J1 Photosynthetic pigments and the nature of light

Key Notes

The nature of light

Sunlight is made up of high-energy photons that can energize molecules capable of absorbing their energy. Light can also be described as a wave motion, with the longest wavelengths having the lowest energy.

Photosynthetic pigments

Chlorophyll *a* is the major photosynthetic pigment. It has a porphyrin ring structure containing a central magnesium atom and a long hydrocarbon tail. Accessory pigments pass their harvested energy to chlorophyll *a*. Blue and red light are absorbed most. Absorption of light energizes an electron in the chlorophyll, the energy being transferred to an electron acceptor.

The reaction center

The pigments are grouped into photosystems in the thylakoid membrane. Two reaction center chlorophylls are surrounded by pigment molecules of the antenna complex. Energy harvested by this complex is passed by resonance energy transfer to the reaction center chlorophylls, which pass on the electron to an electron acceptor.

Related topics

Plastids and mitochondria (B3)
Major reactions of photosynthesis (J2)
C3 and C4 plants and CAM (J3)

The nature of light

The energy for **photosynthesis** is derived from sunlight, which originates from the exothermic reactions taking place in the sun. Light has the properties of both a wave motion and of particles (**photons** or **quanta**). The amount of energy contained in a photon is inversely proportional to the wavelength, short wavelengths having higher energy than long wavelengths. In order to photosynthesize, plants must convert the energy in light to a form in which it can be used to synthesize carbohydrate.

Photosynthetic pigments

Plants appear green because **chlorophyll** absorbs blue and red light and reflects green. This can be shown as an **absorption spectrum**, in which absorbance is plotted against wavelength (*Fig. 1*). The **action spectrum** of photosynthesis, i.e. the photosynthetic activity at different wavelengths, is also shown and corresponds to the absorption spectrum.

When a chlorophyll molecule is struck by a photon, it absorbs energy. This energizes an electron within the chlorophyll that may be used in photosynthesis or return to its original energy state with a loss of heat and transmission of light of lower wavelength.

The major photosynthetic pigments are the chlorophylls (*Fig. 2*). A chlorophyll molecule is made up of a 'head' group, a nitrogen-containing **porphyrin**

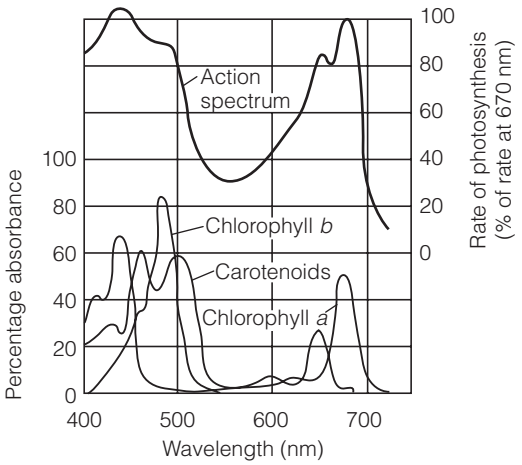


Fig. 1. Absorption spectra of three major pigments of photosynthesis: chlorophyll a, *chlorophyll* b *and carotenoids, together with the action spectrum of photosynthesis. The absorption spectrum represents the degree to which the pigment is able to absorb energy at each wavelength of light; the action spectrum represents rate of photosynthesis at each wavelength (Govindjee, unpublished data, 1961; redrawn with permission of Govindjee, University of Illinois at Urbana, Illinois, USA).*

ring structure, with a **magnesium atom** at its center, and a **tail of hydrocarbons**, which anchors the molecule to a membrane. Chlorophyll *a* is the main pigment of photosynthesis. Most chloroplasts also contain **accessory pigments**, pigments that broaden the range of wavelengths at which light can be absorbed and that pass the energy obtained to chlorophyll *a* or protect against damage. **Chlorophyll *b***, **carotenoids** and **xanthophylls** are examples of these pigments.

The reaction center

To harvest the energy of light, the pigments of photosynthesis must be arranged so that the energy is focused to a point from which it can be used. Energy absorbed by the pigment molecules is transferred to one of a central pair of chlorophyll *a* molecules (termed the **reaction center chlorophylls**) by **resonance energy transfer** (*Fig. 3*). From here, the high energy electron is passed on to an **electron acceptor**. The pigments are arrayed in flat sheets in the thylakoid membrane, orientated to capture the incoming radiation. Each reaction center is surrounded by 200–400 pigment molecules, the **antenna complex**, and the whole structure constitutes a **photosystem**. The thylakoids are stacked in **grana** held within the **stroma** of the chloroplast (Topic B3).

There are two types of photosystem, known as **photosystem I** (**PS-I**) and **photosystem II** (**PS-II**). PS-I was the first to be discovered, and the reaction center chlorophylls in it are known as $\mathbf{P}_{700}$ because they absorb maximally at 700 nm. The reaction center chlorophylls of PS-II absorb maximally at 680 nm ($\mathbf{P}_{680}$). The functions of PS-I and PS-II are explained in Topic J2.

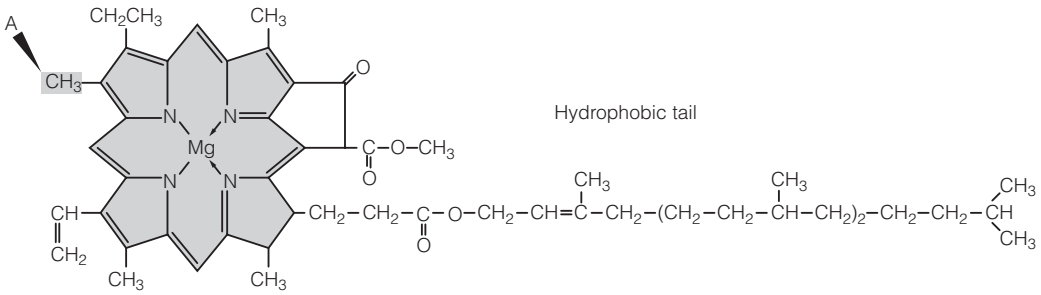


Fig. 2. The structure of chlorophyll. Chlorophyll b *differs from chlorophyll* a *by the substitution of a CHO group for the CH_3 marked at position A.*

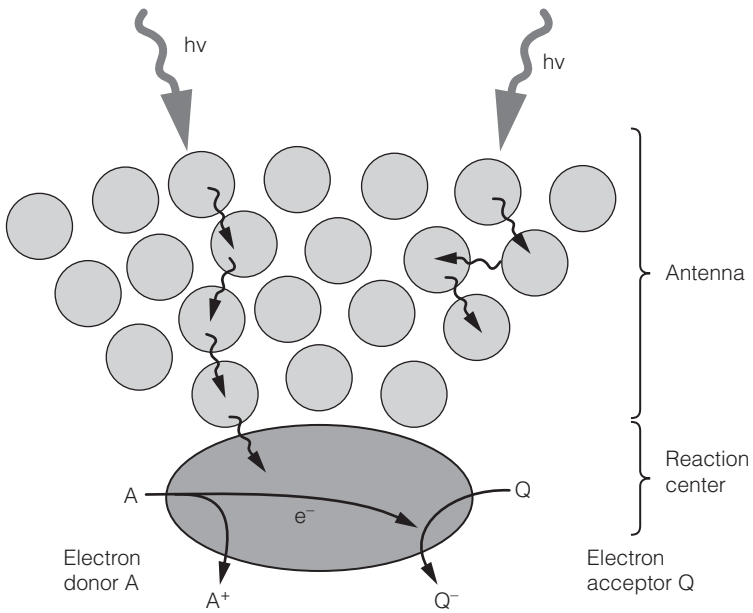


Fig. 3. The reaction center. Chlorophyll and accessory pigments are grouped around a central pair of reaction center chlorophylls. The absorbed energy is collected and conveyed to the central pair of reaction center chlorophylls by resonance energy transfer (RET; arrows). The energized electron from an electron donor, A, in the reaction center is then passed on to an electron acceptor, Q. (Redrawn from Hopkins (1998) Introduction to Plant Physiology*, 2nd Edn, John Wiley & Sons.)*

J2 Major reactions of photosynthesis

Key Notes

The light reactions

The energy of light is used to energize electrons in the reaction center chlorophyll molecules of a photosystem. The electrons are then passed on to an electron transport chain. The missing electrons in the reaction center are replenished when $2H_2O$ is split to O_2 , $4H^+$ and $4e^-$. The electron moves through the electron transport chain until it energizes the cytochrome *b*/*f* complex to pump protons into the thylakoid lumen and is then passed to photosystem I (PS-I) where it is re-energized and passed to NADP reductase, generating NADPH. PS-I can also function alone to transport H^+. Adenosine triphosphate (ATP) is generated by H^+ passing through the enzyme ATP synthase located in the thylakoid membrane. The two products of the light reactions are therefore NADPH and ATP.

