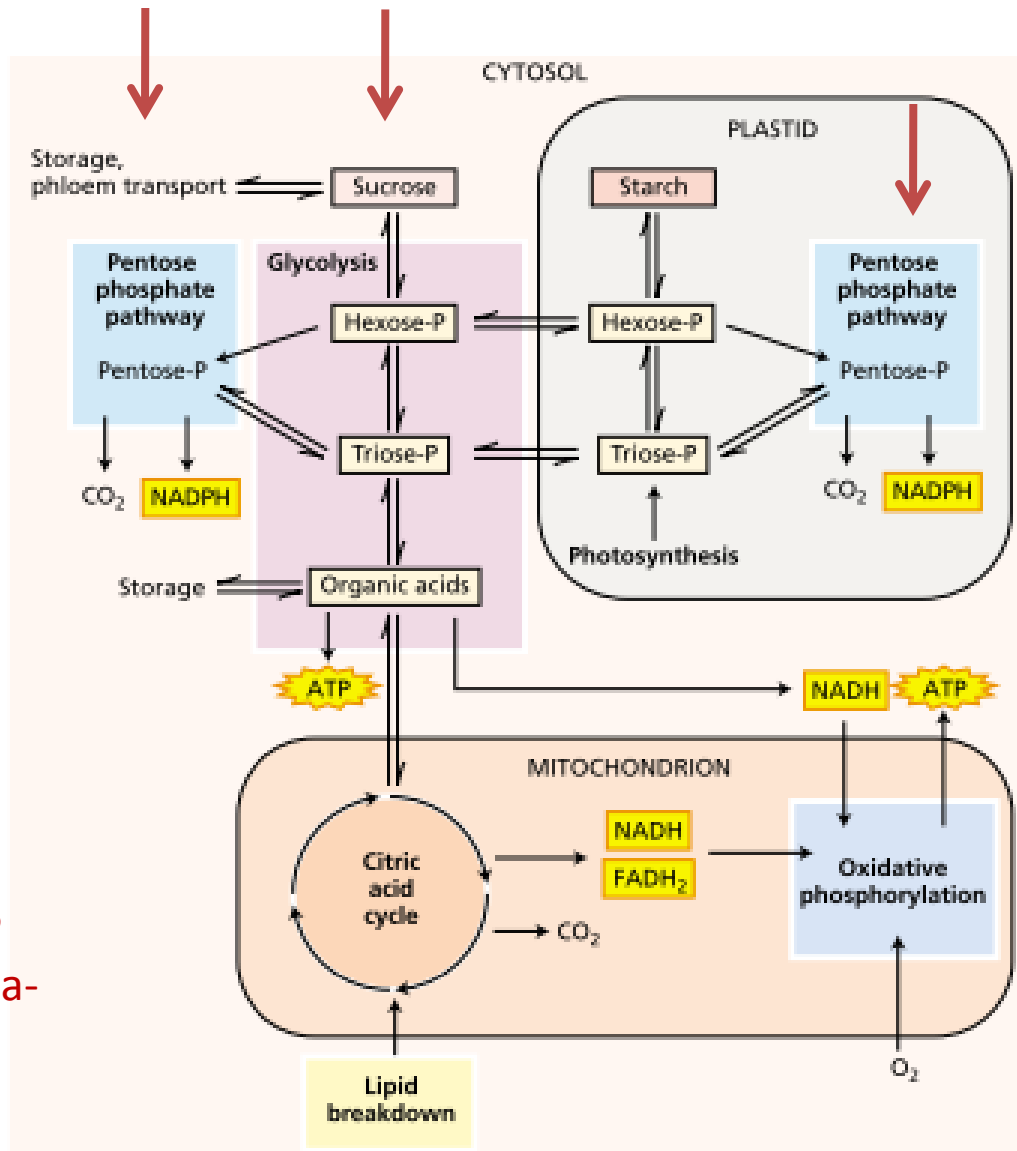
OVERVIEW OF PLANT RESPIRATION

Substrates for respiration are generated by other cellular processes and enter the respiratory pathways.

Glycolysis and **the pentose phosphate pathways** in the cytosol and plastid convert sugars to organic acids, via hexose phosphates and triose phosphates, generating NADH or NADPH and ATP.
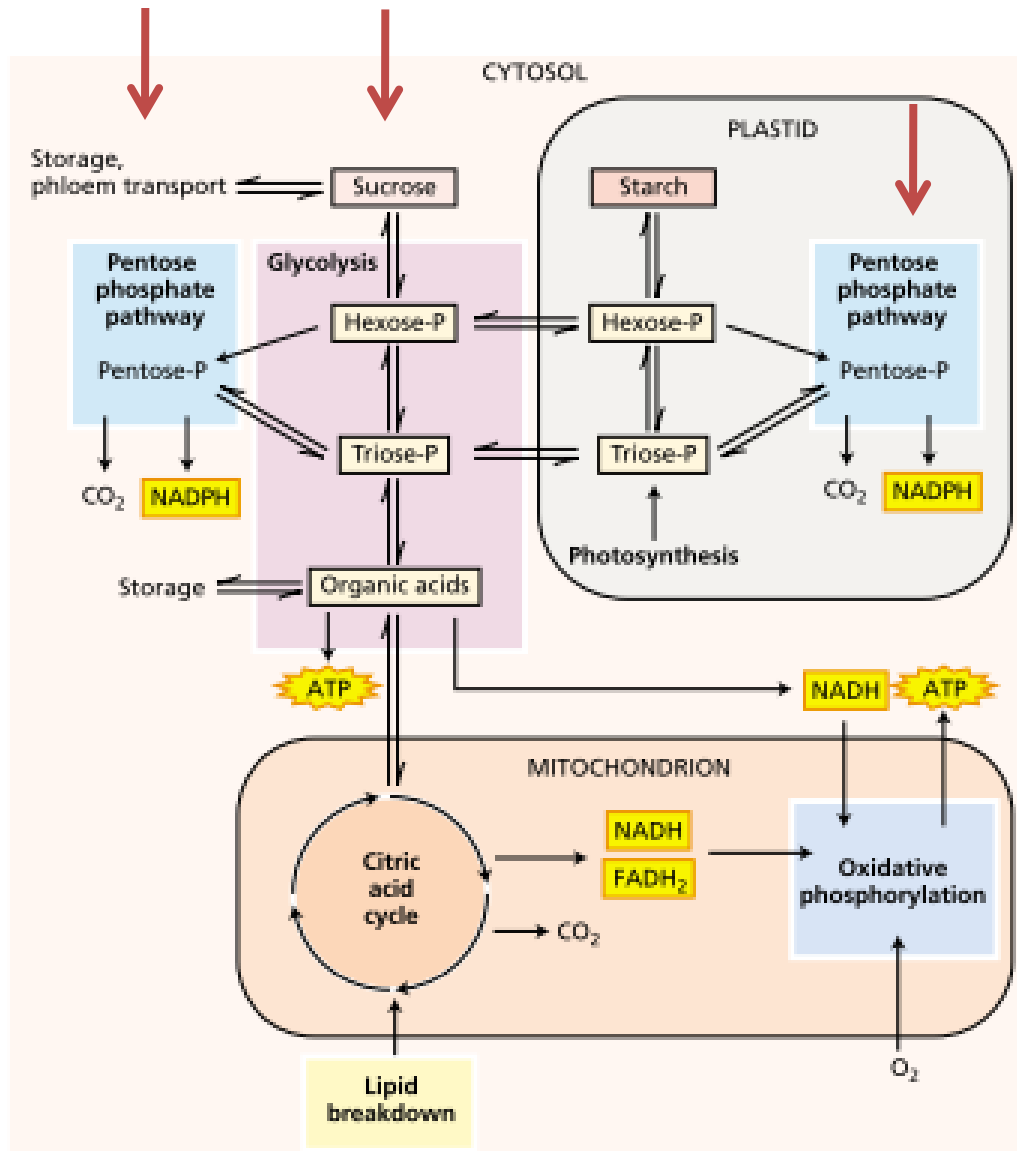
OVERVIEW OF PLANT RESPIRATION

The **organic acids** are oxidized in the mitochondrial citric acid cycle, and the NADH and FADH$_2$ produced provide the energy for ATP synthesis by the electron transport chain and ATP synthase in oxidative phosphorylation.
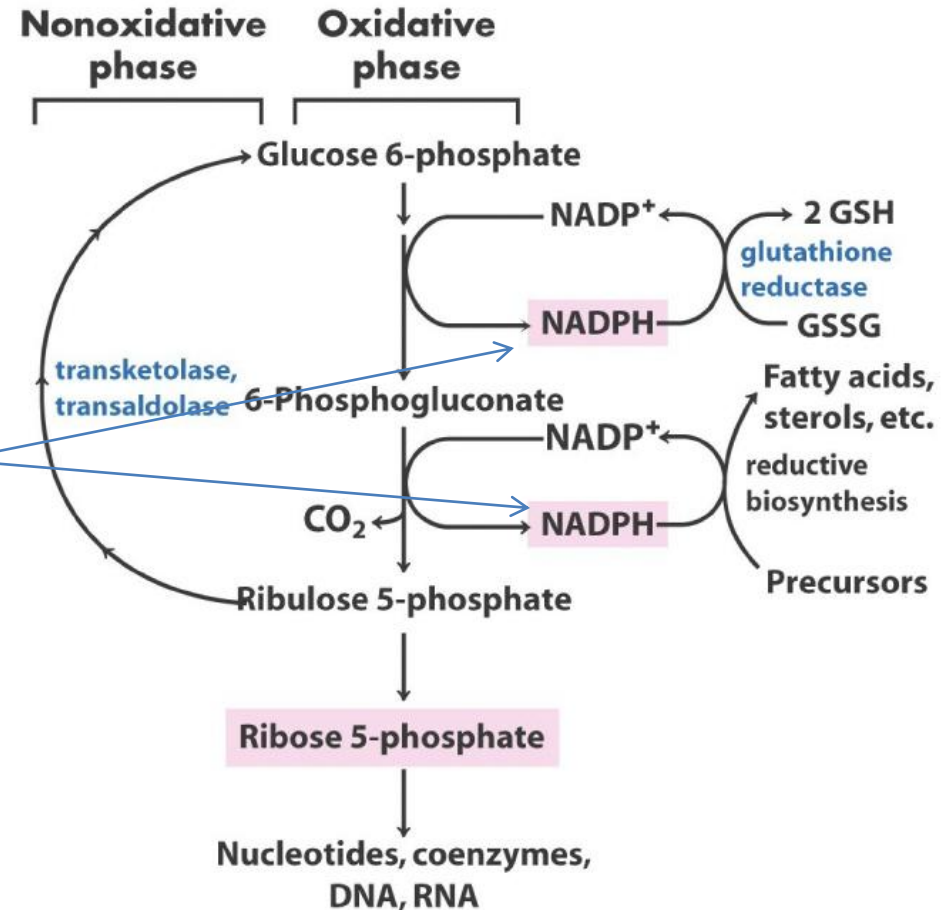
OVERVIEW OF PLANT RESPIRATION

- Self study in details

In the **pentose phosphate pathway**, also located both in the cytosol and the plastid:

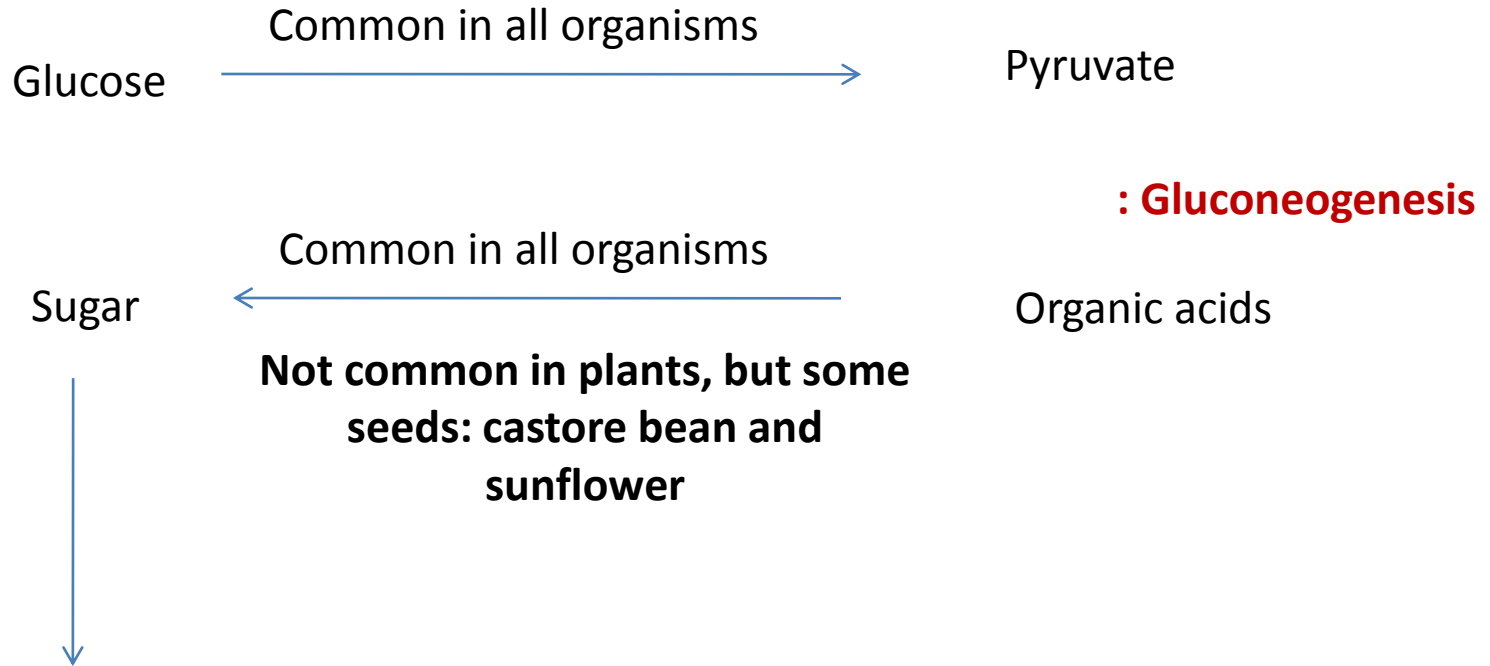the six-carbon glucose-6-phosphate is initially oxidized to the five-carbon ribulose-5-phosphate.

The carbon is lost as CO_2, and reducing power is conserved in the form of two molecules of another reduced pyridine nucleotide, NADPH.

In the following near-equilibrium reactions, ribulose-5-phosphate is converted into three- to seven-carbon sugars.

GLYCOLYSIS: A CYTOSOLIC AND PLASTIDIC PROCESS

Glycolysis:

Glucose → Common in all organisms → Pyruvate

: Gluconeogenesis

Sugar ← Common in all organisms ← Organic acids

**Not common in plants, but some seeds: castore bean and sunflower**

store a significant quantity of their carbon reserves in the form of oils (triacylglycerols)

After the seed germinates, much of the oil is converted by gluconeogene sis to sucrose, which is then used to support the growing seedling.

In the initial phase of glycolysis, gluconeogenesis overlaps with the pathway for synthesis of sucrose from photosynthetic triose phosphate

ATP-dependent phosphofructokinase is essentially irreversible

An additional enzyme, fructose-1,6-bis-phosphatase, converts fructose-1,6-bisphosphate to fructose-6-phosphate and P_i during gluconeogenesis
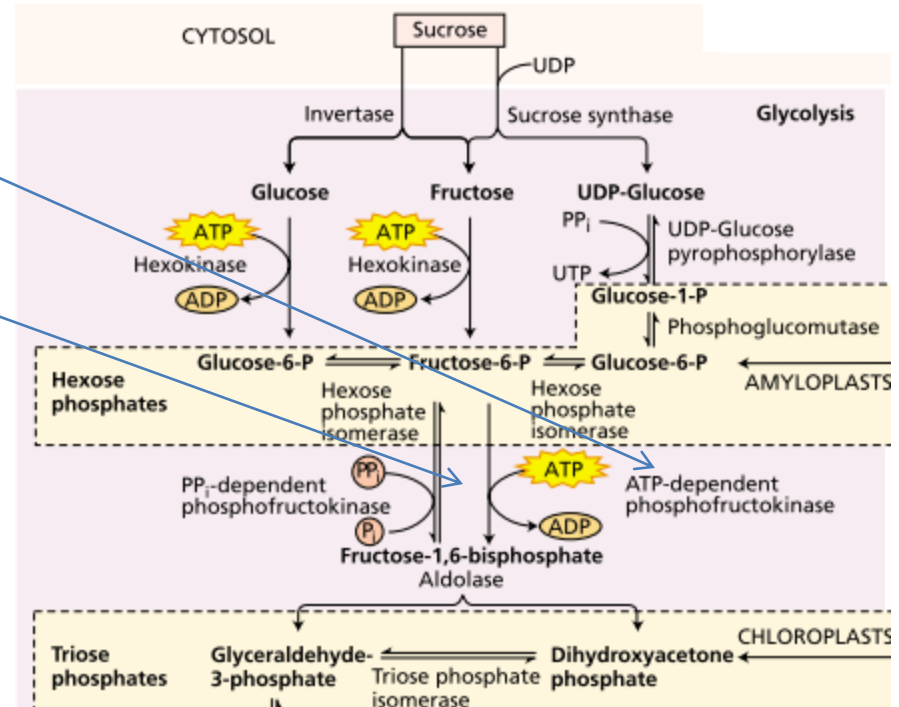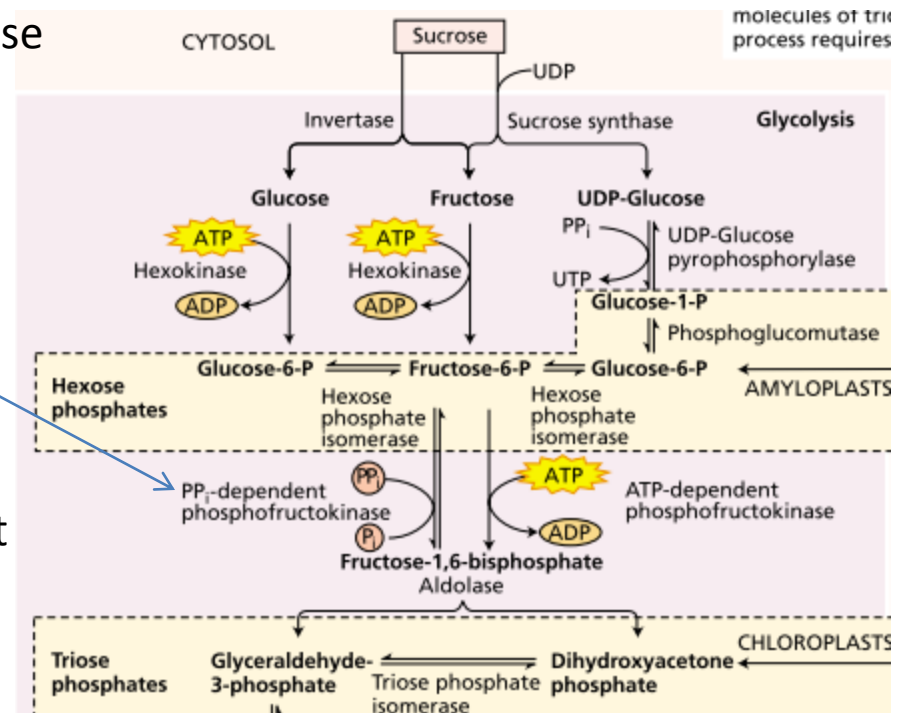

ATP-dependent phosphofructokinase and fructose-1,6-bisphosphatase represent a major control point of carbon flux through the glycolytic/gluconeogenic pathways in both plants and animals, as well as in sucrose synthesis in plants

In plant a PP_i-dependent phosphofructokinase (pyrophosphate:fructose-6-phosphate 1-phosphotransferase), which catalyzes the following reversible reaction
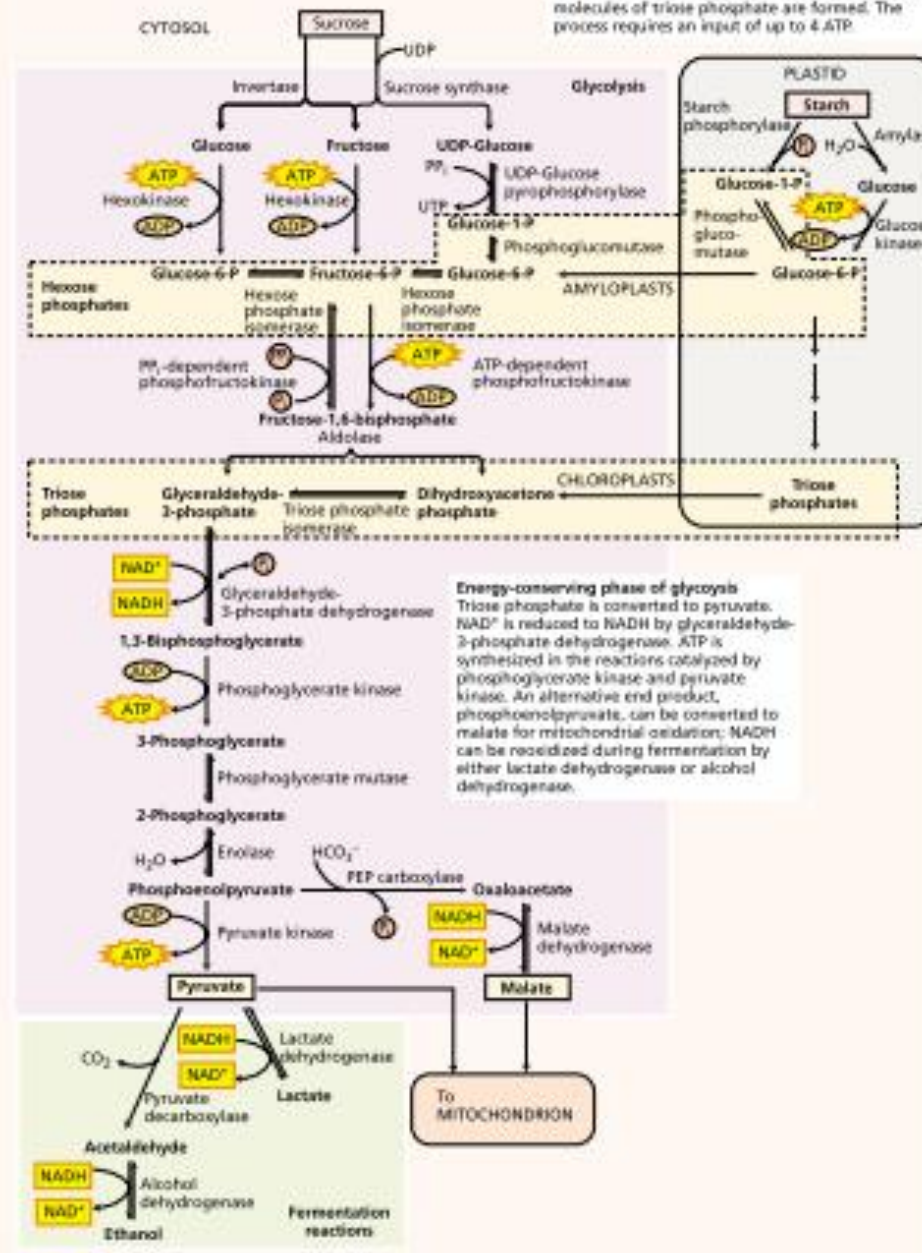
$$\text{Fructose-6-P} + PP_i \leftrightarrow \text{fructose-1,6-P}_2 + P_i$$

The reaction catalyzed by the PPi-dependent phospho-fructokinase is readily reversible, but it is unlikely to operate in sucrose synthesis

(A)

CYTOSOL

Sucrose

UDP

Invertase   Sucrose synthase   **Glycolysis**

PLASTID

Starch phosphorylase   Starch   Amylase

P_i H_2O

Glucose   Fructose   UDP-Glucose

ATP   ATP PP_i UDP-Glucose pyrophosphorylase

Hexokinase   Hexokinase   UTP

ADP   ADP   Glucose-1-P   Phosphoglucomutase

Glucose-1-P   Glucose

ATP   Glucose kinase

Phospho-gluco-mutase   ADP

Glucose-6-P   Fructose-6-P   Glucose-6-P   AMYLOPLASTS   Glucose-6-P

Hexose phosphates

Hexose phosphate isomerase   Hexose phosphate isomerase

PP_i-dependent phosphofructokinase   ATP   ATP-dependent phosphofructokinase

ADP

Fructose-1,6-bisphosphate   Aldolase

CHLOROPLASTS

Triose phosphates   Glyceraldehyde-3-phosphate   Dihydroxyacetone phosphate   Triose phosphates

Triose phosphate isomerase

NAD⁺ P_i

NADH   Glyceraldehyde-3-phosphate dehydrogenase

1,3-Bisphosphoglycerate

ADP   Phosphoglycerate kinase

ATP

3-Phosphoglycerate

Phosphoglycerate mutase

2-Phosphoglycerate

H_2O Enolase HCO_3^-

PEP carboxylase   Oxaloacetate

Phosphoenolpyruvate P_i NADH   Malate dehydrogenase

ADP   Pyruvate kinase   NAD⁺

ATP

Pyruvate   Malate

CO_2 NADH   Lactate dehydrogenase

NAD⁺   Lactate

Pyruvate decarboxylase

Acetaldehyde

NADH   Alcohol dehydrogenase

NAD⁺   Fermentation reactions

Ethanol

To MITOCHONDRION

Fermentative metabolism

In the Absence of O_2, plants and other organisms can further metabolize pyruvate by carrying out one or more forms of **fermentative metabolism**

In **alcoholic fermentation** (common in plants, but more widely known from brewer's yeast), the two enzymes pyruvate decarboxylase and alcohol dehydrogenase act on pyruvate, ultimately producing ethanol and CO_2 and oxidizing NADH in the process.
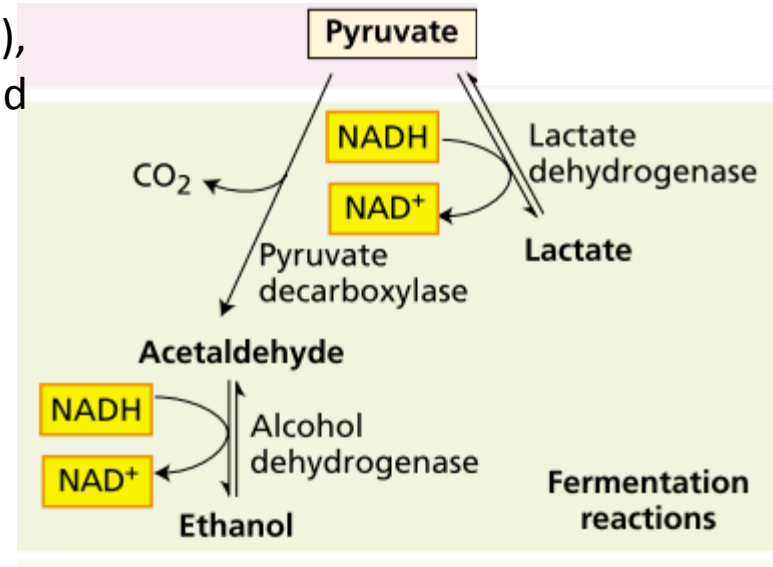

In **lactic acid fermentation** (common to mammalian muscle but also found in plants), the enzyme lactate dehydrogenase uses NADH to reduce pyruvate to lactate, thus regenerating NAD^+.

Fermentative metabolism

In corn the initial response to low oxygen is lactic acid fermentation, but the subsequent response is alcoholic fermentation.

Ethanol is thought to be a less toxic end product of fermentation because it can diffuse out of the cell, whereas lactate accumulates and promotes acidification of the cytosol.
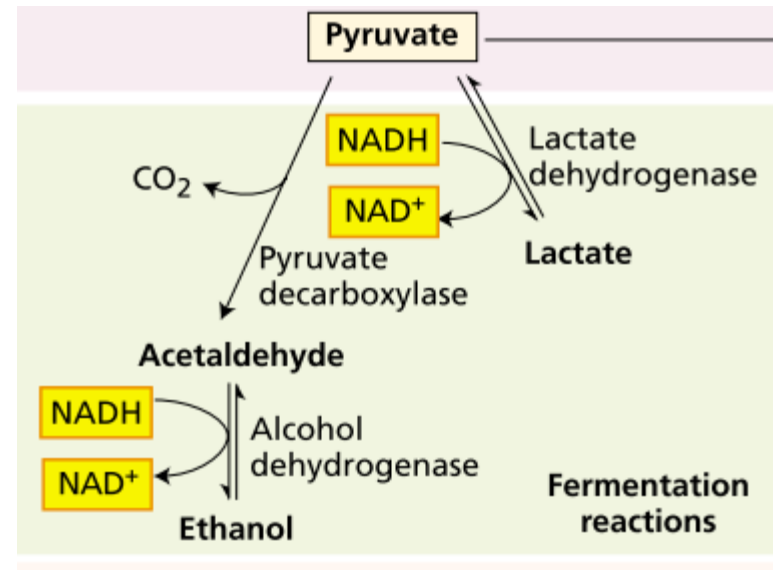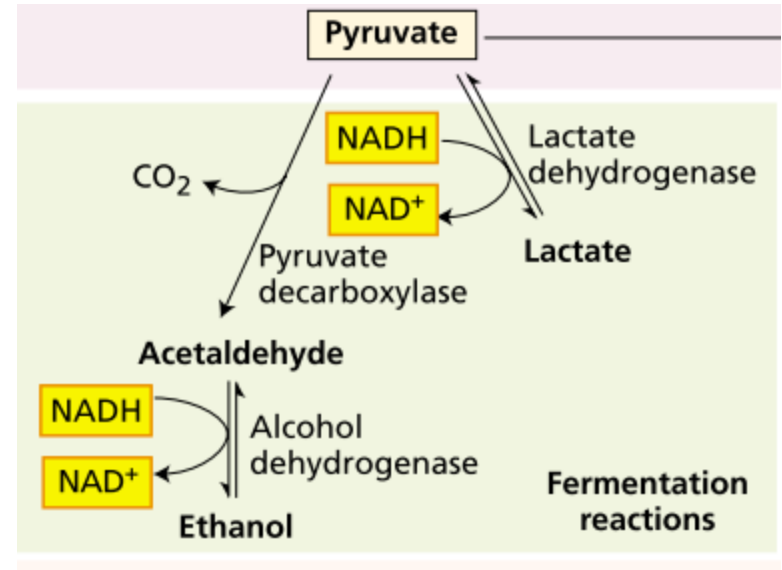
Fermentative metabolism

Fermentation Does Not Liberate All the Energy Available in Each Sugar Molecule

The standard free-energy change (ΔG^0 ') for the complete oxidation of sucrose is -5760 kJ mol-1 (1380 kcal mol-1) coming from 32 ATP.

Given the net synthesis of four molecules of ATP for each sucrose molecule that is converted to ethanol (or lactate), the efficiency of anaerobic fermentation is only about 4%.

Most of the energy available in sucrose remains in the reduced by-product of fermentation: lactate or ethanol.

Fermentative metabolism

Glucose/sucrose

Pasteur effect: The higher rates of glycolysis result from changes in glycolytic metabolite levels, as well as from increased expression of genes encoding enzymes of glycolysis and fermentation

Glycolysis

Pyruvate

Fermentation

Less No. ATP production

Constant no. ATP production necessary for cell survival

How Plant Glycolysis Is Controlled?

Animals, AMP and ATP are major effectors

The cytosolic concentration of PEP, which is a potent inhibitor of the plant ATP-dependent phosphofructokinase, is a more important regulator of plant glycolysis.