The carbon-fixation reactions

The carbon fixation reactions (Calvin cycle) in the stroma of the chloroplast uses ATP and NADPH to fix CO_2 as carbohydrate in a cyclic process which does not directly require light. The cycle involves (i) carboxylation, in which Ribulose bisphosphate carboxylase/oxygenase (Rubsico) carboxylates 5-carbon ribulose bisphosphate using CO_2 to give a transient 6-carbon compound, which forms two molecules of 3-carbon 3-phosphoglycerate; (ii) reduction, where NADPH and ATP are used to form two molecules of glyceraldehyde 3-phosphate; and (iii) regeneration, where one molecule of 3-carbon glyceraldehyde 3-phosphate is converted to 5-carbon ribulose bisphosphate using ATP. Overall, fixation of three molecules of CO_2 requires 6NADPH and 9ATP and leads to the net synthesis for export of one glyceraldehyde 3-phosphate.

Photorespiration

Ribulose bisphosphate carboxylase/oxygenase also has oxygenase activity which generates 3-phosphoglycerate and 2-phosphoglycolate. The overall efficiency of photosynthesis is decreased by about 25% as a consequence. The photorespiratory cycle partially recovers the fixed carbon and involves the peroxisomes and mitochondria. It results in the loss of CO_2 and the use of ATP to convert the 2-phosphoglycolate to 3-phosphoglycerate which is converted to ribulose 1,5-bisphosphate by the Calvin cycle.

Related topics

Plastids and mitochondria (B3)
Photosynthetic pigments and the nature of light (J1)
C3 and C4 plants and CAM (J3)

The light reactions

In photosystem II (PS-II) (Topic J1) a pair of electrons energized by light are passed from the reaction center chlorophyll to an electron transport chain. These

electrons are replaced by a unique process called **photolysis** in which water is oxidized to yield molecular oxygen. The overall reaction, termed the **S state mechanism** is as follows:

$$2H_2O \rightarrow O_2 + 4H^+ + 4\ e^-$$

It requires manganese and is energized by PS-II. The protons generated are released into the lumen of the **thylakoid**. The high energy electrons are captured by an electron acceptor and passed on to the $\mathbf{P_{680}}$ **chlorophyll** (the reaction center chlorophyll in PS-II, having an absorption maximum at 680 nm; Topic J1).

The electrons then move through an **electron transport chain** located in the thylakoid membrane. The first stage is **plastoquinone**, a quinone molecule which is able to move within the membrane. Plastoquinone accepts two electrons and two protons to form PQH_2. The electrons are then passed to the **cytochrome *b*/*f*** complex. This is a proton pump and pumps H^+ into the **thylakoid lumen** (*Fig. 1*). The electron is then transferred to **plastocyanin**, a copper-containing protein that accepts electrons, by the copper cycling between Cu^{2+} and Cu^+ that then supplies it to **PS-I**. It is energized again by light and transported by another electron acceptor, **ferredoxin**, a protein. The electron is then passed on to the enzyme nicotinamide adenine dinucleotide phosphate (**NADP**) **reductase**, that reduces $NADP^+$ to nicotinamide adenine dinucleotide phosphate (reduced form; NADPH). Overall, two photons absorbed by PS-II result in: the oxidation of a water molecule to give O_2 and the release of H^+ into the lumen of the thylakoid; the formation of NADPH by the reduction of $NADP^+$; and the transport of H^+ into the lumen of the thylakoid via the cytochrome *b*/*f* complex. The process, known as **non-cyclic electron flow**,

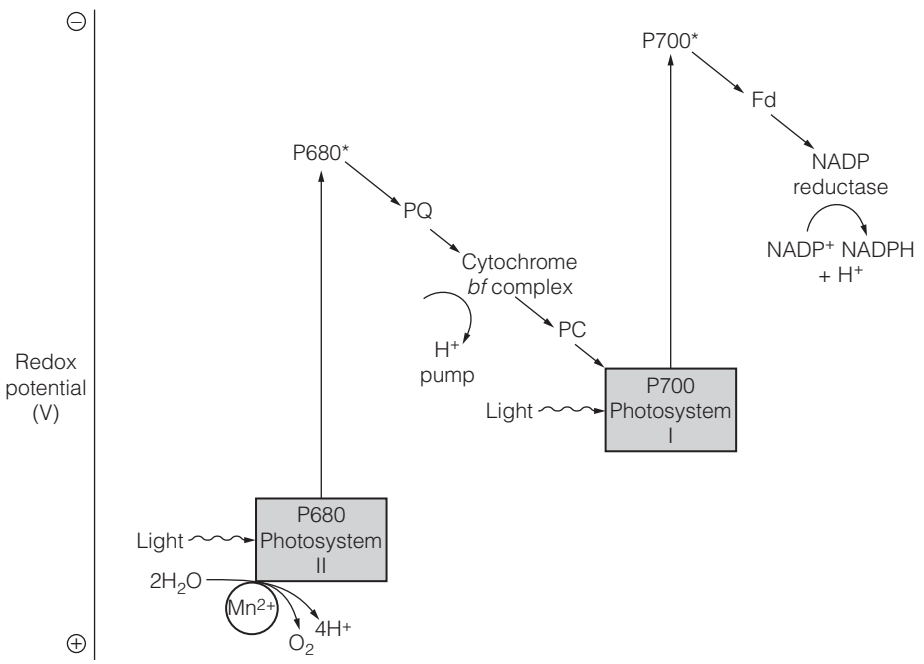


Fig. 1. The Z-scheme of non-cyclic photophosphorylation.

produces NADPH and a proton gradient across the thylakoid membrane. NADPH is used directly in the **Calvin cycle** (below). The proton gradient is used to drive **adenosine triphosphate** (**ATP**) **synthase**, the enzyme that makes ATP.

The second photosystem, PS-I, can work independently of PS-II. This occurs when electrons are transferred from cytochrome *b/f* back to P_{700} via plastocyanin and re-energized by light. This process, termed **cyclic electron flow** is illustrated in *Fig. 2*. As the electrons never reach NADP reductase, the system only generates a proton gradient.

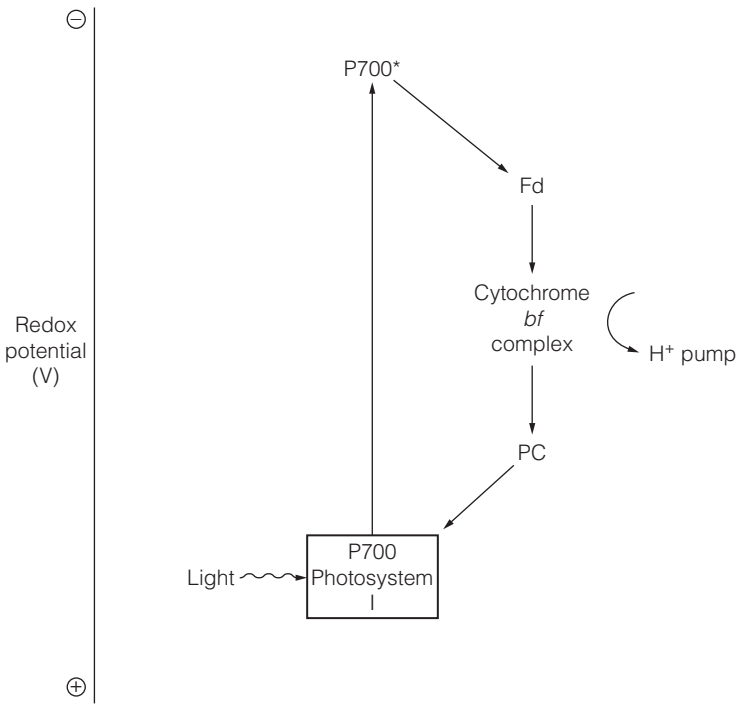


Fig. 2. Cyclic phosphorylation in green plants.