In plants, therefore, the control of glycolysis comes from the "bottom up" **with primary regulation** at the level of PEP metabolism by pyruvate kinase and PEP carboxylase and **secondary regulation** exerted by PEP at the conversion of fructose-6-phosphate to fructose-1,6-bisphosphate

In animals, the primary control operates at the phosphofructokinase, and secondary control at the pyruvate kinase.
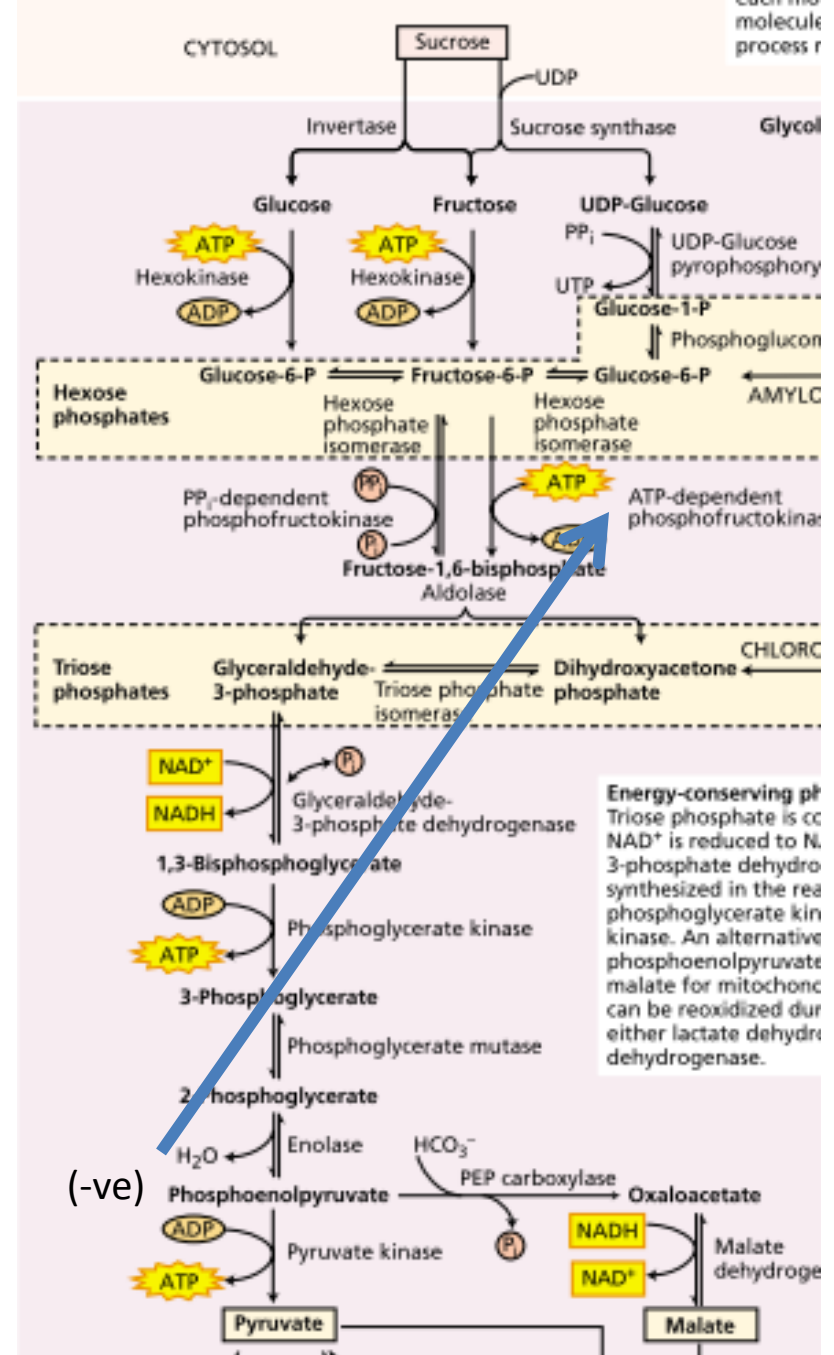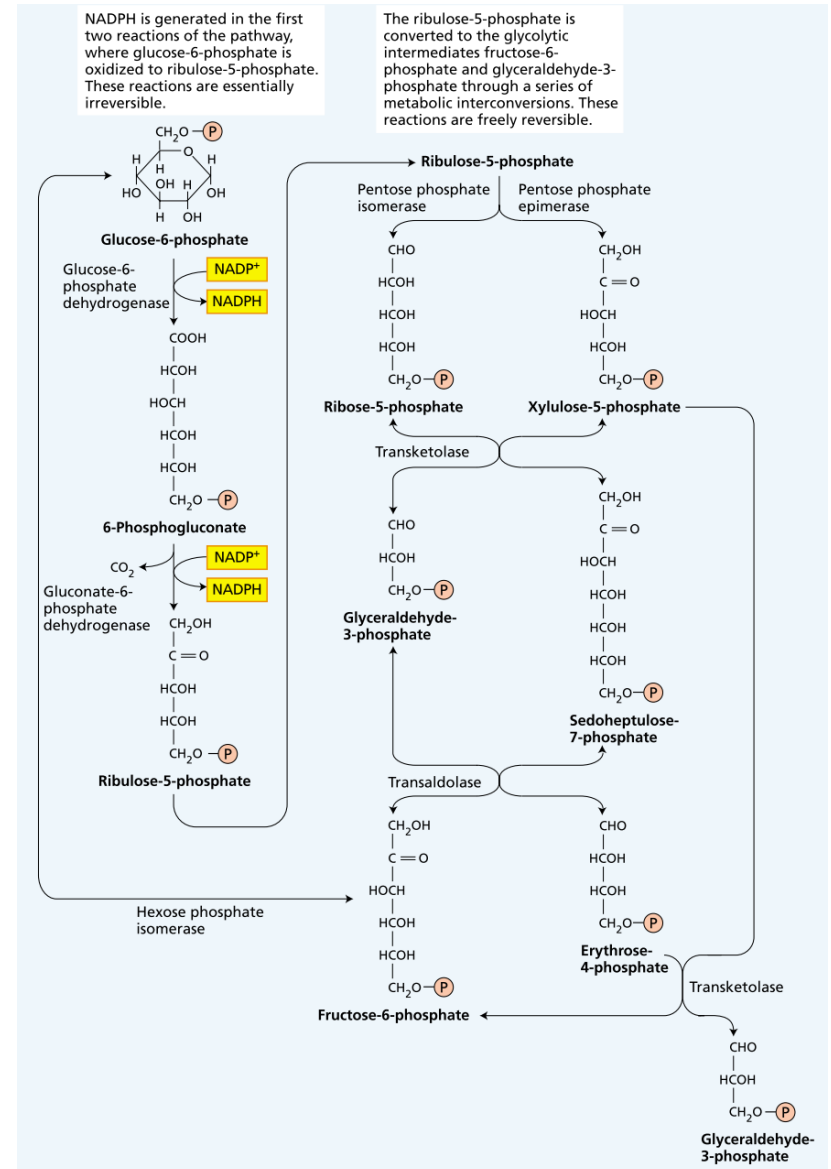
The Pentose Phosphate Pathway Produces NADPH and Biosynthetic Intermediates

The glycolytic pathway is not the only route available for the oxidation of sugars in plant cells.

the oxidative pentose phosphate pathway
Or hexose monophosphate shunt

The reactions are carried out by soluble enzymes present in the cytosol and in plastids.

Generally, the pathway in plastids predominates over the cytosolic pathway

The Pentose Phosphate Pathway Produces NADPH and Biosynthetic Intermediates

The first two reactions of this pathway involve the oxidative events that convert the six-carbon glucose-6-phosphate to a five-carbon sugar, ribulose-5-phosphate, with loss of a CO2 molecule and generation of two molecules of NADPH (not NADH).

The remaining reactions of the pathway convert ribulose-5-phosphate to the glycolytic intermediates glyceraldehyde-3-phosphate and fructose-6-phosphate

The net result is the complete oxidation of one glucose-6-phosphate molecule to CO2 with the concomitant synthesis of 12 NADPH molecules.
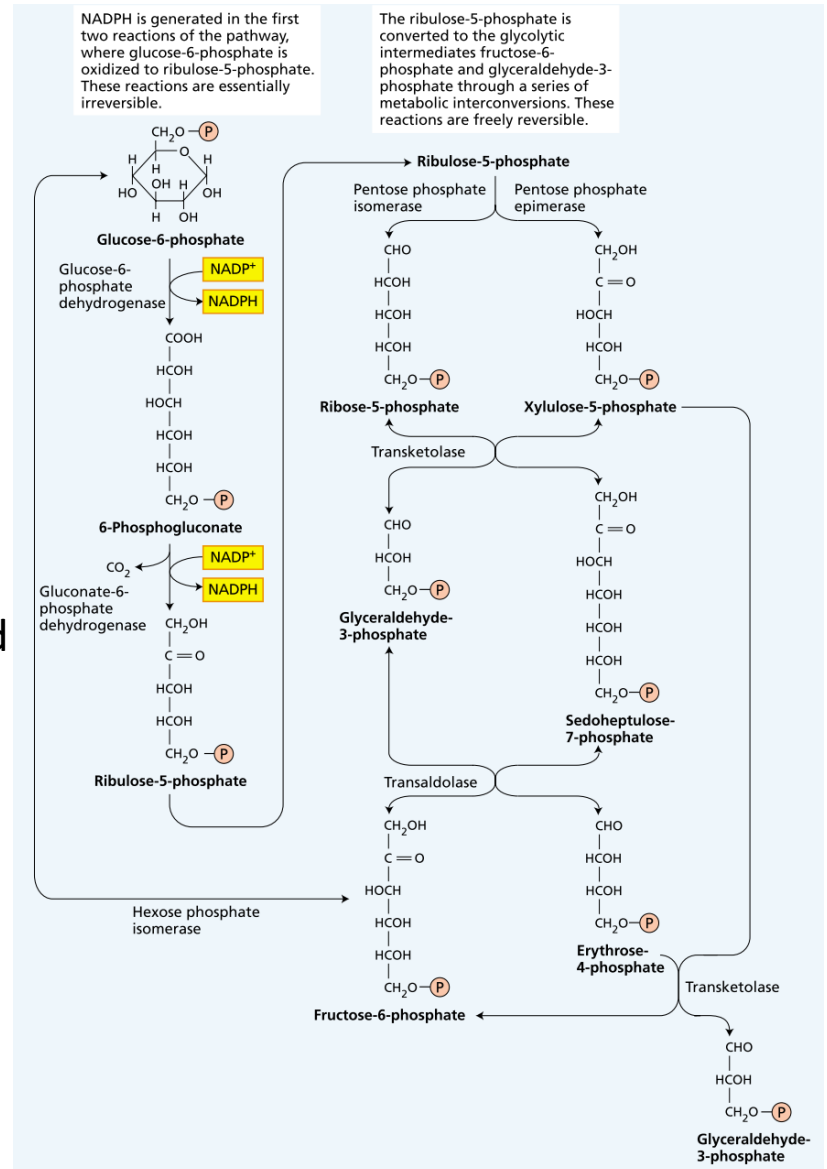
The Pentose Phosphate Pathway Produces NADPH and Biosynthetic Intermediates

The oxidative pentose phosphate pathway plays several roles in plant metabolism:

•NADPH is thought to drive reductive steps associated with various biosynthetic reactions that occur in the cytosol.

•electrons from NADPH may end up reducing O2 and generating ATP.

•The pathway produces ribose-5-phosphate, a precursor of the ribose and deoxyribose needed in the synthesis of RNA and DNA, respectively.

• Erythrose-4-phosphate, combines with PEP in the initial reaction that produces plant phenolic compounds, including the aromatic amino acids and the precursors of lignin, flavonoids, and phytoalexins

• During the early stages of greening, before leaf tissues become fully photoautotrophic, the oxidative pentose phosphate pathway is thought to be involved in generating Calvin cycle intermediates.

THE CITRIC ACID CYCLE: A MITOCHONDRIAL MATRIX PROCESS

Self study
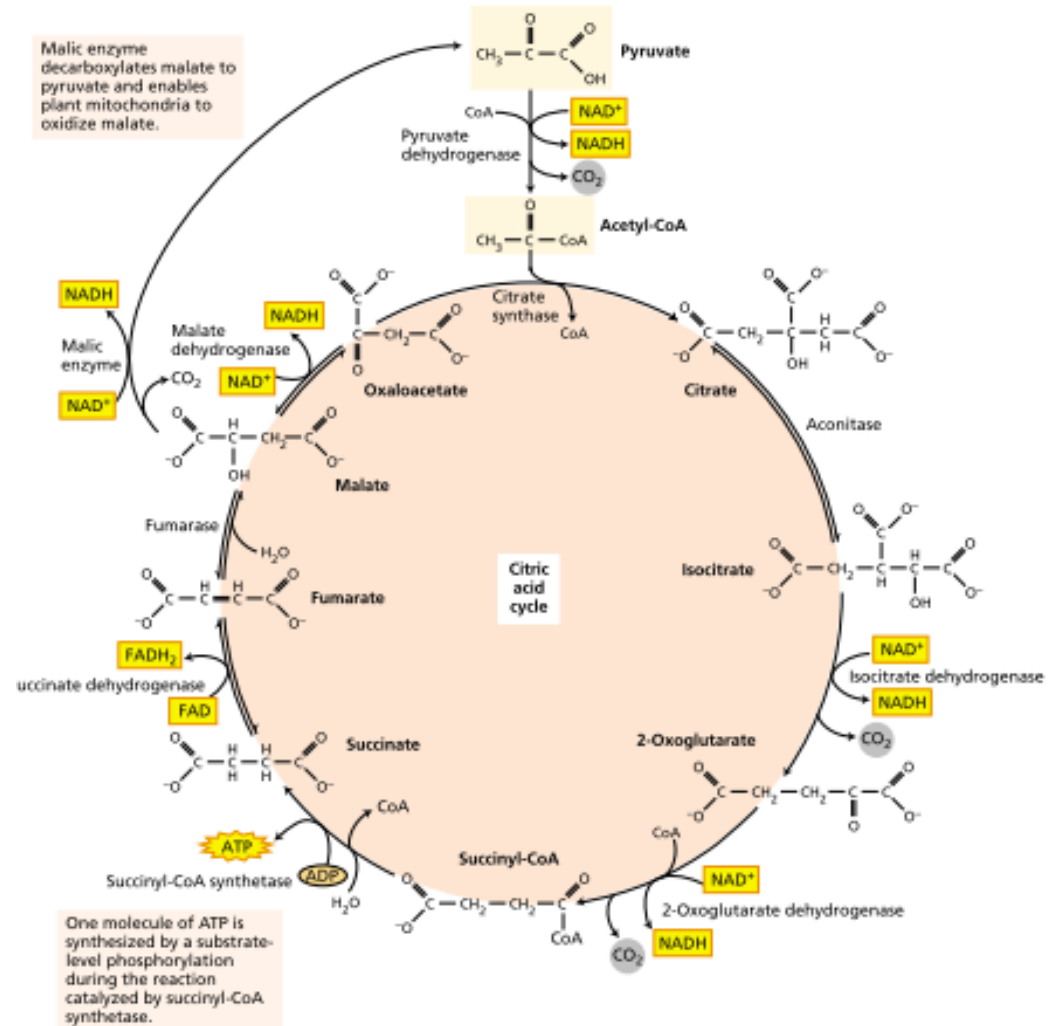
The Citric Acid Cycle of Plants Has Unique Features

- the step catalyzed by succinyl-CoA synthetase produces ATP in plants and GTP in animals.

- A feature of the plant citric acid cycle that is absent in many other organisms is the significant activity of NAD+ malic enzyme

$$\text{Malate} + \text{NAD}^+ \rightarrow \text{pyruvate} + CO_2 + \text{NADH}$$

The presence of NAD+ malic enzyme enables plant mitochondria to operate alternative pathways for the metabolism of PEP derived from glycolysis.
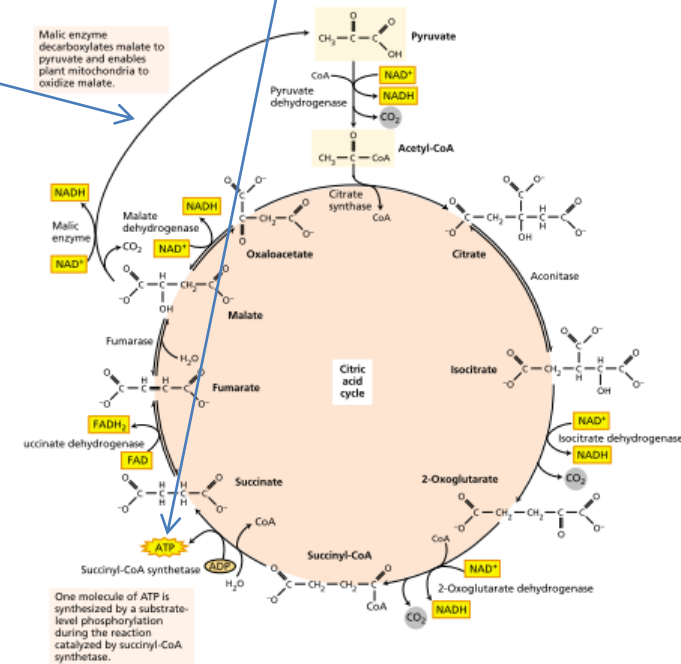
The Citric Acid Cycle of Plants Has Unique Features

malate can be synthesized from PEP in the cytosol via the enzymes PEP carboxylase and malate dehydrogenase

Malic enzyme makes it possible for plant mitochondria to oxidize both malate (A) and citrate (B) to CO2 without involving pyruvate delivered by glycolysis.
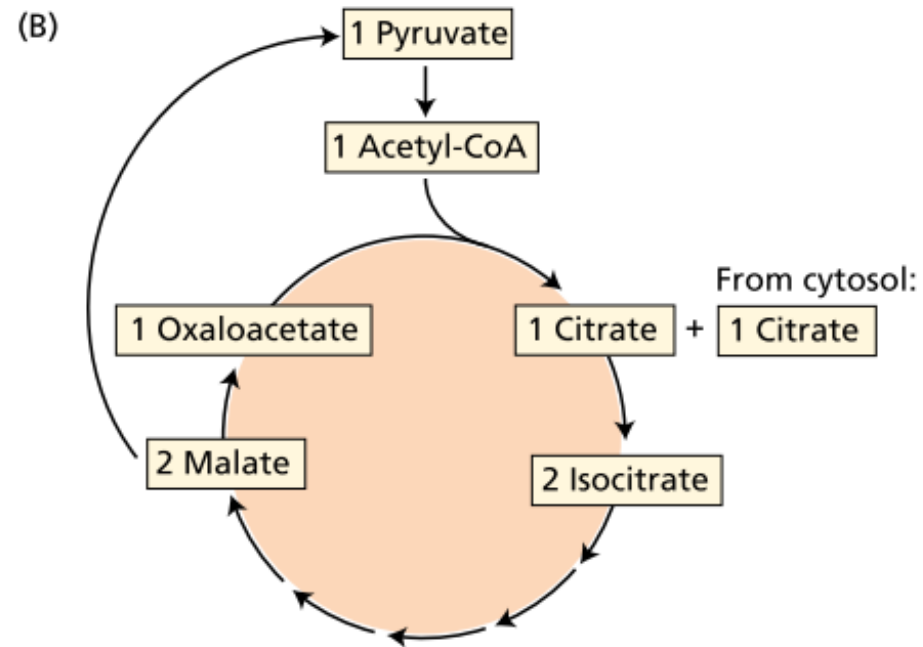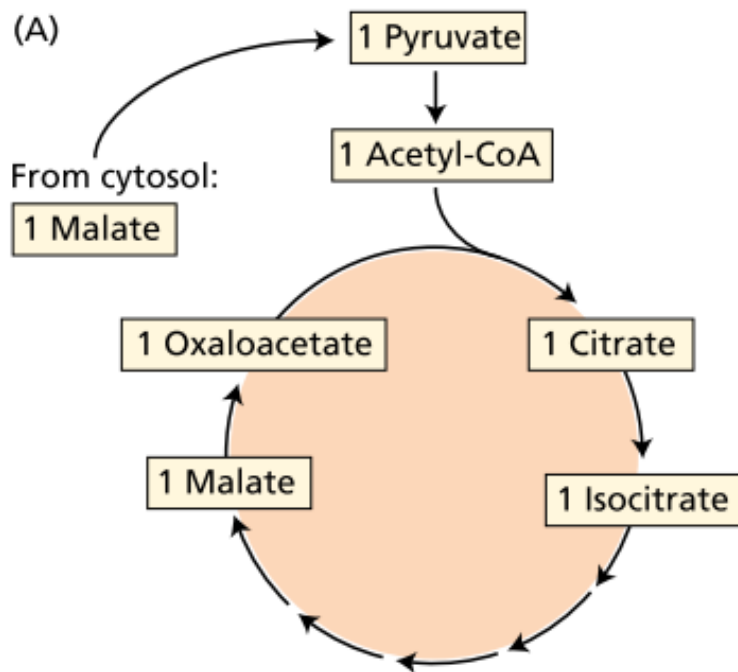
The Citric Acid Cycle of Plants Has Unique Features

The joint action of PEP carboxylase and pyruvate kinase can convert glycolytic PEP to 2-oxoglutarate, which is used for nitrogen assimilation

Reactions that can replenish intermediates in a metabolic cycle are known as **anaplerotic.**

crassulacean acid metabolism (CAM) , store significant levels of malate in their central vacuole.

(C)

2 PEP

1 Pyruvate

1 Acetyl-CoA

1 Oxaloacetate   1 Citrate

1 Malate   1 Isocitrate

2-Oxoglutarate

Nitrogen assimilation
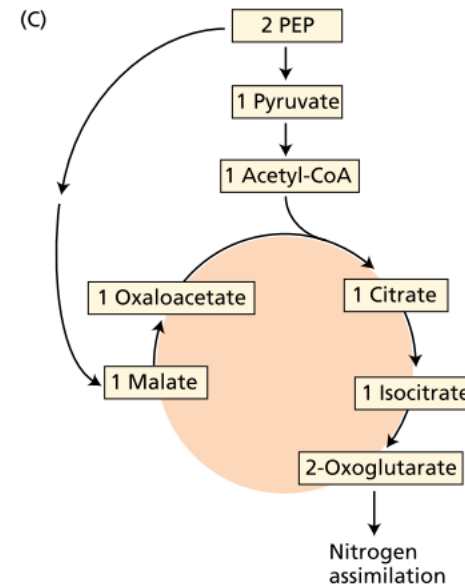
ELECTRON TRANSPORT AND ATP SYNTHESIS AT THE INNER MITOCHONDRIAL MEMBRANE

Self study

Although fundamentally similar in all aerobic cells, the electron transport chain of plants (and fungi) contains multiple NAD(P)H dehydrogenases and an alternative oxidase not found in mammalian mitochondria.
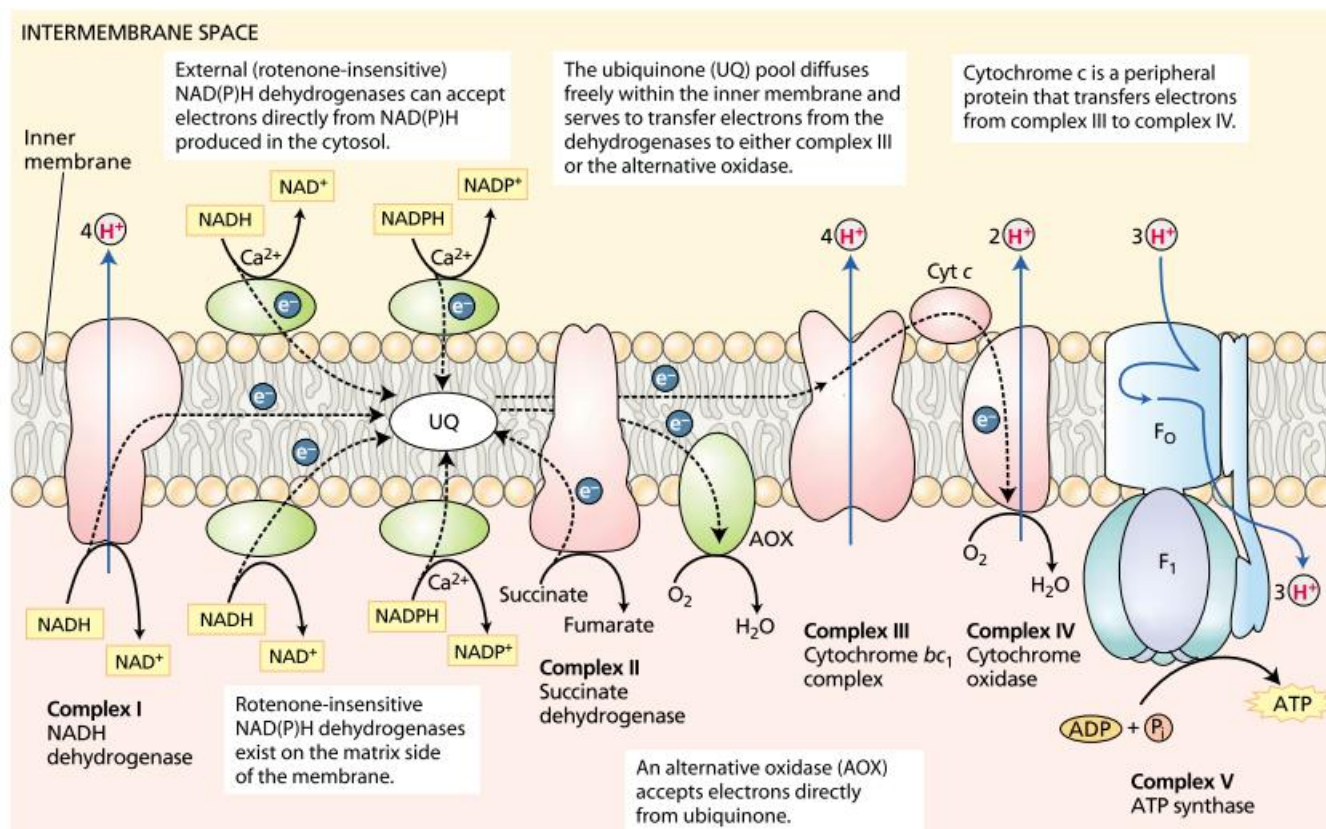
Some Electron Transport Enzymes Are Unique to Plant Mitochondria

• Two NAD(P)H dehydrogenases, both Ca^{2+}-dependent, attached to the outer surface of the inner membrane facing the intermembrane space can oxidize cytosolic NADH and NADPH.
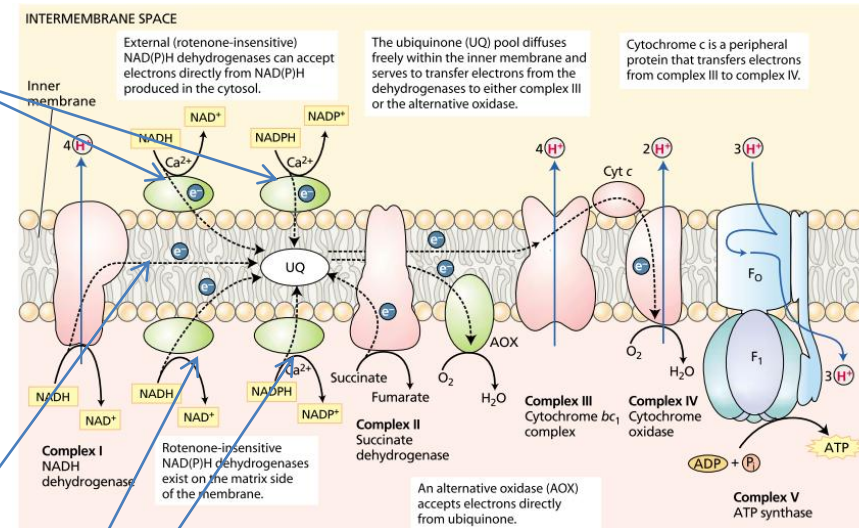
• Plant mitochondria have two pathways for oxidizing matrix NADH.

-Electron flow through complex I, is sensitive to inhibition by several compounds, including rotenone and piericidin.

-- In addition, plant mitochondria have a rotenone-resistant dehydrogenase, ND_{in}(NADH), for the oxidation of NADH derived from citric acid cycle substrates.

INTERMEMBRANE SPACE

Inner membrane

External (rotenone-insensitive) NAD(P)H dehydrogenases can accept electrons directly from NAD(P)H produced in the cytosol.

The ubiquinone (UQ) pool diffuses freely within the inner membrane and serves to transfer electrons from the dehydrogenases to either complex III or the alternative oxidase.

Cytochrome c is a peripheral protein that transfers electrons from complex III to complex IV.

Complex I NADH dehydrogenase

Rotenone-insensitive NAD(P)H dehydrogenases exist on the matrix side of the membrane.

Complex II Succinate dehydrogenase

An alternative oxidase (AOX) accepts electrons directly from ubiquinone.

Complex III Cytochrome bc_1 complex

Complex IV Cytochrome oxidase

Complex V ATP synthase

Some Electron Transport Enzymes Are Unique to Plant Mitochondria

• An NADPH dehydrogenase, ND_{in}(NADPH), is present on the matrix surface.

• Most, if not all, plants have an "alternative" respiratory pathway for the reduction of oxygen. This pathway involves the so-called alternative oxidase that, unlike cytochrome c oxidase, is insensitive to inhibition by cyanide, azide, or carbon monoxide
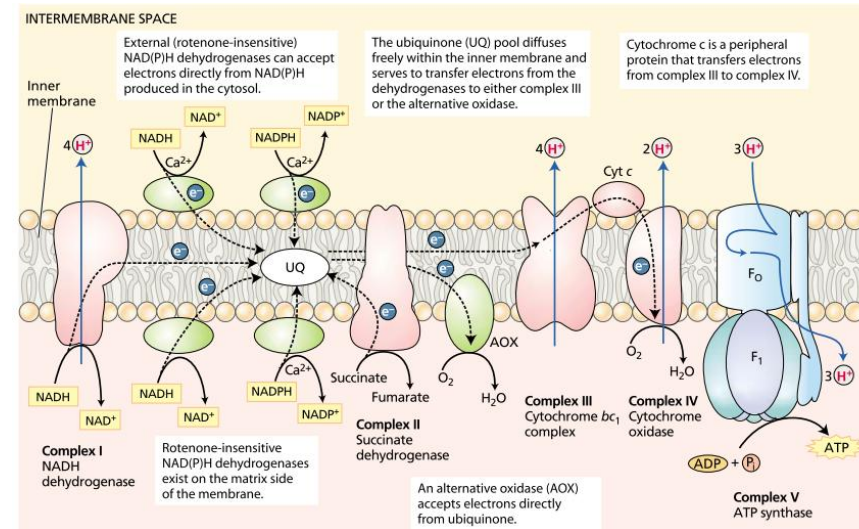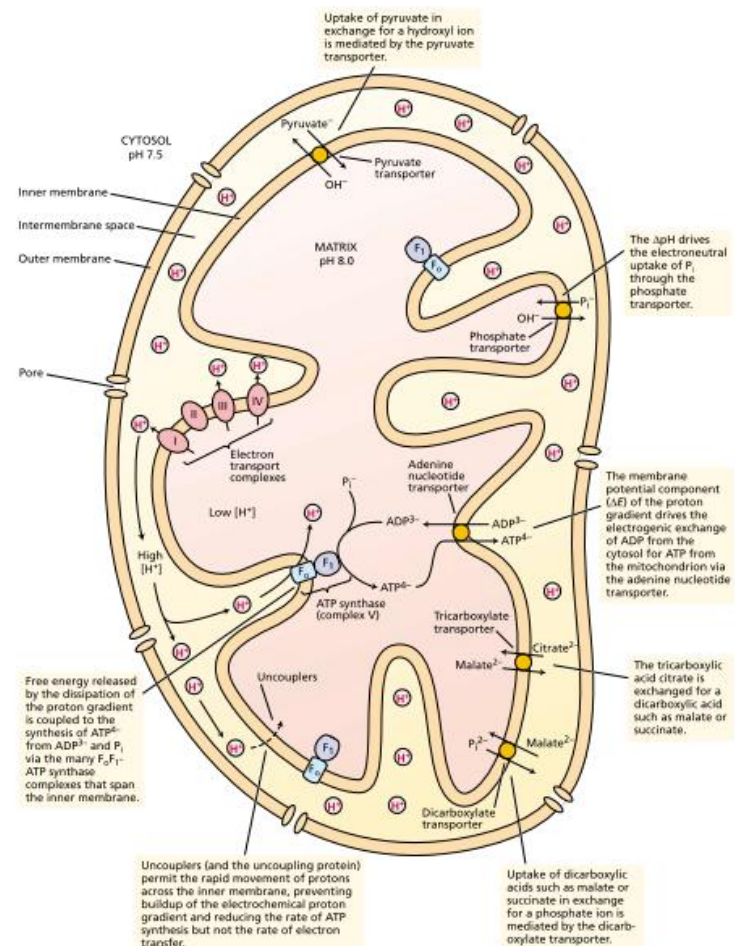
ATP Synthesis in the Mitochondrion Is Coupled to Electron Transport

Transporters Exchange Substrates and Products

Aerobic Respiration Yields about 60 Molecules of ATP per Molecule of Sucrose

Self study

Mitochondrial Genome

First complete sequencing of plant mitochondrial DNA (mtDNA) in *Arabidopsis thaliana*

Some characteristics of the plant mitochondrial genetic system are not generally found in the mitochondria of animals, protozoans, or even fungi.