ATP is produced by **ATP synthase** (*Fig. 3*). This is a large protein complex located in the thylakoid membrane. As the protons flow down the electrochemical gradient from the thylakoid lumen into the stroma, the energy is used to synthesize ATP by the phosphorylation of adenosine diphosphate (ADP) by the ATP synthase complex. ATP synthesis driven by cyclic electron flow (PS-I only) is termed **cyclic photophosphorylation**, while ATP synthesis driven by non-cyclic electron flow (PS-I and PS-II) is **non-cyclic photophosphorylation**.

The carbon-fixation reactions

The next stages of photosynthesis do not require light and are termed the **carbon-fixation reactions**. They do require the ATP and NADPH generated by the light reactions and result in the incorporation (fixation) of carbon into carbohydrates. The carbon-fixation reactions in many plants occur in the stroma of the chloroplast by the Calvin cycle.

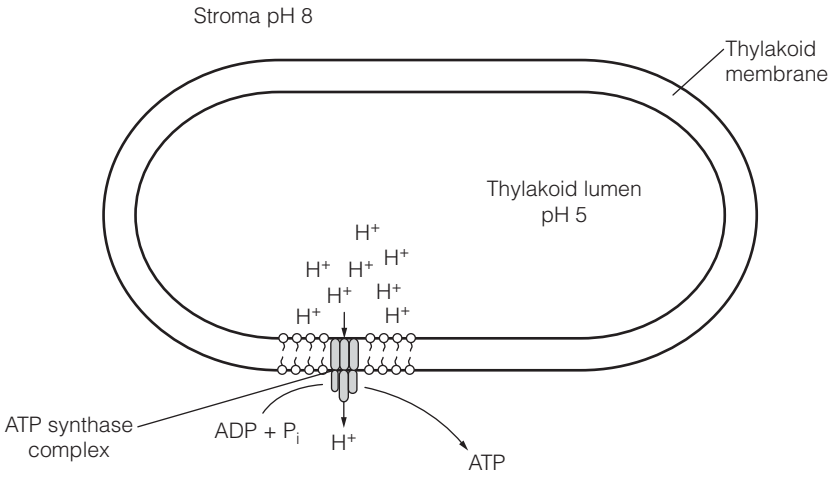


Fig. 3. ATP synthase.

The Calvin cycle

The **Calvin cycle** has three stages: **carboxylation**, the incorporation of CO_2; **reduction**, utilizing ATP and NADPH; and **regeneration** where the CO_2 acceptor is formed again. The entire cycle, together with the number of moles of each molecule produced and the number of moles of ATP and NADPH used is shown in *Fig. 4*.

Stage 1: Carboxylation

$$\text{Ribulose bisphosphate (5C)} + CO_2 \rightarrow 2 \times \text{3-phosphoglycerate (3C)}$$

In this stage, a carbon atom from CO_2 is added to one molecule of **5-C ribulose bisphosphate** by the enzyme **ribulose bisphosphate carboxylase/oxygenase** (**Rubisco**) to yield two molecules of **3-C 3-phosphoglycerate**. The enzyme is the world's most abundant protein, often constituting around 40% of the soluble protein in a leaf. Rubisco is a **CO_2 acceptor**, which binds with sufficient affinity to ensure carboxylation of ribulose 1,5-bisphosphate. The reaction is energetically favourable, so the cycle runs in favor of 3-phosphoglycerate without additional energy input.

Stage 2: Reduction

$$\text{3-phosphoglycerate (3C)} \rightarrow \text{1,3-bisphosphoglycerate (3C)} \rightarrow \text{glyceraldehyde 3-phosphate (3C)}$$

The process involves two enzymes, **3-phosphoglycerate kinase** and **NADP glyceraldehyde-3-phosphate dehydrogenase**. In the first enzymatic reaction, one mole of ATP is used and in the second, one mole of NADPH is used for each mole of 3-phosphoglycerate. **Glyceraldehyde-3 phosphate** is a 3-carbon sugar, some of which is used in the next stages of the cycle and some removed as the product of the cycle (*Fig. 4*).

Stage 3: Regeneration

Regeneration involves the steps from glyceraldehyde-3-phosphate to ribulose 1,5-bisphosphate. Most of the stages are energetically favourable and do not

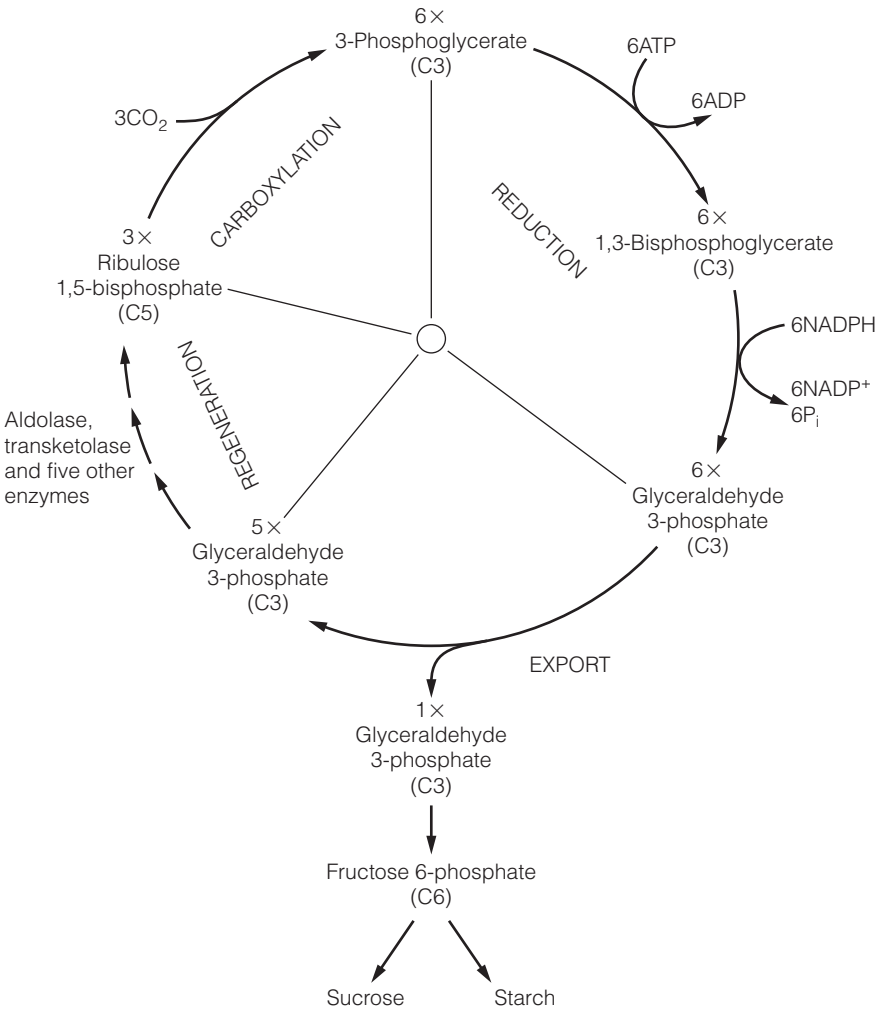


Fig. 4. Key stages of the Calvin cycle.

consume further ATP or NADPH. The pathway involves the activity of seven enzymes in total. Finally, ribulose 5-phosphate (5C) is produced, which is phosphorylated by the enzyme **ribulose 5-phosphate kinase** using ATP to generate ribulose 1,5-bisphosphate (5C) ready for carboxylation.

Photorespiration

Rubisco can either carboxylate ribulose bisphosphate, giving 3-phosphoglycerate or can oxygenate it to give a 2-carbon sugar 2-phosphoglycolate and a 3-carbon sugar 3-phosphoglycerate (*Fig. 5*). In equal concentrations of CO_2 and O_2, carboxylation is favored over oxygenation by about 80:1; however, at ambient CO_2 concentrations, the ratio falls to 3:1. The rate of assimilation of carbon by a leaf is therefore the result of two opposing pathways; the Calvin cycle and photorespiration**.** The overall effect of photorespiration is a reduction of about 25% in carbon assimilation.

3-phosphoglycerate is salvaged for carboxylation by the Calvin cycle (see above), but recovery of the phosphoglycolate requires the enzymes of the

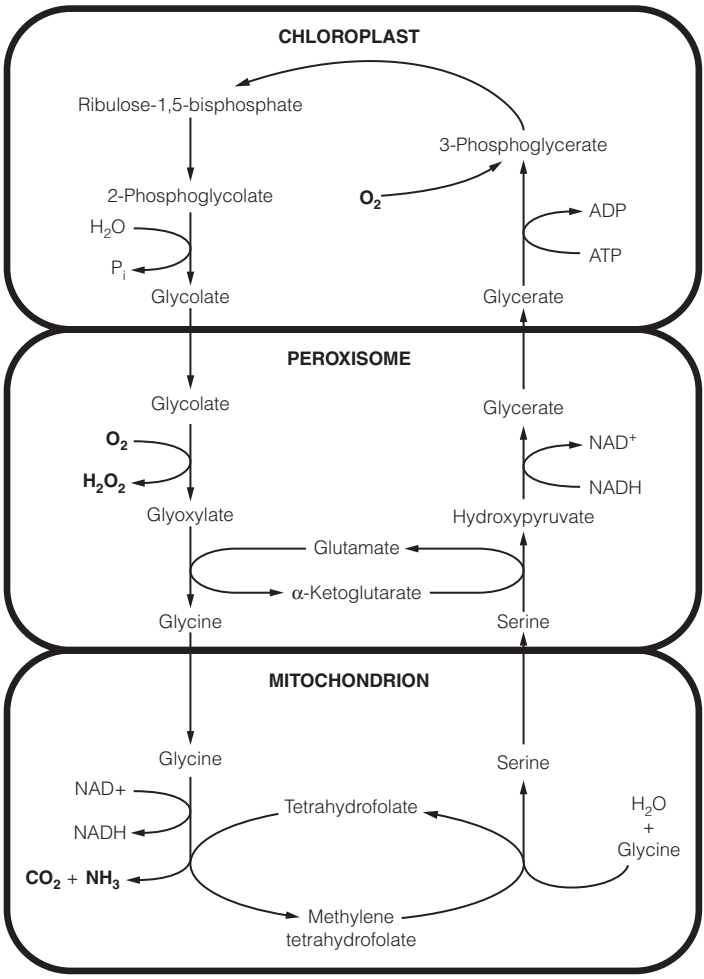


Fig. 5. The photorespiratory carbon oxidation cycle.

photorespiratory cycle which are located in peroxisomes (Topic B1) and mitochondria (Topic B3). The stages are shown in *Fig. 5*. Overall, the pathway consumes oxygen and ATP; equal amounts of NADH are used up in the peroxisome and produced in the mitochondrion.

The function of photorespiration is unknown; it may be a consequence of the structure and reaction mechanism of Rubisco; alternatively, it may be a safety mechanism to protect the photosystems in conditions where light intensity is high and carbon dioxide low. Some plants show a modified form of photosynthesis termed C4 in which photorespiration does not occur (Topic J3).

J3 C3 AND C4 PLANTS AND CAM

Key Notes

CO_2 concentration and water conservation

Land plants have to open their stomata to admit CO_2. This means water loss is inevitable while photosynthesis occurs. Atmospheric concentrations of CO_2 do not saturate Rubisco and it therefore functions at less than its maximal rate. C4-photosynthesis and crassulacean acid metabolism (CAM) are two adaptations which decrease water loss.

C4 anatomy

C4 plants show Krantz anatomy, a ring of bundle-sheath cells containing chloroplasts surrounding the leaf veins. Surrounding mesophyll cells also contain chloroplasts and are in close contact with the bundle sheath cells by plasmodesmata.

C4 biochemistry

C4 plants carry out the functions of the Calvin cycle in the bundle sheath cells. Rubisco in these cells is supplied with CO_2 released from the C4 compounds malic acid or aspartic acid generated in the mesophyll cells and transported through the plasmodesmata. CO_2 is first fixed by phosphoenolpyruvate (PEP)-carboxylase, which has a high affinity for HCO_3^-. The effect of the system is to increase the efficiency of CO_2 fixation and reduce the requirement for stomatal opening.

CAM anatomy

CAM plants show adaptations to drought and are succulents, having fleshy leaves with a minimum surface area to volume ratio. The photosynthetic cells have a substantial vacuole in which C4 acids are stored.

CAM biochemistry

In CAM plants, the stages of CO_2 fixation by PEP-carboxylase and of the Calvin cycle occur in the same cells but at different times. CO_2 is fixed at night and the C4 compounds formed are stored in the leaf cell vacuole. The C4 compounds break down to release CO_2 during the day permitting the Calvin cycle to function when stomata are closed.

Distribution of CAM and C4 photosynthesis

Both C4 and CAM are adaptations to drought occurring in a wide range of species and families, generally from arid zones. Some families of plants contain C3, C4 and CAM members.

Related topics

Plants and water (I1)
Water retention and stomata (I2)
Major reactions of photosynthesis (J2)

CO_2 concentration and water conservation

Land plants have a dilemma: allowing a free diffusion of CO_2 into leaf cells without excessive water loss. The plant's environment is often most desiccating when light intensities are highest, meaning that stomata close during times when CO_2 could be used most effectively. In addition, the photosynthetic

apparatus of many plants showing **C3 photosynthesis**, the type of photosynthesis described in Topic H2 (so called because its first stage involves formation of two C3 sugars) operates maximally at CO_2 concentrations above that found in the atmosphere. Two adaptations have been described which minimize water loss and maximize CO_2 usage; they are known as the **C4-syndrome** (**C4 photosynthesis**), so called because CO_2 is fixed to give 4-carbon compounds, and **crassulacean acid metabolism** (**CAM**).

C4 anatomy

In a typical C3 leaf, the majority of chloroplasts are distributed throughout the palisade mesophyll (below the epidermis) and the spongy mesophyll. These cells are somewhat randomly arranged between large gas-spaces that connect to the stomatal pores (Topic C4). In the leaf of a C4 plant, the vascular bundles are surrounded by a ring of **bundle-sheath cells** containing chloroplasts. These are surrounded by loosely packed mesophyll cells and air-spaces (Topic C5). This is known as **'Krantz' anatomy** (German for 'a wreath'). The bundle-sheath and mesophyll cells are interconnected by many plasmodesmata (Topic B1) and no bundle sheath cell is separated by more than a few cells from a mesophyll cell.

C4 biochemistry

In a C4 leaf, the first product of CO_2 fixation is a **4-carbon acid**. This is produced by the action of an additional cycle, the **Hatch/Slack pathway**, found in the mesophyll cells. The first stage of this pathway is catalyzed by the enzyme **phosphoenolpyruvate** (**PEP**) **carboxylase**. PEP-carboxylase uses $\mathbf{HCO_3^-}$ (formed when CO_2 dissolves in the cytoplasm) and **PEP** as substrates, yielding the C4 acid **oxaloacetate** which is converted to either **malate** or **aspartate** (both C4 acids) and they are transported directly to the bundle sheath cells, where the C4 acid is decarboxylated to yield a C3-acid and CO_2. At this stage, the CO_2 released is fixed by the Calvin cycle and the C3 acid transported back to the mesophyll cell (*Fig. 1*). The system therefore functions as a C3 pathway to which a 'CO_2 concentrator' has been added, transporting CO_2 into the bundle sheath cells, and generating a high CO_2 environment for Rubisco. The system has two major effects. First, it reduces photorespiration to undetectable levels as the Rubisco is saturated with CO_2 giving conditions in which its oxygenase function is inhibited (Topic J2). This improves photosynthetic efficiency by up to 30%. Second, Rubisco is able to function at optimal CO_2 concentrations, well above atmospheric levels. PEP-carboxylase is also saturated at the concentration of HCO_3^- in the cytosol which results from atmospheric CO_2.

There is an energy cost to C4, however. The regeneration of the C3 acid PEP from the C3-acids transported requires the consumption of adenosine triphosphate (ATP) with the cleavage of both phosphates to yield adenosine monophosphate (AMP).

CAM anatomy

CAM plants are generally adapted to survive drought; they are succulents with fleshy leaves and few air spaces. Unlike C4 plants, they lack the physical compartmentation of photosynthesis into two cell types, but instead fix CO_2 in the night as C4 acids that are stored in a vacuole which occupies much of their photosynthetic cells' volume. The stomata of CAM plants are closed during the most desiccating periods of the day and are open at night.