• **RNA processing differs between plant mitochondria and mitochondria from most other organisms.**
- Several plant mitochondrial genes contain introns, and some genes are even split between separate transcript molecules, which must be joined by splicing.

•**the plant mitochondrial genetic system is that it strictly observes the universal genetic code, showing none of the deviations found in mtDNA in all other kingdoms.**

Plant mitochondrial genomes are generally much larger than those of animals.

Plants Have Several Mechanisms That Lower the ATP Yield (skip)

Respiration Is Tightly Coupled to Other Pathways (skip)

RESPIRATION IN INTACT PLANTS AND TISSUES (Skip)

Mitochondrial Respiration Is Controlled by Key Metabolites

 plant respiratory rates are
controlled from
the "bottom up" by the cellular
level of ADP

ADP initially regulates the rate of
electron transfer and ATP
synthesis, which in turn regulates
citric acid cycle activity, which,
finally, regulates the rate of the
glycolytic reactions.
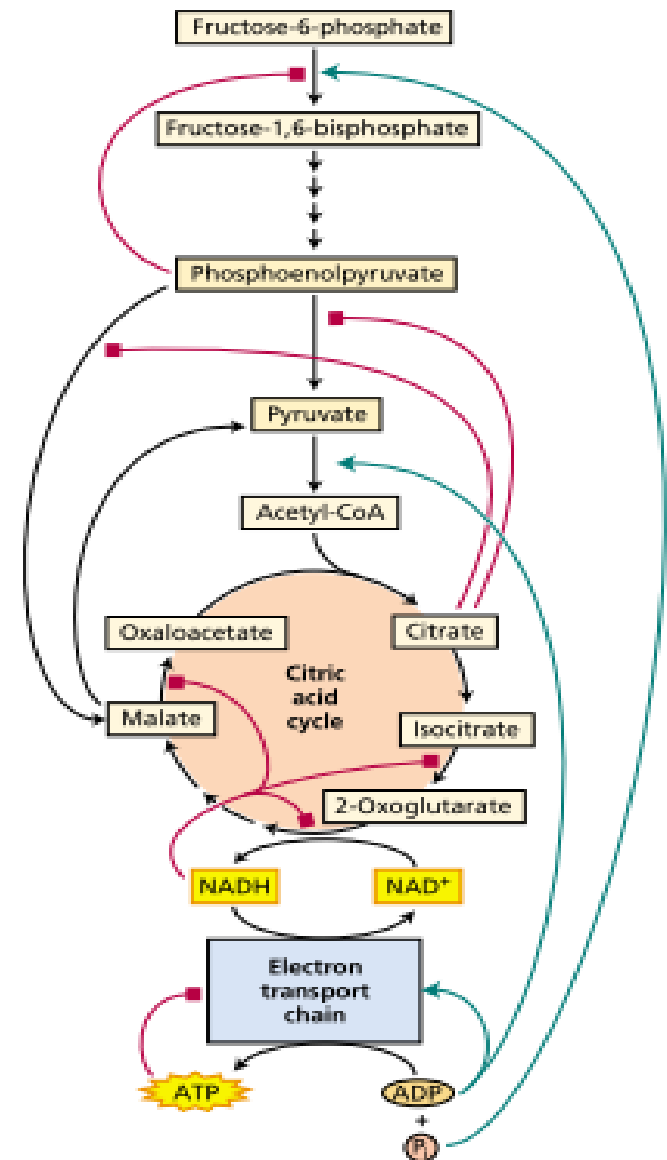
Mitochondrial Respiration Is Controlled by Key Metabolites

Control points exist at all three stages of respiration

1. Regulation of pyruvate dehydrogenase (PDH) activity by reversible phosphorylation and by other metabolites

Pyruvate + CoA + NAD$^+$ ⟶ Acetyl-CoA + CO$_2$ + NADH
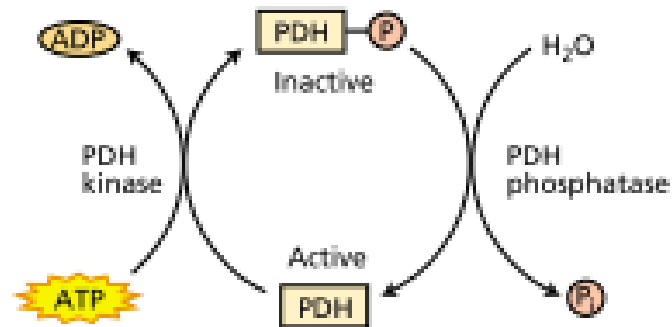
Effect on PDH activity	Mechanism
Activating	
Pyruvate	Inhibits kinase
ADP	Inhibits kinase
Mg^{2+} (or Mn^{2+})	Stimulates phosphatase
Inactivating	
NADH	Inhibits PDH Stimulates kinase
Acetyl CoA	Inhibits PDH Stimulates kinase
NH$_4^+$	Inhibits PDH Stimulates kinase

Mitochondrial Respiration Is Controlled by Key Metabolites

2. The citric acid cycle oxidations, and subsequently respiration, are dynamically controlled by the cellular level of adenine nucleotides.

As the cell's demand for ATP in the cytosol decreases relative to the rate of synthesis of ATP in the mitochondria, less ADP will be available, and the electron transport chain will operate at a reduced rate

This slowdown could be signaled to citric acid cycle enzymes through an increase in matrix NADH, inhibiting the activity of several citric acid cycle dehydrogenases
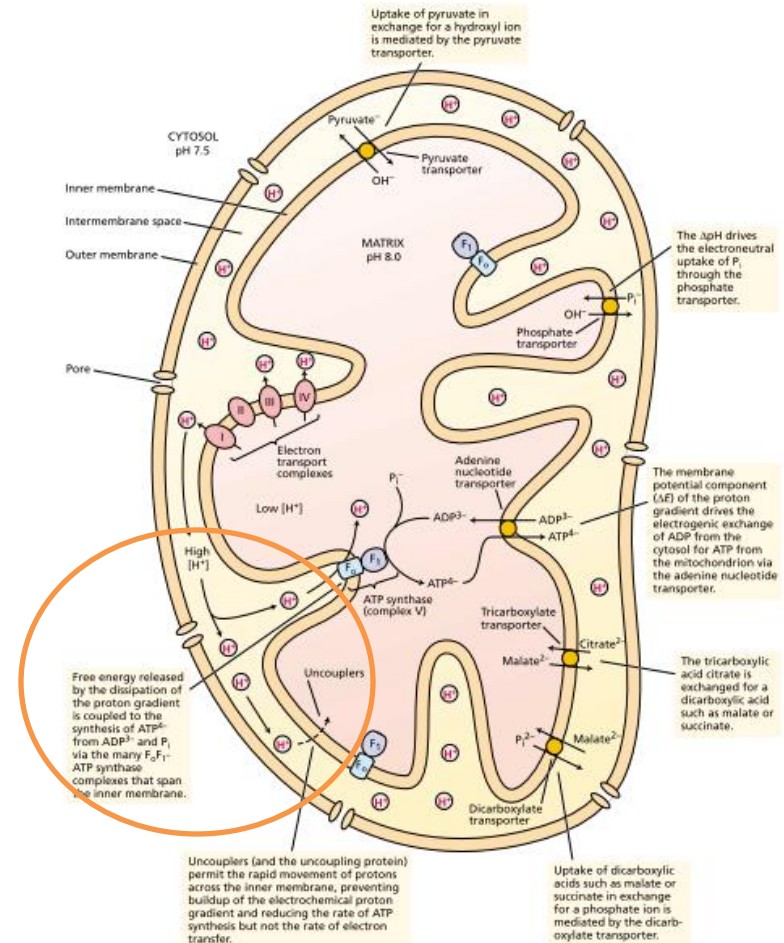
# Mitochondrial Respiration Is Controlled by Key Metabolites

3. The buildup of citric acid cycle intermediates and their derivates, such as citrate and glutamate, inhibits the action of cytosolic pyruvate kinase, increasing the cytosolic PEP concentration, which in turn reduces the rate of conversion of fructose-6-phosphate to fructose-1,6-bisphosphate, thus inhibiting glycolysis..

(-ve)

LIPID METABOLISM

energy storage

Animals ——————————————→ **fats**

plants ——————————————→ **carbon storage**
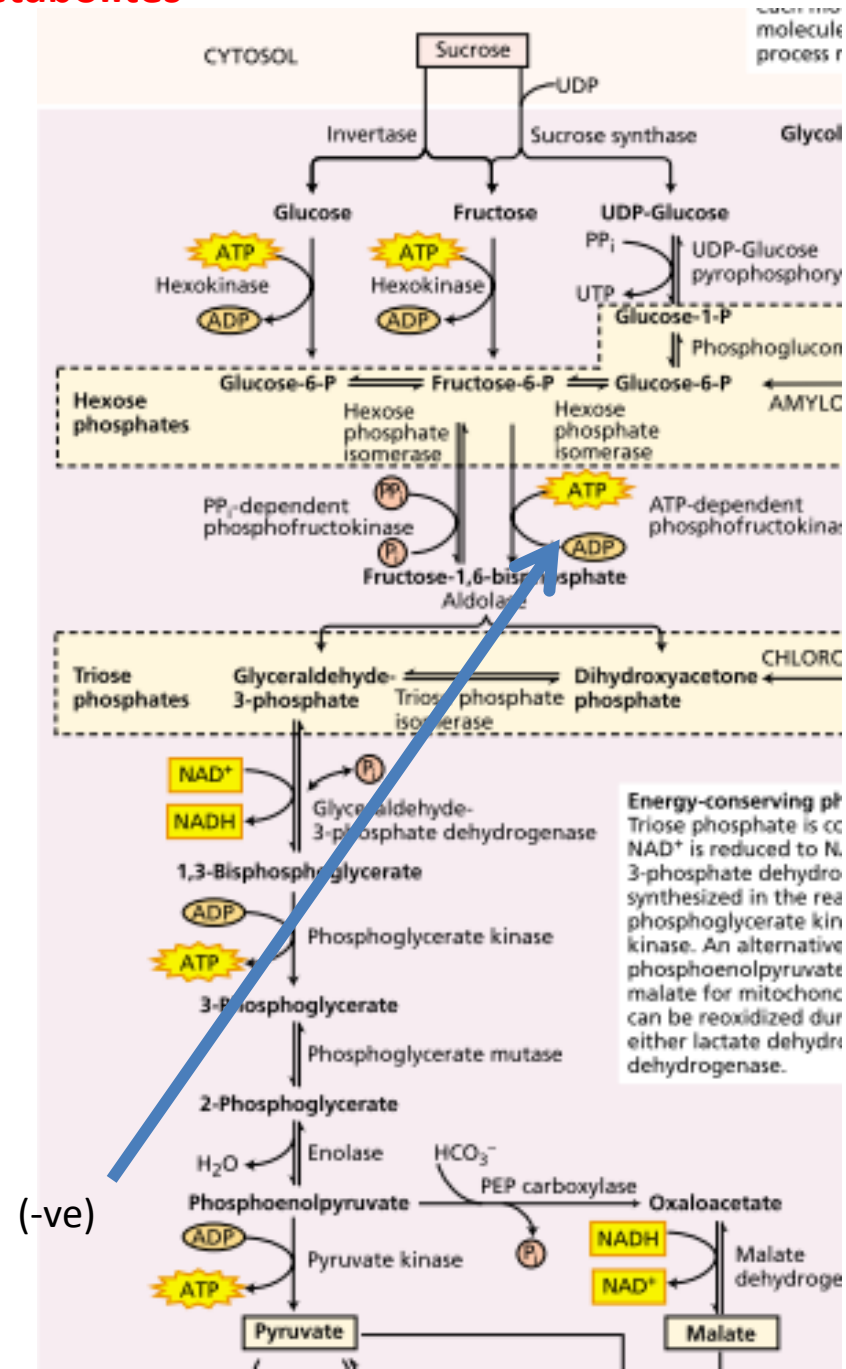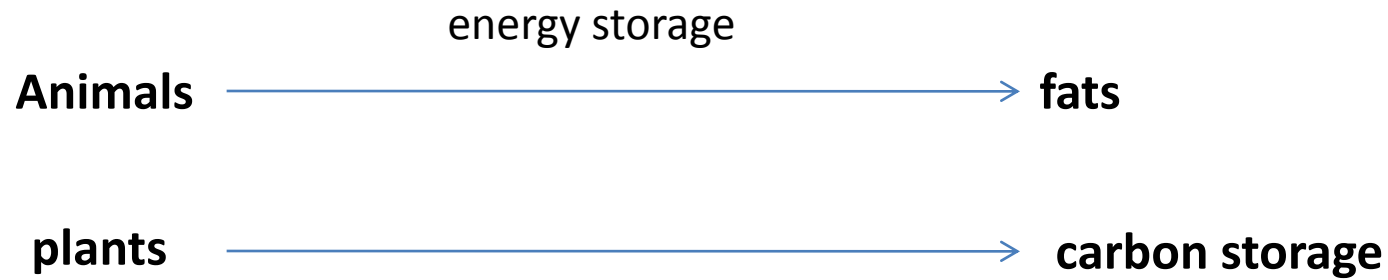
Fats and oils are important storage forms of reduced carbon in many seeds, including those of agriculturally important species such as soybean, sunflower, peanut, and cotton.

Oils often serve a major storage function in non-domesticated plants that produce small seeds.
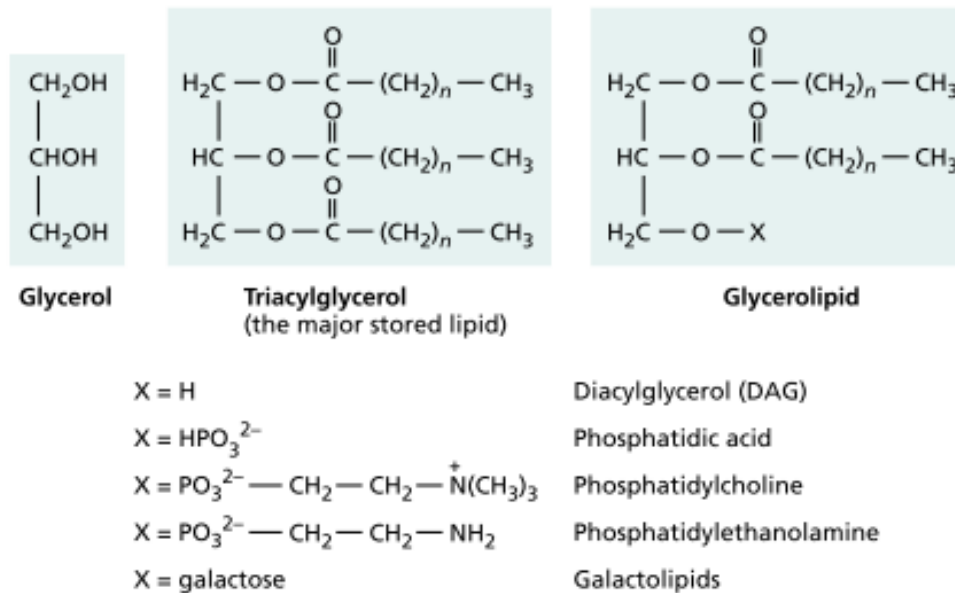
Some fruits, such as olives and avocados, also store fats and oils.