CAM biochemistry

In common with C4 plants, the first stage of CO_2 fixation in a CAM plant involves PEP-carboxylase, which incorporates CO_2 into a C4-compound, oxaloacetate, in the dark. NADPH is used in the conversion of oxaloacetate to

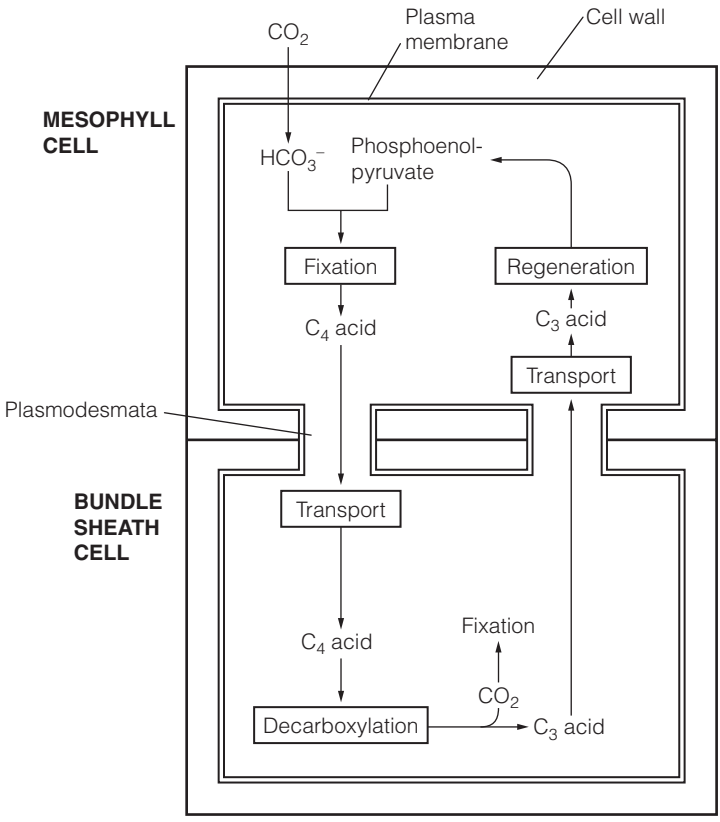


Fig. 1. Photosynthesis in C4 plants. Carbon is fixed from HCO_3^- in the mesophyll cells by PEP-carboxylase to produce C4 acids. These are transported to the bundle sheath cells, where they are broken down to release CO_2 which is fixed by the Calvin cycle. C3 acids produced are returned to the mesophyll cells, where they are converted to phosphoenol-pyruvate with the consumption of ATP.

malate; malate is then stored in the vacuole (*Fig. 2*). In the light, malate is released from the vacuole and broken down to yield CO_2, which is then used in the Calvin cycle. CAM photosynthesis eliminates photorespiration and increases efficiency, though losses result from the energy expended in transporting C4 acids to the vacuole and in the formation of malate. CAM plants may have a major advantage in drought conditions, with the ability to photosynthesize in daylight with closed stomata.

Distribution of CAM and C4 photosynthesis

The C4 syndrome occurs in many plant families. The syndrome is most common in arid environments. C4 plants are distributed throughout the world and C4 crops such as maize have been successfully introduced into temperate climates. C4 plants are found in a number of families (*Table 1*), but by no means all the members of those families are C4 species. CAM plants are similarly distributed in many families, mostly succulents and are distributed in arid zones throughout the world. Some families contain C3, CAM and C4 species. Although there appears to be an advantage to C4 and CAM, many arid zone plants are C3 and use other adaptations to survive.

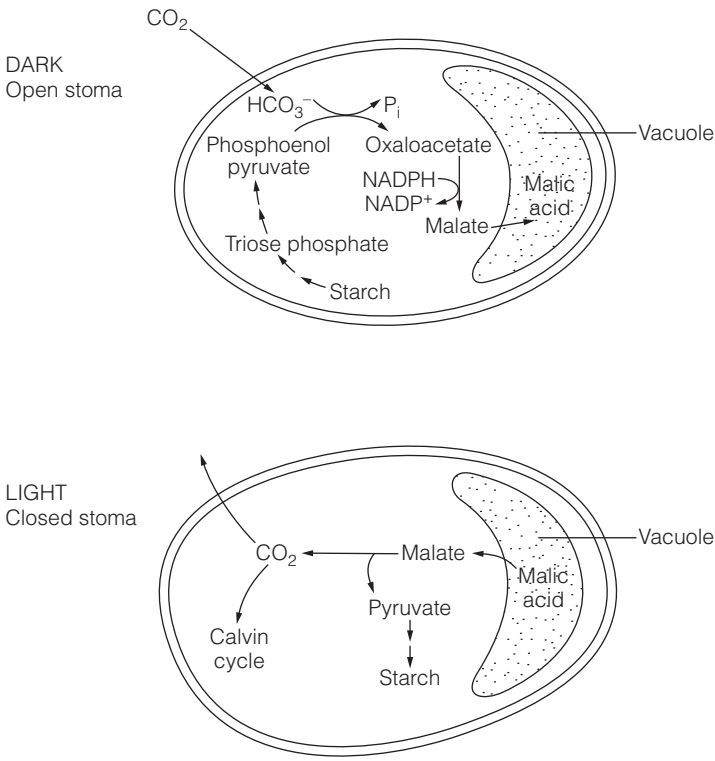


Fig. 2. CAM plants use PEP-carboxylase to fix carbon as a C4 compound. However, carbon fixation and the operation of the Calvin cycle are separated temporally, rather than spatially. C4 acids are synthesized in the dark and deposited in the vacuole. In the day, the C4 compounds are released to supply CO_2 to the Calvin cycle that can function with the stomata fully closed.

Table 1. Examples of C4 and CAM plants

Family	Common examples
C4 plants	
Amaranthaceae	Amaranths
Asteraceae	Asters and daisies
Euphorbiaceae	Euphorbias
Poaceae	Grasses including corn (maize), sugarcane and sorghum
Nyctaginaceae	Bougainvillea
CAM plants	
Agavaceae	Agaves
Asteraceae	Asters and daisies
Cactaceae	Cacti
Crassulaceae	Crassulas
Euphorbiaceae	Euphorbias
Liliaceae	Lilies
Orchidaceae	Orchids
Vitaceae	Grape vines

J4 Respiration and carbohydrate metabolism

Key Notes

Starch degradation

Starch is the major carbohydrate storage product of most plants. It is broken down to 6-carbon sugars by either hydrolytic or phosphorolytic enzymes. Products are exported from the chloroplast to the cytosol for glycolysis.

Glycolysis

Glycolysis breaks glucose (6C) to two molecules of pyruvate (3C). Two molecules of ATP are used and four formed, giving a net yield of 2ATP and 2NADH. In anaerobic conditions, pyruvate is fermented to ethanol and carbon dioxide, with no further ATP production and use of the NADH.

The citric acid cycle

In aerobic conditions, pyruvate binds to coenzyme A (CoA) and enters the citric acid cycle as acetyl CoA. In total, the 3C sugar yields three CO_2, one ATP, three NADH and one $FADH_2$. As each glucose molecule supplies two 3C sugars, it takes two turns of the cycle to fully oxidize glucose.

The electron transport chain

NADH and $FADH_2$ supply energized electrons to the electron transport chain in the mitochondrial inner membrane. The electrons are carried through the chain and result in the pumping of protons across the membrane, giving a proton gradient, which is used to drive the enzyme ATP synthase, which generates ATP by oxidative phosphorylation. In all, about 12 ATP molecules are formed per glucose.

Sources and sinks

Tissues which are net suppliers of carbohydrate to the plant are known as sources; those which are net consumers are sinks. Young leaves are sinks, but become sources when mature. Storage organs are major sinks in a mature plant.

Phloem transport

Phloem transport is driven by a pressure gradient. Active loading of assimilates at the source creates a high solute concentration in the phloem, which results in water influx, creating a high hydrostatic pressure. Assimilate unloading at the sink tissue is accompanied by efflux of water, creating a low hydrostatic pressure. Loading is an active process. Assimilates unload down a concentration gradient maintained by the constant metabolism and incorporation of assimilates into storage reserves at the sinks.