Fats and Oils Store Large Amounts of Energy

1 g of fat or oil ⟶ 40 kJ, or 9.3 kcal, of energy

1 g of starch ⟶ 15.9 kJ, or 3.8 kcal

Triacylglycerols Are Stored in Oleosomes

| Glycerol | Triacylglycerol (the major stored lipid) | Glycerolipid |

X = H   Diacylglycerol (DAG)

$X = HPO_3^{2-}$ Phosphatidic acid

$X = PO_3^{2-} - CH_2 - CH_2 - \overset{+}{N}(CH_3)_3$ Phosphatidylcholine

$X = PO_3^{2-} - CH_2 - CH_2 - NH_2$ Phosphatidylethanolamine

X = galactose   Galactolipids

Fats and oils exist mainly in the form of triacylglycerols   or triglycerides, in which fatty acid molecules are linked by ester bonds to the three hydroxyl groups of glycerol

Triacylglycerols Are Stored in Oleosomes

The carbon chains can be as short as 12 units and as long as 20, but more commonly they are 16 or 18 carbons long.

Oils are liquid at room temperature, primarily because of the presence of unsaturated bonds in their component fatty acids; fats, which have a higher proportion of saturated fatty acids, are solid at room temperature.

TABLE 11.3
Common fatty acids in higher plant tissues

Name[a]	Structure
Saturated Fatty Acids	
Lauric acid (12:0)	$CH_3(CH_2)_{10}CO_2H$
Myristic acid (14:0)	$CH_3(CH_2)_{12}CO_2H$
Palmitic acid (16:0)	$CH_3(CH_2)_{14}CO_2H$
Stearic acid (18:0)	$CH_3(CH_2)_{16}CO_2H$
Unsaturated Fatty Acids	
Oleic acid (18:1)	$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$
Linoleic acid (18:2)	$CH_3(CH_2)_4CH=CH-CH_2-CH=CH(CH_2)_7CO_2H$
Linolenic acid (18:3)	$CH_3CH_2CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7CO_2H$

Triacylglycerols Are Stored in Oleosomes

The composition of fatty acids in plant lipids varies with the species.:

Peanut oil is about 9% palmitic acid, 59% oleic acid, and 21% linoleic acid

Cotton seed oil is 20% palmitic acid, 30% oleic acid, and 45% linoleic acid.

Triacylglycerols in most seeds are stored in the cytoplasm of either cotyledon or endosperm cells in organelles known as oleosomes (also called spherosomes or oil bodies)

Oleosomes have an unusual single layer of phospholipid membrane barrier that separates the triglycerides from the aqueous cytoplasm.

The oleosome is stabilized by the presence of specific proteins, called oleosins, that coat the surface and prevent the phospholipids of adjacent oil bodies from coming in contact and fusing.

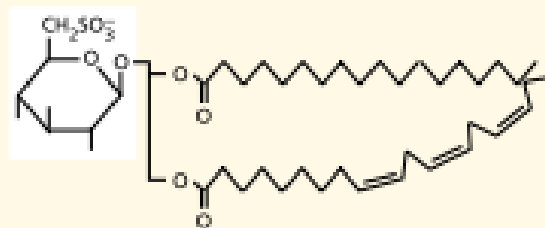**Polar Glycerolipids Are the Main Structural Lipids in Membranes**

The main structural lipids in membranes are the polar glycerolipids

There are two categories of polar glycerolipids:

1. Glyceroglycolipids, in which sugars form the head group
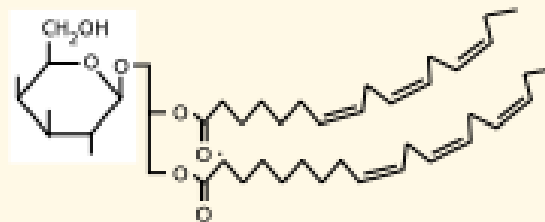
Monogalactosyldiacylglycerol
(18:3 | 16:3)

Sulfolipid (sulfoquinovosyldiacylglycerol)
(18:3 | 16:0)
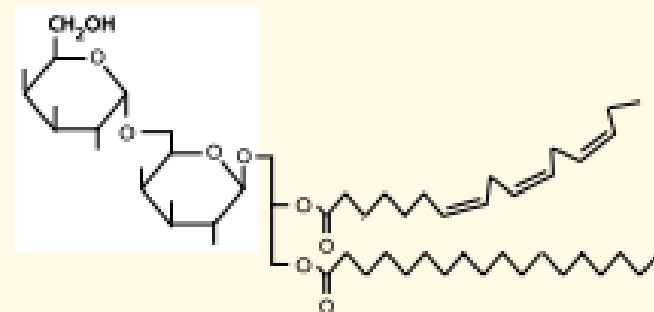
Digalactosyldiacylglycerol
(16:0 | 18:3)

(A) Glyceroglycolipids

2. Glycerophospholipids, in which the head group contains phosphate
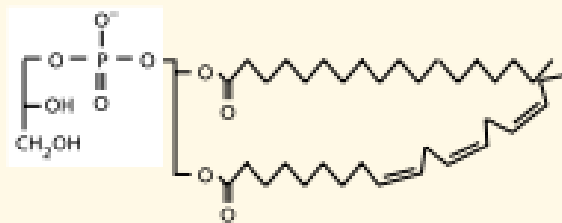
Phosphatidylglycerol
(18:3|16:0)

Phosphatidylcholine
(16:0|18:3)
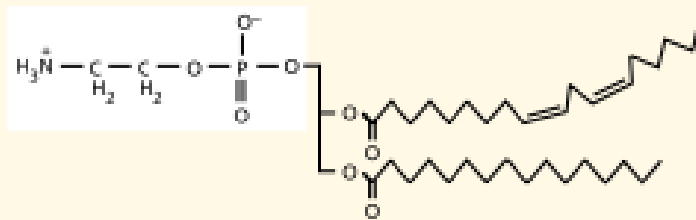
Phosphatidylethanolamine
(16:0|18:2)
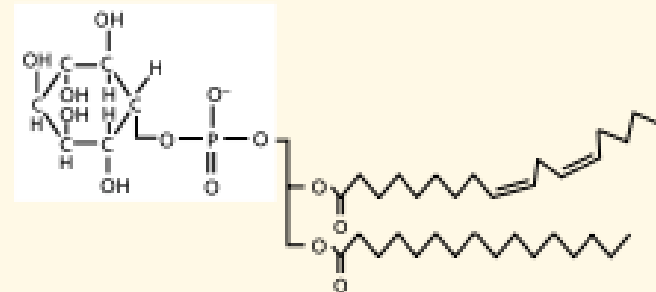
Phosphatidylinositol
(16:0|18:2)
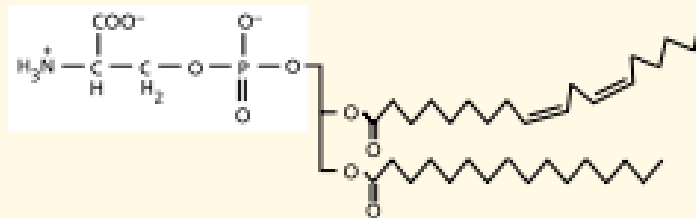
Phosphatidylserine
(16:0|18:2)
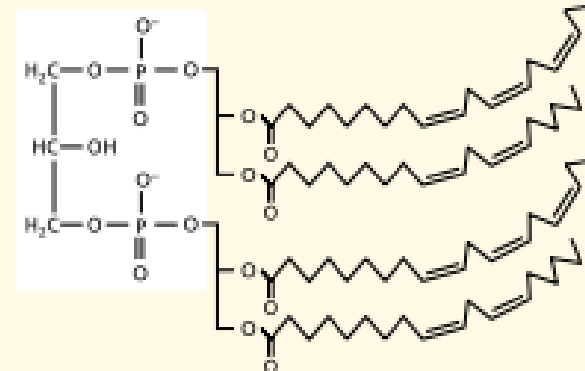
Diphosphatidylglycerol (cardiolipin)
(18:2|18:2)

(B) Glycerophospholipids

Plant membranes have additional structural lipids, including sphingolipids and sterols , but these are minor components.

Other lipids perform specific roles in photosynthesis and other processes: Included among these lipids are chlorophylls, pl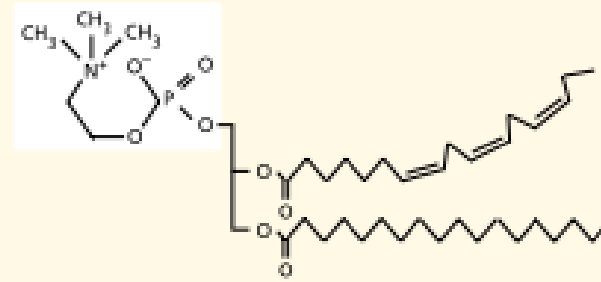astoquinone, carotenoids, and tocopherols, which together account for about **one-third of the lipids in plant leaves.**

TABLE 11.4
Glycerolipid components of cellular membranes

	Lipid composition (percentage of total)		
	Chloroplast	Endoplasmic reticulum	Mitochondrion
Phosphatidylcholine	4	47	43
Phosphatidylethanolamine	—	34	35
Phosphatidylinositol	1	17	6
Phosphatidylglycerol	7	2	3
Diphosphatidylglycerol	—	—	13
Monogalactosyldiacylglycerol	55	—	—
Digalactosyldiacylglycerol	24	—	—
Sulfolipid	8	—	—

Fatty Acid Biosynthesis Consists of Cycles of Two-Carbon Addition

a complex that is collectively referred to as **fatty acid synthase.**

the growing acyl chains are covalently bound to a low-molecular-weight, acidic protein **called acyl carrier protein (ACP).**
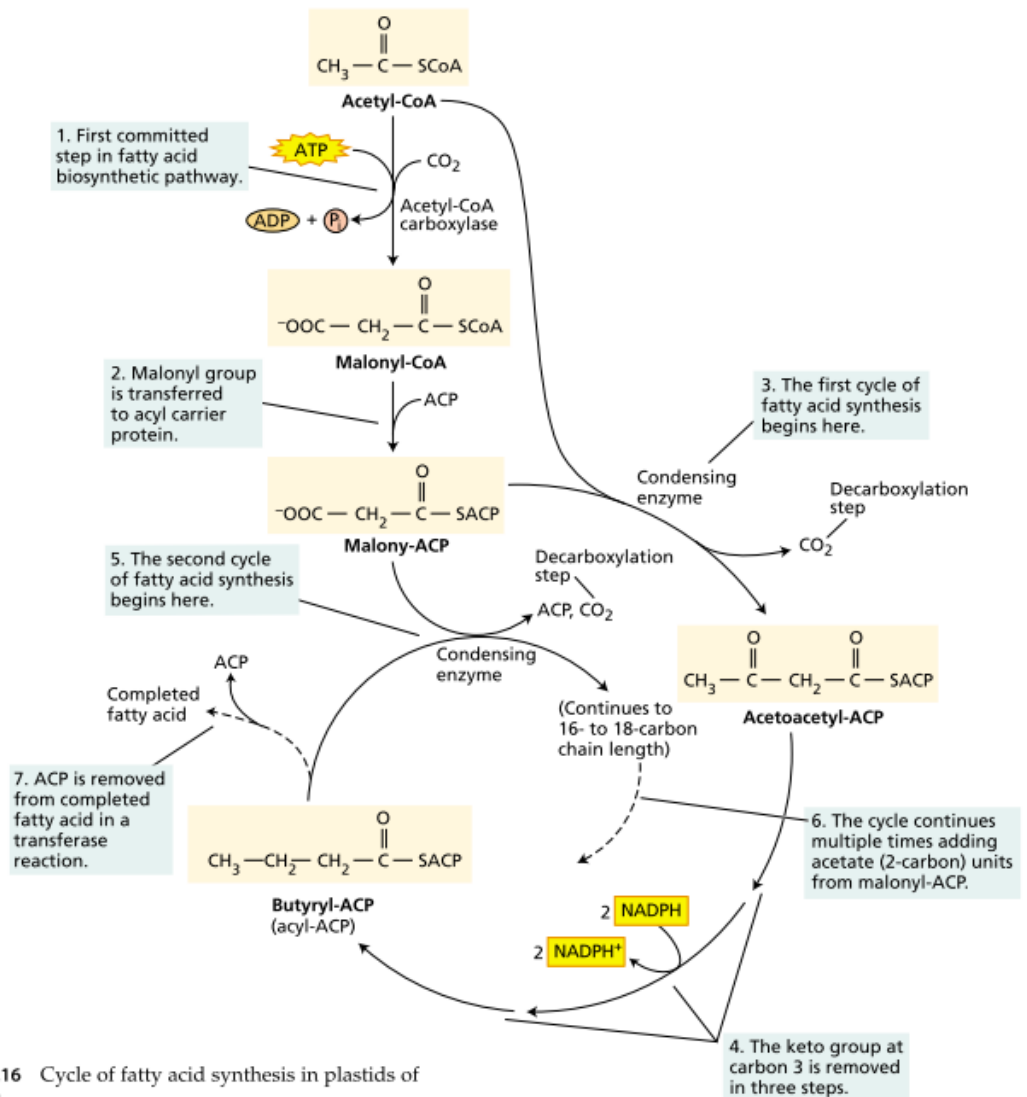
FIGURE 11.16 Cycle of fatty acid synthesis in plastids of plant cells.

Fatty acids may undergo further modification after they are linked with glycerol to form glycerolipids.

Some 16:0-ACP is released from the fatty acid synthase machinery, but most molecules that are elongated to 18:0-ACP are efficiently converted to **18:1-ACP by a desaturase enzyme.**

 The repetition of this sequence of events makes 16:0-ACP and 18:1-ACP the major products of fatty acid synthesis in plastids

 Desaturase isozymes are integral membrane proteins found in the chloroplast and the endoplasmic reticulum (ER).

 Each desaturase inserts a double bond at a specific position in the fatty acid chain, and the enzymes act sequentially to produce the final 18:3 and 16:3 products

Glycerolipids Are Synthesized in the Plastids and the ER

The fatty acids synthesized in the plastid are next used to make the glycerolipids of membranes and oleosomes.

The first steps of glycerolipid synthesis are two acylation reactions that transfer fatty acids from acyl-ACP or acyl-CoA to glycerol-3-phosphate to form phosphatidic acid.

diacylglycerol (DAG)

Phosphatidylinositol
or
phosphatidylglycerol

phosphatidic acid

phatidylethanolamine
or
phosphatidylcholine

Chloroplast
(Prokaryotic pathway)

Fatty acid synthase
and
18:0-ACP Desaturase

16:0-ACP
18:1-ACP

Phosphatidylglycerol ← Phosphatidic acid (PA)

Digalactosyldiacyl-glycerol

Monogalactosyl-diacylglycerol

Diacylglycerol (DAG)

Sulfolipid

In simple terms, the biochemistry involves two pathways referred to as the prokaryotic (or chloroplast) pathway and the eukaryotic (or ER) pathway.

1. In chloroplasts, the prokaryotic pathway utilizes the 16:0- and 18:1-ACP products of chloroplast fatty acid synthesis to synthesize phosphatidic acid and its derivatives. **Alternatively, the fatty acids may be exported to the cytoplasm as CoA esters.**
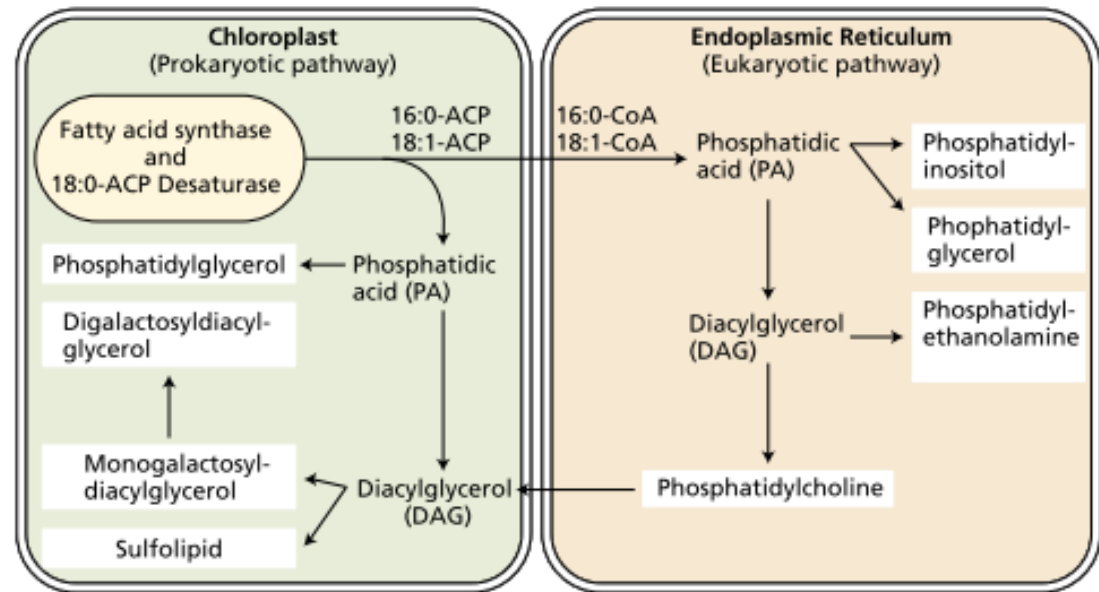
2. In the cytoplasm, the eukaryotic pathway uses a separate set of acyltransferases in the ER to incorporate the fatty acids into phosphatidic acid and its derivatives.

In some higher plants, including Arabidopsis and spinach, the two pathways contribute almost equally to chloroplast lipid synthesis.

In many other angiosperms, however, **phosphatidylglycerol is the only product of the prokaryotic pathway**, and the remaining chloroplast lipids are synthesized entirely by the eukaryotic pathway.

The biochemistry of triacylglycerol synthesis in oilseeds is generally the same as described for the glycerolipids 16:0- and 18:1-ACP are synthesized in the plastids of the cell and exported as CoA thioesters for incorporation into DAG in the endoplasmic reticulum
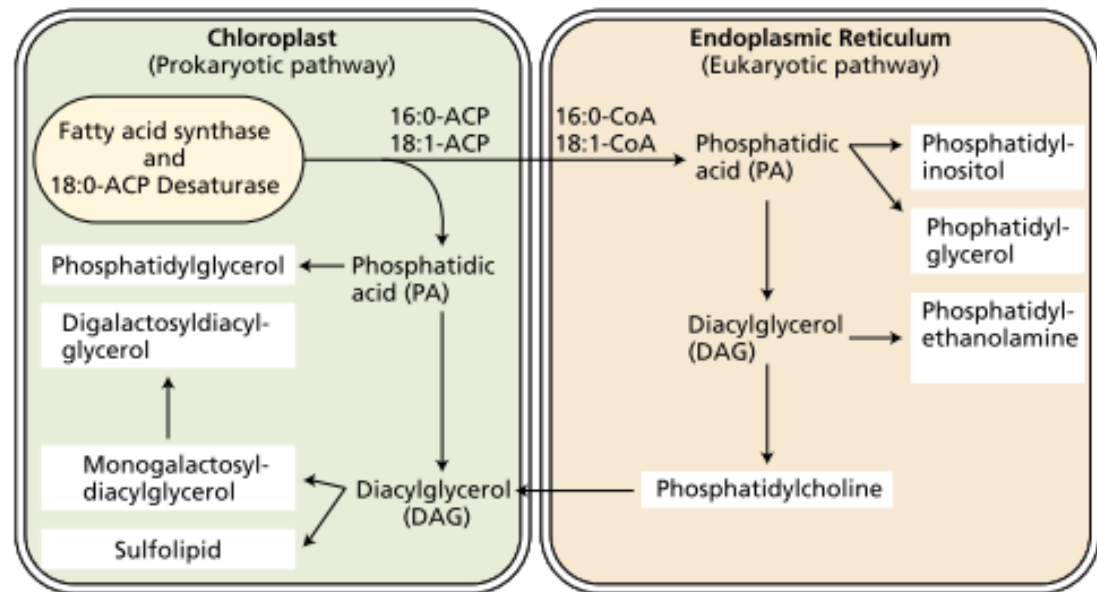
Lipid Composition Influences Membrane Function

Why lipid diversity is needed?

lipid composition and the ability of organisms to adjust to temperature changes

chill-sensitive plants experience sharp reductions in growth rate and development at temperatures between 0 and 12°C. Many economically important crops, such as cotton, soybean, maize, rice, and many tropical and subtropical fruits, are classified as chill sensitive.

In contrast, most plants that originate from temperate regions are able to grow and develop at chilling temperatures and are classified as chill-resistant plants.

at lower temperatures ⟶ decrease in lipid fluidity ⟶ chilling injury

a liquid-crystalline phase ⟶ gel phase
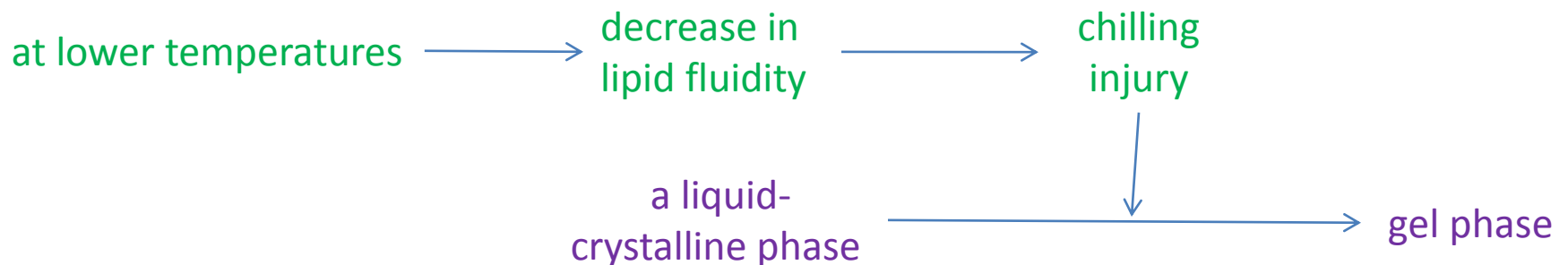
The degree of unsaturation of the fatty acids would determine the temperature at which such damage occurred

Membrane Lipids Are Precursors of Important Signaling Compounds

Plants, animals, and microbes all use membrane lipids as precursors for compounds that are used for intracellular or long-range signaling.

-Jasmonate derived from linolenic acid (18:3) activates plant defenses against insects and many fungal pathogens.

-- Phosphatidylinositol-4,5-bisphosphate (PIP_2) is the most important of several phosphorylated derivatives of phosphatidylinositol known as phosphoinositides. In animals, receptor-mediated activation of phospholipase C leads to the hydrolysis of PIP_2 to inositol trisphosphate (IP_3) anddiacylglycerol, which both act as intracellular secondary messengers.

The action of IP_3 in releasing Ca2+ into the cytoplasm (through calcium-sensitive channels in the tonoplast and other membranes) and thereby regulating cellular processes has been demonstrated in several plant systems, including the stomatal guard cells

Storage Lipids Are Converted into Carbohydrates in Germinating Seeds

After germinating, oil-containing seeds metabolize stored triacylglycerols by converting lipids to sucrose.

Plants are not able to transport fats from the endosperm to the root and shoot tissues of the germinating seedling, so they must convert stored lipids to a more mobile form of carbon, generally sucrose.

This process involves several steps that are located in different cellular compartments:
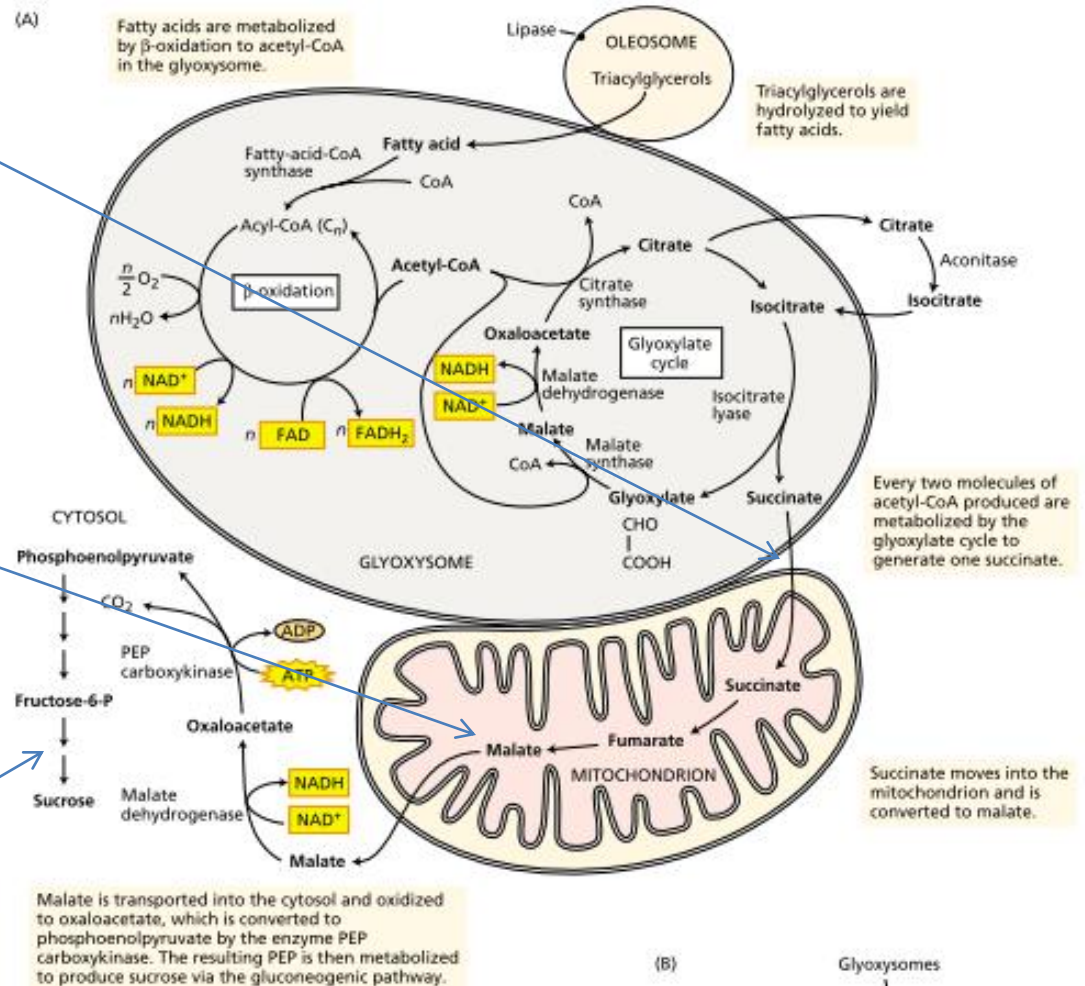- oleosomes,
- glyoxysomes,
- mitochondria,
- cytosol.

The conversion of lipids to sucrose in oilseeds is triggered by germination and begins with the hydrolysis of triacylglycerols stored in the oil bodies to free fatty acids, followed by oxidation of the fatty acids to produce acetyl-CoA

Fatty acids are oxidized in a type of peroxisome called a glyoxysome. Acetyl-CoA is metabolized in the glyoxysome to produce succinate, which is transported from the glyoxysome to the mitochondrion

mitochondrion, where it is converted first to oxaloacetate and then to malate.

The process ends in the cytosol with the conversion of malate to glucose via gluconeogenesis, and then to sucrose.

(A)

Fatty acids are metabolized by β-oxidation to acetyl-CoA in the glyoxysome.

Lipase — OLEOSOME
Triacylglycerols

Triacylglycerols are hydrolyzed to yield fatty acids.

Fatty-acid-CoA synthase   Fatty acid
CoA
Acyl-CoA (C_n)
$\frac{n}{2}O_2$ β-oxidation
nH_2O
n NAD$^+$
n NADH n FAD n FADH$_2$

CoA
Acetyl-CoA   Citrate
Citrate synthase
Oxaloacetate   Glyoxylate cycle
NADH   Malate dehydrogenase
NAD$^+$
Malate   Malate synthase
CoA
Glyoxylate   Succinate
CHO
|
COOH

Citrate   Aconitase
Isocitrate   Isocitrate
Isocitrate lyase

Every two molecules of acetyl-CoA produced are metabolized by the glyoxylate cycle to generate one succinate.

CYTOSOL
Phosphoenolpyruvate   GLYOXYSOME
CO$_2$
ADP
PEP carboxykinase   ATP
Fructose-6-P
Oxaloacetate
Sucrose   Malate dehydrogenase   NADH   NAD$^+$
Malate

Succinate
Fumarate
Malate
MITOCHONDRION

Succinate moves into the mitochondrion and is converted to malate.

Malate is transported into the cytosol and oxidized to oxaloacetate, which is converted to phosphoenolpyruvate by the enzyme PEP carboxykinase. The resulting PEP is then metabolized to produce sucrose via the gluconeogenic pathway.

(B)   Glyoxysomes

Lipase hydrolysis.

The initial step in the conversion of lipids to carbohydrate is the breakdown of triglycerides stored in the oil bodies by the enzyme lipase, which, at least in castor bean endosperm, is located on the half-membrane that serves as the outer boundary of the oil body.

The lipase hydrolyzes triacylglycerols to three molecules of fatty acid and glycerol.
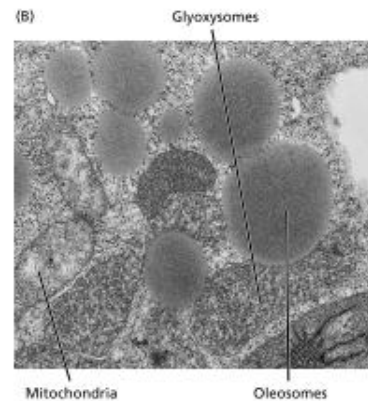
During the breakdown of lipids, oil bodies and glyoxysomes are generally in close physical association

(B)

Glyoxysomes

Mitochondria   Oleosomes

Fatty acids are metabolized by β-oxidation to acetyl-CoA in the glyoxysome.

Lipase — OLEOSOME

Triacylglycerols

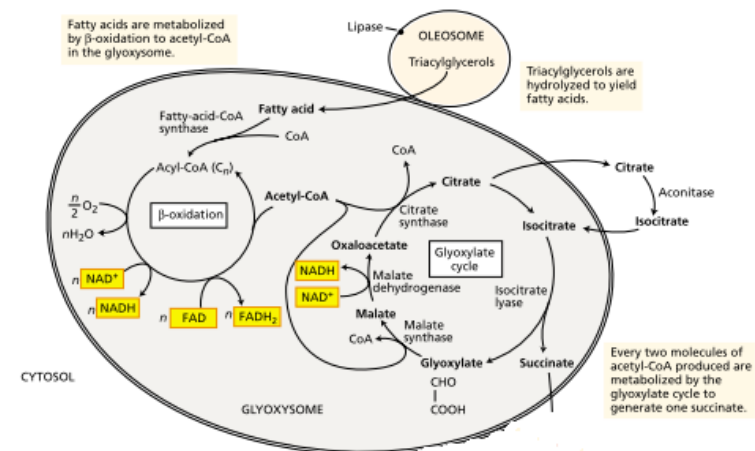Triacylglycerols are hydrolyzed to yield fatty acids.

Fatty-acid-CoA synthase   Fatty acid

CoA

CoA

Acyl-CoA (C_n)

$\frac{n}{2}O_2$

nH_2O

β-oxidation

Acetyl-CoA

Citrate

Citrate synthase

Citrate

Aconitase

Isocitrate

Isocitrate

Oxaloacetate

Glyoxylate cycle

n NAD⁺

n NADH

NADH

NAD⁺

Malate dehydrogenase

Isocitrate lyase

n FAD n FADH₂

Malate

Malate synthase

CoA

Glyoxylate

CHO

COOH

Succinate

Every two molecules of acetyl-CoA produced are metabolized by the glyoxylate cycle to generate one succinate.

CYTOSOL

GLYOXYSOME

β-Oxidation of fatty acids.

After hydrolysis of the triacylglycerols, the resulting fatty acids enter the glyoxysome, where they are activated by conversion to fatty-acyl-CoA by the enzyme fatty-acyl-CoA synthase.