Related topics

Plastids and mitochondria (B3)

Amino acid, lipid, polysaccharide and secondary product metabolism (J5)

Starch degradation

The chief carbohydrate storage products from photosynthesis are **sugars** and **starch**. These are respired by plant cells to provide ATP. **Respiration** occurs in all cells, whether photosynthetic or not. Starch is made up of glucose polymers, either as long, straight chain molecules, **amylose**, or in highly branched form, **amylopectin**. Starch is mostly deposited in plastids. *Fig. 1* shows the two major pathways for starch breakdown, either involving hydrolytic enzymes,

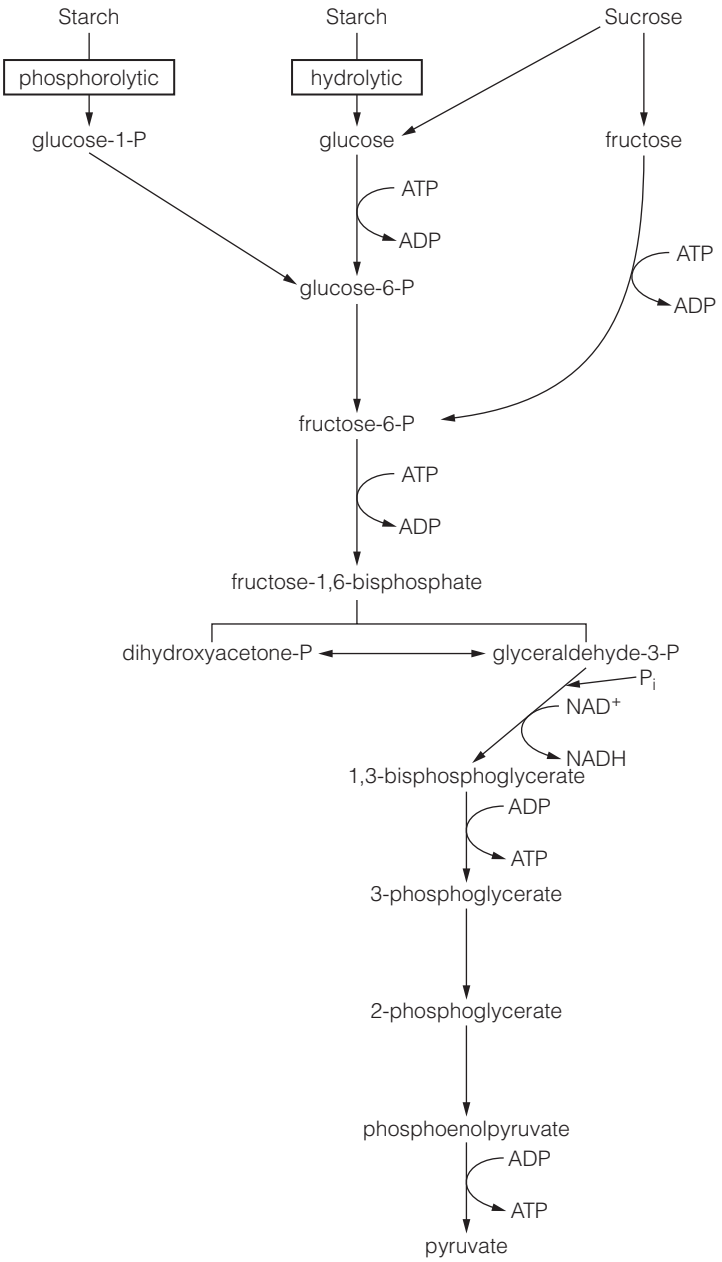


Fig. 1. The major pathways of starch degradation in a plant cell, involving either hydrolytic or phosphorylytic enzymes. All pathways lead into glycolysis.

α-amylase, dextrinase, α-glucosidase or phosphorolytic enzymes, starch phosphorylase. Starch breakdown occurs initially in the plastid. The products are exported to the cytoplasm by a glucose transporter and a triose-P transporter in the chloroplast envelope.

Glycolysis

Glycolysis occurs in the cytoplasm without the consumption of oxygen. The products of starch breakdown, or sucrose, must be converted to a 6-carbon sugar phosphorylated at both ends for glycolysis. This 6-carbon sugar is **fructose 1,6-bisphosphate**; it is produced by the enzyme **aldolase** which adds a phosphate group taken from ATP to fructose-6-P (*Fig. 1*). Production of fructose 1,6-bisphosphate consumes two molecules of ATP.

Fructose 1,6-bisphosphate is cleaved into **two 3-carbon sugars**, each having one phosphate: **dihydroxyacetone-P** and **glyceraldehyde-3-P**. They are readily interconvertible and glyceraldehyde-3-P is then phosphorylated again to generate **1,3-bisphosphoglycerate**, a 3-carbon sugar with phosphate at both ends. This step generates NADH and requires inorganic phosphate. The 1,3-bisphosphoglycerate is then converted to **pyruvate** in stages which yield two molecules of ATP (four per initial glucose as each 6-carbon glucose has generated two 3-carbon sugars). The net ATP yield from glycolysis is therefore two molecules (four produced, two consumed) per molecule of glucose.

In the presence of oxygen, pyruvate is respired in the citric acid cycle (see below) in the mitochondrion. In anaerobic conditions (for instance in a root in flooded soil) it is **fermented** to yield carbon dioxide and ethanol. NADH is oxidized to NAD^+, recycling the NADH produced in glycolysis. The total yield of anaerobic respiration is therefore limited to two ATP molecules per molecule of glucose (*Table 1*).

The citric acid cycle

The next stage of respiration, the **citric acid cycle** (sometimes known as the **Krebs cycle**) requires oxygen and occurs in the mitochondrion (*Fig. 2*). Its substrate is the pyruvate generated by glycolysis. **Pyruvate** is combined with **coenzyme A** (**CoA**) to generate **acetyl CoA** and liberate CO_2. The 2C compound is combined with **4C oxaloacetate** to generate **6C citrate**. CoA is released for reuse. Citrate is converted back to oxaloacetate in seven stages, with the production of one ATP, three NADH and one flavin adenine dinucleotide (reduced form; $FADH_2$). The cycle also liberates two CO_2; the pyruvate is therefore completely oxidized to yield three molecules of CO_2 and all the energy of the C-C bonds liberated.

Table 1. The maximum overall energy yield from the oxidation of one molecule of glucose

	Cytosol	Matrix of mitochondrion	Electron transport and ATP synthesis	Total
Glycolysis	2ATP			2ATP
	2NADH		4ATP	4ATP
Pyruvate to acetyl CoA		2NADH	6ATP	6ATP
Citric acid cycle		2ATP		2ATP
		6NADH	18ATP	18ATP
		$2FADH_2$	4ATP	4ATP
Total				36ATP

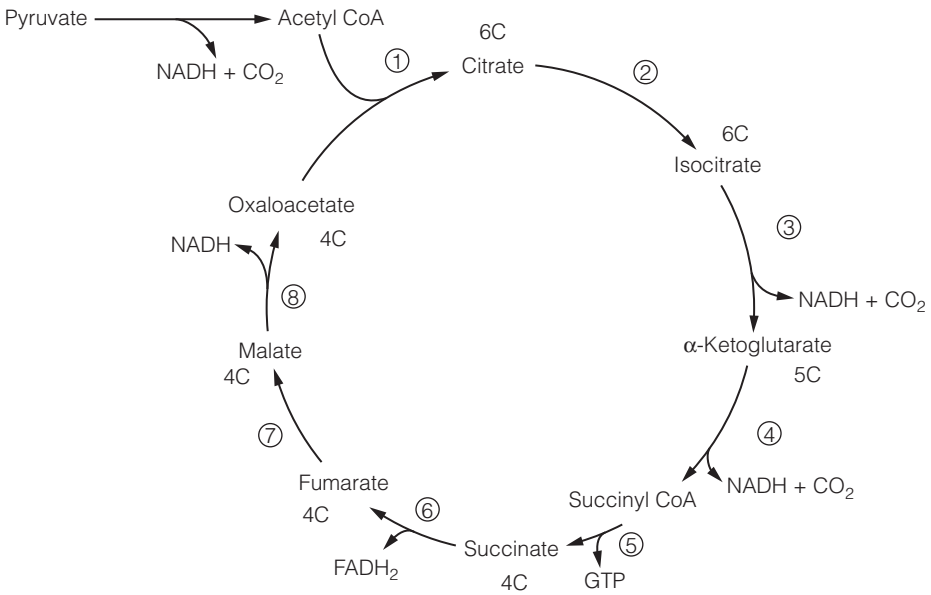


Fig. 2. The citric acid cycle. Two carbons enter the cycle as the acetyl group of acetyl CoA and two carbons are released (as CO_2). NADH and $FADH_2$ are generated. The steps involve the following enzymes: (1) citrate synthase; (2) aconitase; (3) isocitrate dehydrogenase; (4) α-ketoglutarate dehydrogenase; (5) succinyl CoA synthase; (6) succinate dehydrogenase; (7) fumarase; (8) malate dehydrogenase.

The electron transport chain

The mitochondrial **electron transport chain** generates **ATP** from the products of the citric acid cycle. In it, electrons removed from glucose are transported through a series of electron carriers located in the mitochondrial inner membrane until they react with protons and oxygen to give water. As the electrons pass through the electron transport chain, protons are pumped into the intermembrane space, generating a proton-motive force that then drives the synthesis of ATP. The key components of the electron transport chain are illustrated in *Fig. 3a*. Finally, the proton motive force is used to synthesize ATP from ADP by **ATP-synthase** (*Fig. 3b*). This process is known as **oxidative phosphorylation**.

Sources and sinks

Carbohydrate is exported from the photosynthetic tissue of the plant via the phloem. Net exporters are **source tissues**. Tissues which are net consumers or accumulating stores are **sink tissues**. Plants use a variety of storage products, including starch, protein and oils (lipids). All these storage products are produced in pathways originating from intermediates in glycolysis and the citric acid cycle. Major sink tissues include storage organs such as tubers, seeds and fruits. Newly growing tissues, including young leaves, are also sink tissues; a leaf will develop from being a sink to a source as the balance between energy requirements for growth and export from photosynthesis changes.

Phloem transport

Sugars move rapidly (0.05–0.25 m h^{-1}) in the phloem (Topic C1 details the structure of phloem). Movement may be **bi-directional** in the same group of tubes. The best model to describe phloem transport is the **pressure-flow model**. It is proposed that the driving force for transport in the phloem results from an osmotic gradient between the source and the sink ends of the tube. *Fig. 4* shows

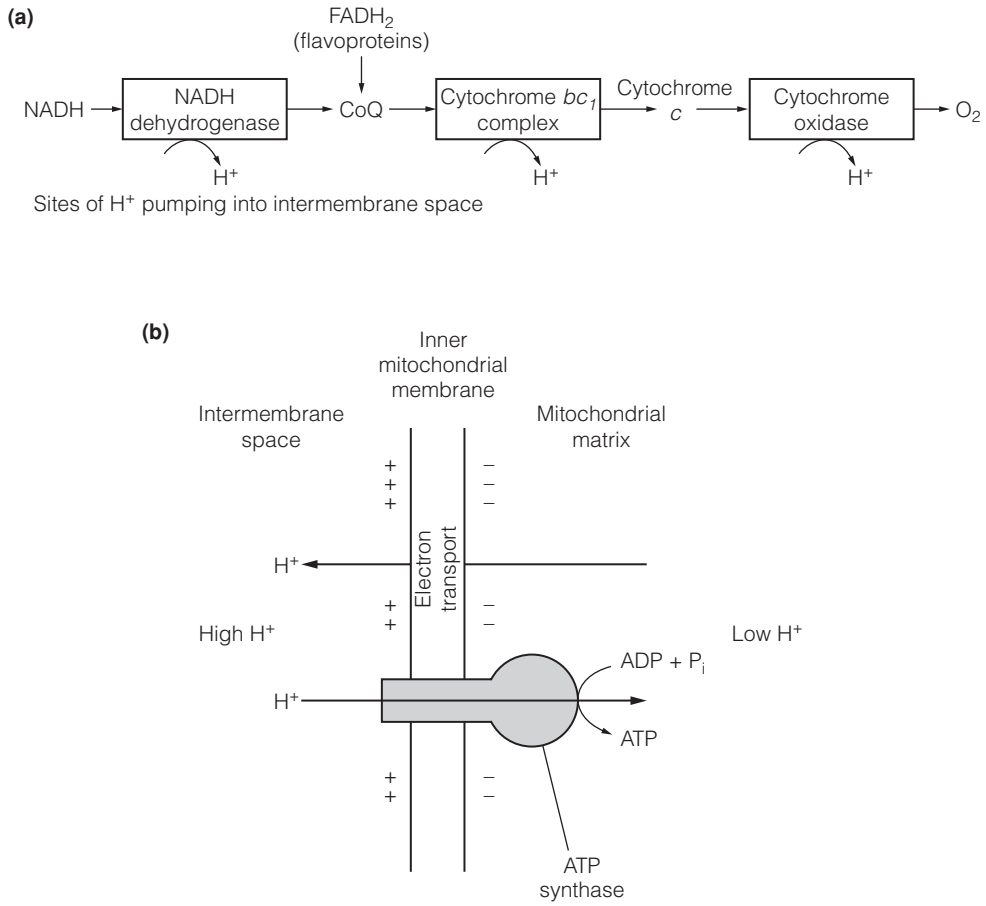


Fig. 3. ATP generation in the mitochondrion. (a) As electrons pass through the electron transport chain, protons (H^+) are transported out of the mitochondrial matrix and into the intermembrane space. (b) The energy stored in the resulting proton gradient across the membrane is used to generate ATP as protons flow through the ATP synthase complex.

the predicted development of the turgor gradient that drives transport. The presence of sieve plates and the associated **P-protein** that seals the sieve plate if the tube is damaged helps to maintain the pressure gradient.

The key processes in phloem transport are **loading** and **unloading**, which create the pressure gradient. Sugars are concentrated in the phloem by active transport; a proton-pumping ATPase establishes a proton gradient and sucrose is carried into the companion cells/phloem by a sucrose/proton cotransporter (Topic I3). Phloem unloading also requires metabolic energy; sucrose may leave the phloem passively and be converted to glucose and fructose by the enzyme **acid invertase**, in which case glucose and fructose will be transported into the sink; alternatively, sucrose may leave the phloem, either via **plasmodesmata** or via a **sucrose transporter**. If the sugars are rapidly metabolized within the sink (e.g. to form starch), a concentration gradient favoring sink loading will be maintained.

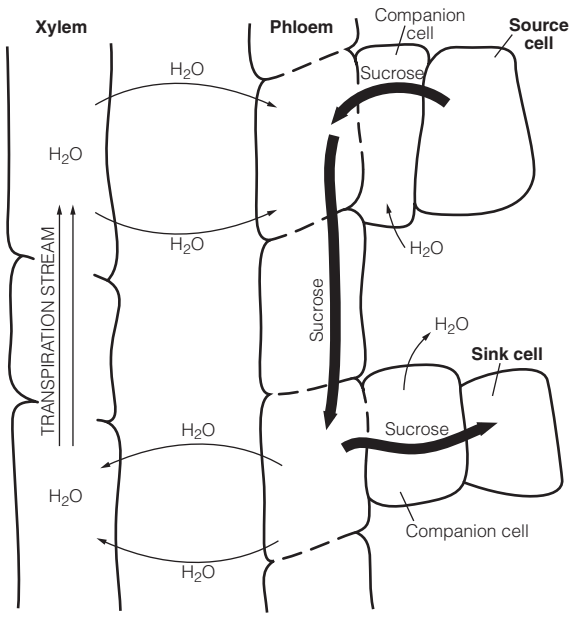


Fig. 4. Transport in the phloem. Sucrose is actively loaded into the companion cells and phloem tubules by sucrose/proton co-transporters. This increases the solute concentration resulting in an influx of water, generating a high turgor pressure at the site of loading. Sucrose is removed at the sink tissue giving a low turgor pressure.

J5 Amino acid, lipid, polysaccharide and secondary product metabolism

Key Notes

Role of the citric acid cycle

Acetyl CoA, pyruvate and citric acid cycle intermediates are the starting point for the production of amino acids, lipids, polysaccharides and secondary products in plant metabolism.

Amino acid biosynthesis

Production of amino acids is linked to the assimilation of nitrogen by the plant. Nitrate is converted to ammonium by nitrate reductase and ammonium is then incorporated into glutamine and glutamate, either by the glutamine synthase-glutamate synthase (GS-GOGAT) pathway or by glutamate dehydrogenase (GDH). Ammonium is toxic and is converted to organic nitrogen compounds in the root. Nitrate may be converted to ammonium in the roots, or is carried to shoots and leaves and either stored in the vacuole or converted to ammonium. Other amino compounds are formed by transamination reactions.