Fatty-acyl-CoA is the initial substrate for the β-oxidation series of reactions, in which C_n fatty acids are sequentially broken down to n/2 molecules of acetyl-CoA

This reaction sequence involves the reduction of $1/2\ O_2$ to H_2O and the formation of 1 NADH and 1 $FADH_2$ for each acetyl-CoA produced.
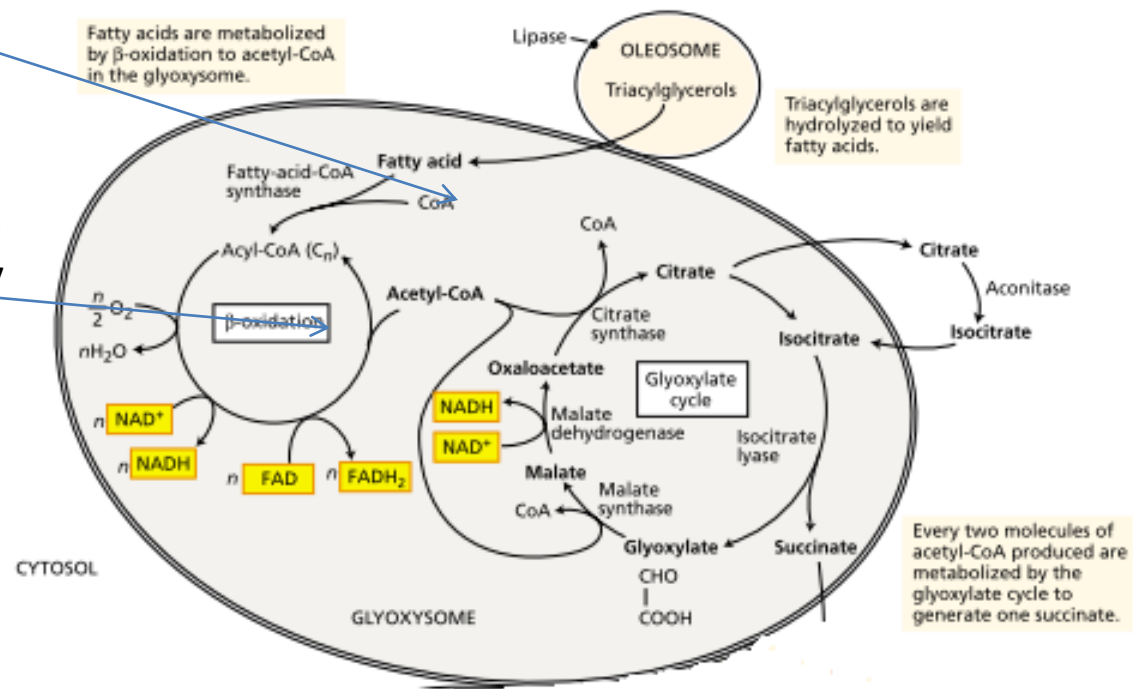
β-Oxidation of fatty acids.

In mammalian tissues, the four enzymes associated with β-oxidation are present in the mitochondrion; in plant seed storage tissues, they are localized exclusively in the glyoxysome.

Interestingly, in plant vegetative tissues (e.g., mung bean hypocotyl and potato tuber), the β-oxidation reactions are localized in a related organelle, the peroxisome

The glyoxylate cycle.

The function of the glyoxylate cycle is to convert two molecules of acetyl-CoA to succinate
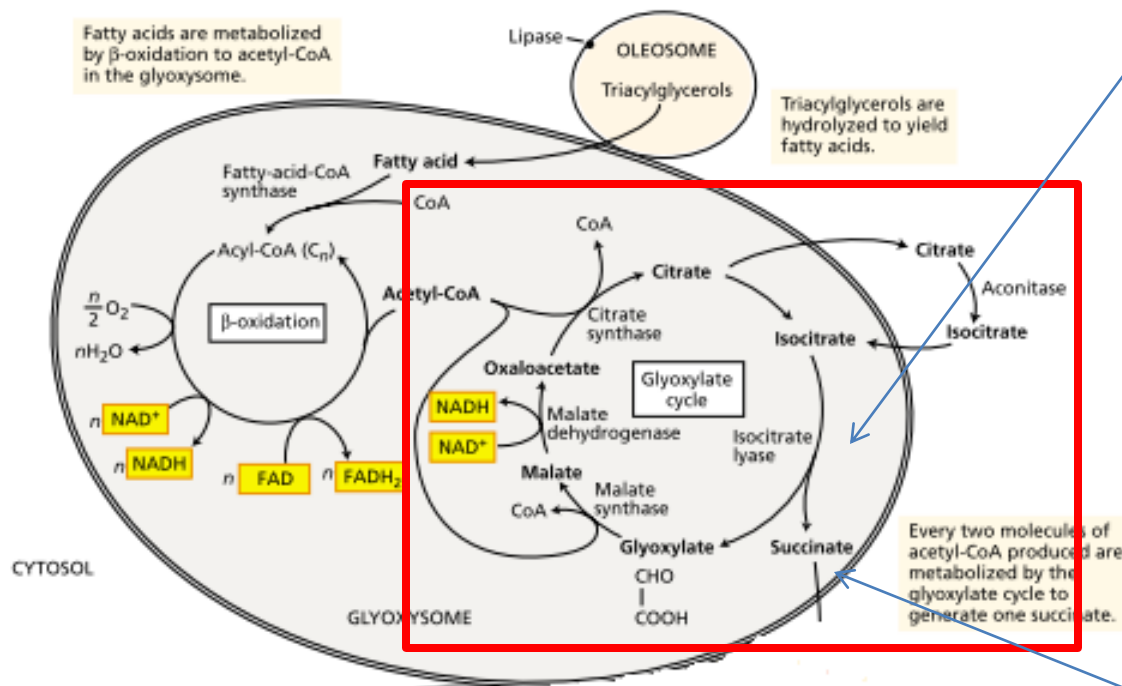
Initially, the acetyl-CoA reacts with oxaloacetate to give citrate, which is then transferred to the cytoplasm for iso merization to isocitrate by aconitase.
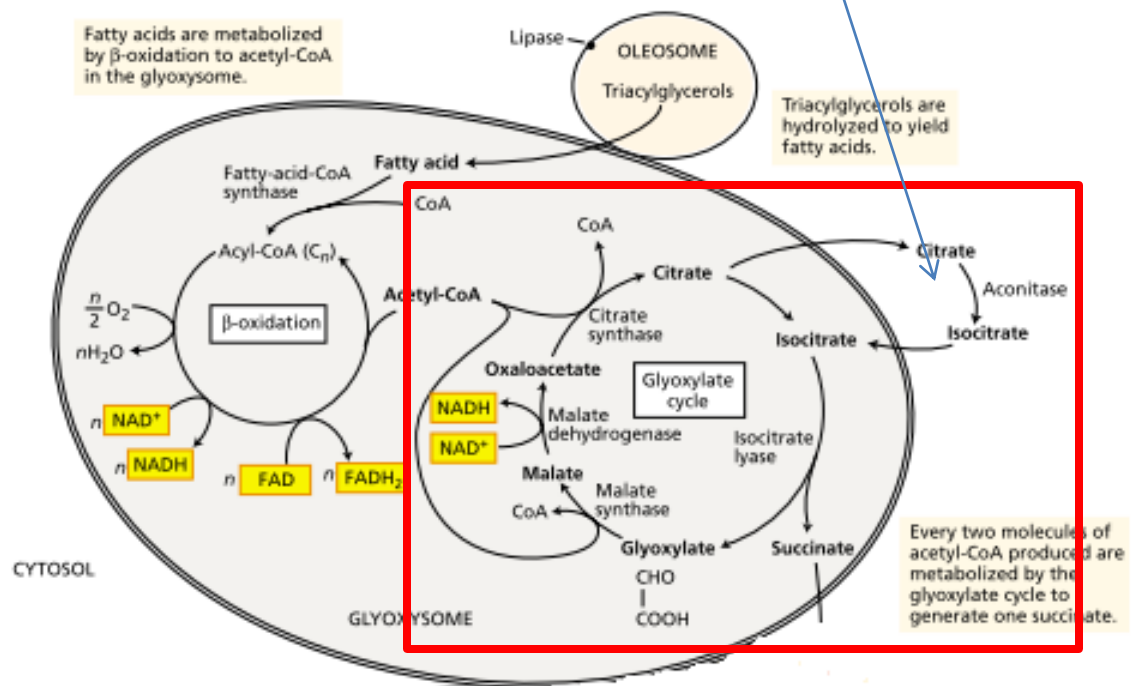
The glyoxylate cycle.

Isocitrate is reimported into the peroxisome and converted to malate by two reactions that are unique to the glyoxylate pathway.

First isocitrate (C6) is cleaved by the enzyme isocitrate lyase to give succinate (C4) and glyoxylate (C2).

Fatty acids are metabolized by β-oxidation to acetyl-CoA in the glyoxysome.

Triacylglycerols are hydrolyzed to yield fatty acids.

Every two molecules of acetyl-CoA produced are metabolized by the glyoxylate cycle to generate one succinate.

This succinate is exported to the motochondria.

The glyoxylate cycle.
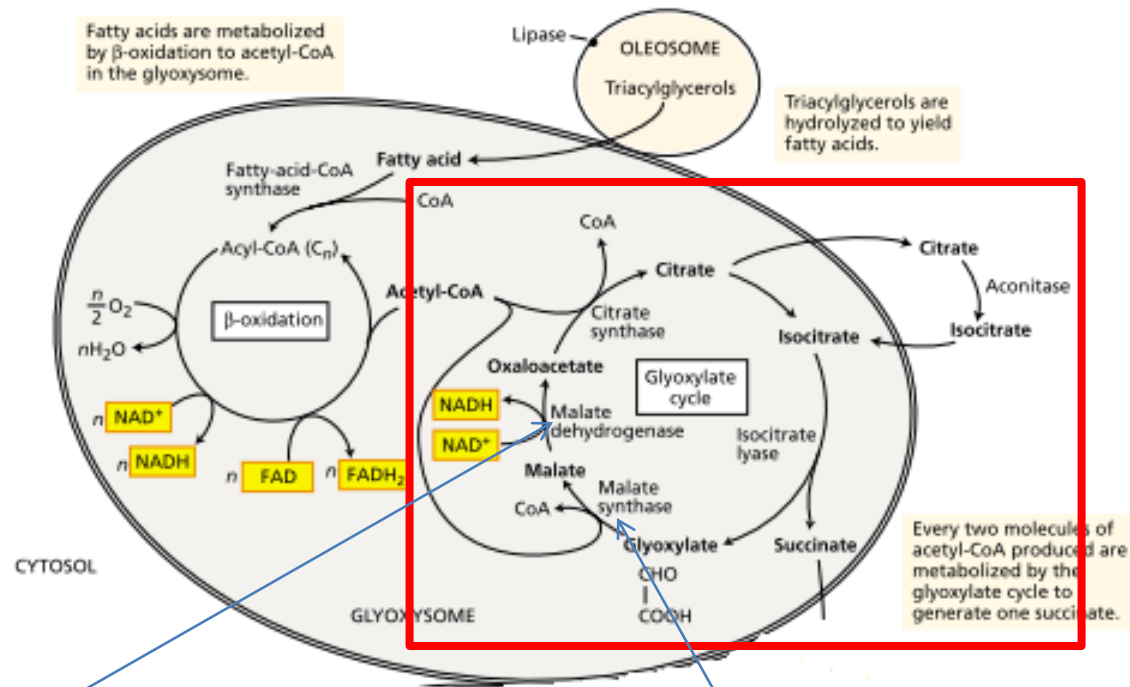
Malate is then oxidized by malate dehydrogenase to oxaloacetate, which can combine with another acetyl-CoA to continue the cycle

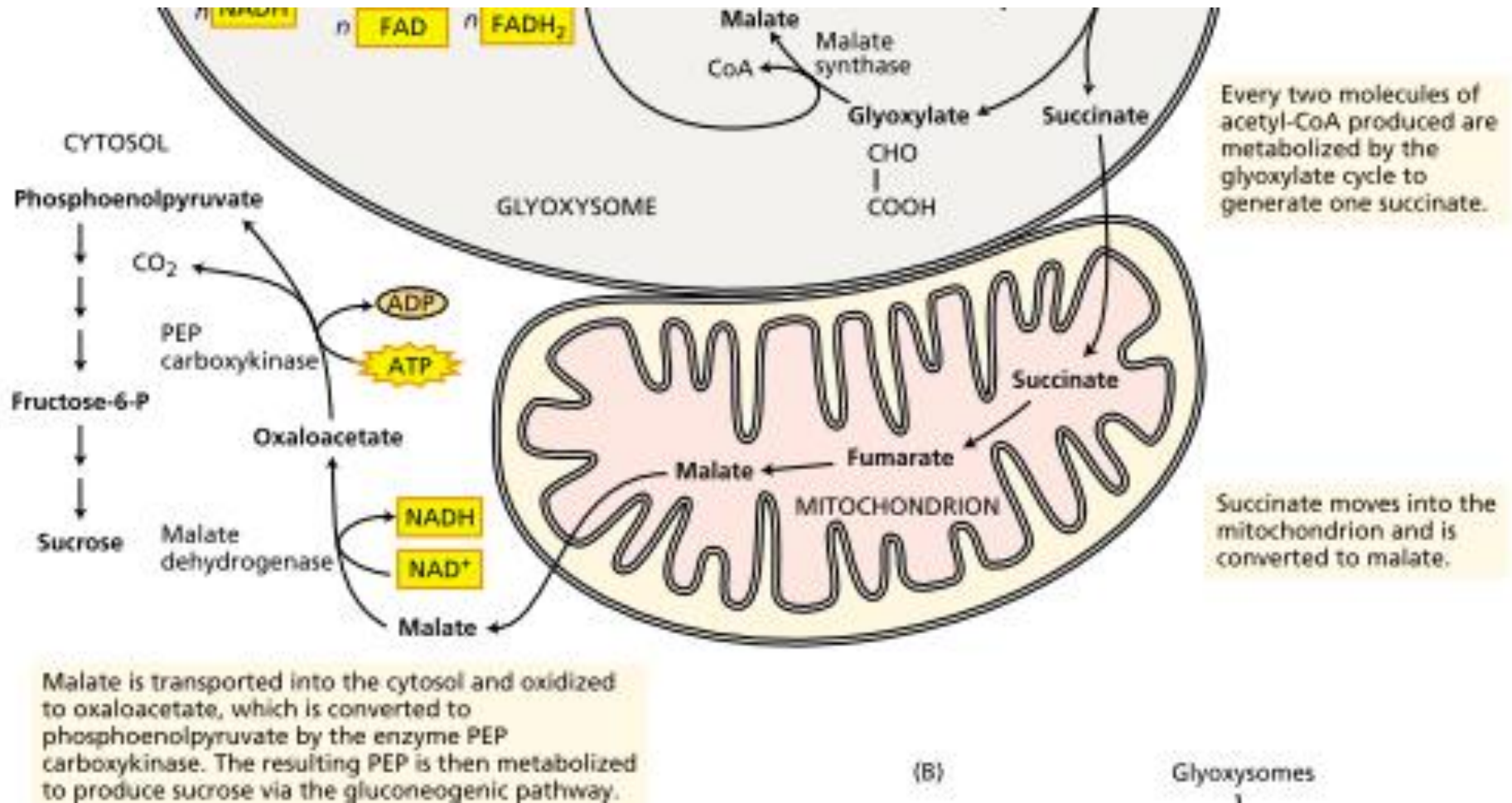Next malate synthase combines a second molecule of acetyl-CoA with glyoxylate to produce malate.

The mitochondrial role

CYTOSOL

Phosphoenolpyruvate

CO_2

ADP

PEP carboxykinase

ATP

Fructose-6-P

Oxaloacetate

Sucrose   Malate dehydrogenase

NADH

NAD+

Malate

n FAD n FADH$_2$

Malate

CoA ← Malate synthase

Glyoxylate ← Succinate

CHO
|
COOH

GLYOXYSOME

Succinate

Malate ← Fumarate

MITOCHONDRION

Every two molecules of acetyl-CoA produced are metabolized by the glyoxylate cycle to generate one succinate.

Succinate moves into the mitochondrion and is converted to malate.

Malate is transported into the cytosol and oxidized to oxaloacetate, which is converted to phosphoenolpyruvate by the enzyme PEP carboxykinase. The resulting PEP is then metabolized to produce sucrose via the gluconeogenic pathway.

(B)   Glyoxysomes

Sucrose is the final product of this process, and the primary form of reduced carbon translocated from the cotyledons to the growing seedling tissues.

Not all seeds quantitatively convert fat to sugar