Lipid biosynthesis

Plants synthesize a wide variety of lipids, including membrane lipids, cuticular waxes and seed storage lipids (mostly triacylglycerols). Synthesis of glycerolipids occurs in two stages: addition of the fatty acid chains to glycerol-3-phosphate and addition of a head group. Triacylglycerols consist of a glycerol to which three fatty acid chains have been added and are synthesized in the endoplasmic reticulum. They are stored in oil bodies, small lipid droplets with a surrounding coating of lipid and protein.

Sucrose, polysaccharides and starch

Plant cells produce monosaccharides, from 3-carbon trioses to 6-carbon hexoses. Sucrose is a disaccharide, made of glucose and fructose. Starch is a polysaccharide made up of α-(1–4) and α-(1–6) branched D-glucose residues. Cellulose is made up of β-D-glucose. Sucrose is synthesized in the cytoplasm either by sucrose phosphate synthase and sucrose phosphate phosphatase or by sucrose synthase.

Plant secondary products

A secondary product is one that is not involved in primary metabolism. They are generally produced in specialized tissues, with highly developed multi-enzyme pathways for their production. Plant secondary products include alkaloids, terpenoids and phenolic compounds. Many are involved in plant defenses against herbivory or fungal pathogens; others are of economic importance as medicinal and industrial compounds.

Related topics

Respiration and carbohydrate metabolism (J4)

Plant cell and tissue culture (O2)
Functions of mineral nutrients (I5)

Role of the citric acid cycle

Fig. 1 illustrates that **pyruvate**, **acetyl CoA** and the **citric acid cycle** (Topic J4) are central in the production of many compounds. The activity of each of the pathways depends on substrate availability (usually monosaccharide) and on the tissue. As the pathways are often complex and involve many enzymes, initiating secondary product metabolism involves the developmental activation of many genes. Such gene expression and the production of secondary metabolites may be enhanced by stress, wounding, pathogen attack and herbivory.

Amino acid biosynthesis

Production of **amino acids** and other nitrogen-containing compounds is directly linked to the assimilation of nitrogen by the plant. **Nitrogen** is taken up as either nitrate or ammonium, the nitrate being converted by nitrate reductase into ammonium. **Ammonium** is incorporated into **glutamine** and **glutamate**, either by the **glutamine synthase-glutamate synthase (GS-GOGAT)** pathway or by **glutamate dehydrogenase** (**GDH**) (Topic I5). Ammonium is toxic and is converted to organic nitrogen compounds in the root. Nitrate is converted to ammonium in the roots, or carried to shoots and leaves and either stored in the vacuole or converted to ammonium there.

Roots have **glutamine synthase** (**GS**) in cytosol and plastids. Root plastids also have glutamate synthase that uses NADH as electron donor (**NADH-GOGAT**). If a root is supplied with nitrate, expression of **ferredoxin-dependent** (**Fd**)**-GOGAT** in plastids is induced.

Shoots have GS in the cytosol and chloroplasts. The chloroplast form takes ammonium generated by photorespiration, preventing it becoming toxic. Shoots and leaves express Fd-GOGAT in chloroplasts. Chloroplasts of shoots and leaves also contain GDH which synthesizes glutamate from ammonium and 2-oxoglutarate.

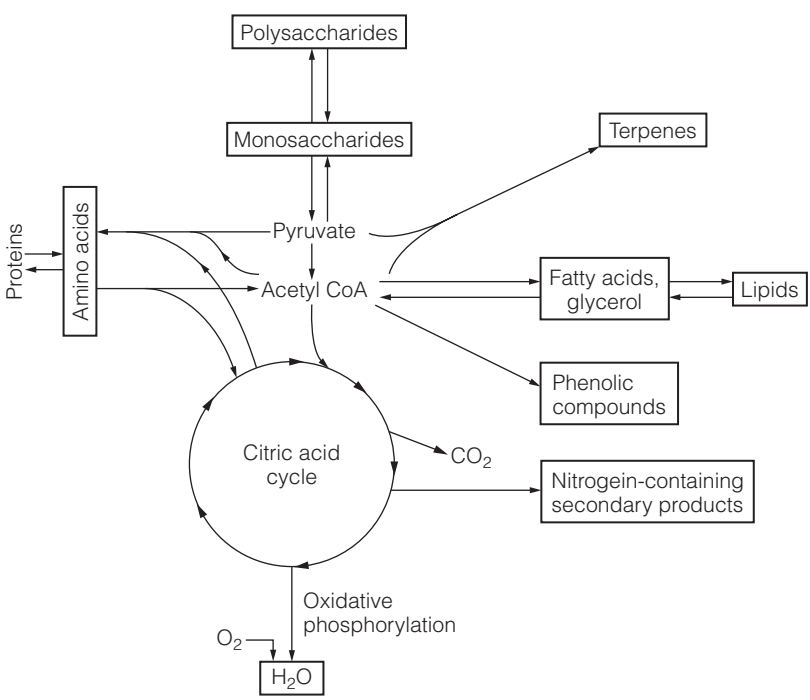


Fig. 1. Major plant products and their origins in metabolism.

Transamination reactions involve the transfer of an amino group from one compound to another. For instance, **asparagine synthase** (**AS**; *Fig. 2*) converts aspartate and glutamine to asparagine and glutamate. Asparagine contains a high quantity of nitrogen (2N) for each carbon (4C) present, compared with glutamate (1N:5C) or glutamine (2N:5C). Expression of the AS gene is repressed (inhibited) by high light and high carbohydrate production, so the plant makes nitrogen compounds with low quantities of nitrogen. When light is low and carbohydrate is scarce, carbon is conserved by the synthesis of compounds with a much higher nitrogen content.

Lipid biosynthesis

Plants synthesize a wide variety of lipids, including: membrane lipids, in which long-chain fatty acids, commonly 16–18 carbons in length, are esterified to glycerol; the waxes of the cuticle and suberin of the endodermis; and the storage lipids of seeds (most commonly triacylglycerols).

Plants use acetyl CoA as the basic building block for assembling **long-chain fatty acids**. Acetyl CoA is produced by **pyruvate dehydrogenase** present both in plastids and mitochondria. In the chloroplast, **pyruvate** is produced from 3-phosphoglycerate from the Calvin cycle; in non-photosynthetic tissue, it originates from glycolysis. Synthesis of glycerolipids occurs in two stages: addition of the fatty acid chains to glycerol-3-phosphate and the addition of a head group. Glycerol-3-phosphate is derived in stages originating from glyceraldehyde-3-phosphate. In photosynthetic tissue, the chloroplast is the chief source of fatty acids, which may be used directly in the chloroplast or exported to the cytoplasm. Plant cells can synthesize **glycerolipids** at the endoplasmic reticulum (ER) and in mitochondria as well as in plastids; all three of these organelles are believed to be inter-connected and lipids traffic between them and to the other cellular membranes.

Seeds make **triacylglycerols**, which are **storage oils**, and frequently very important human foods. Up to 60% of the dry weight of a seed may be in the form of storage oils. Triacylglycerols consist of a glycerol to which three fatty acid chains have been added (*Fig. 3*). They are stored in oil bodies, small lipid droplets with a surrounding coating of lipid and protein. The oil is first synthesized in the ER.

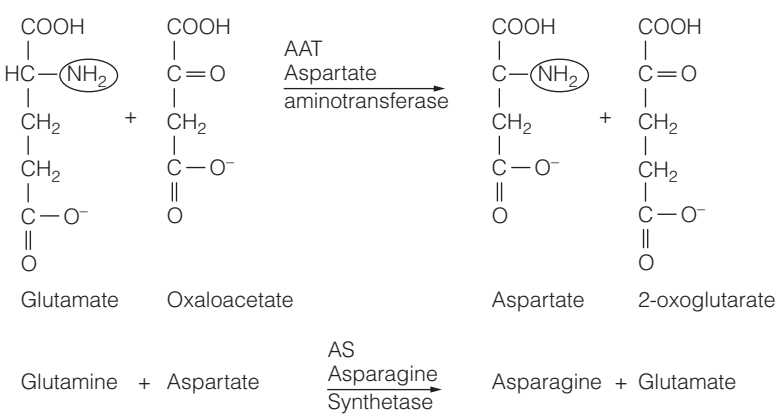


Fig. 2. Other amino acids are synthesized by transamination reactions which occur in various organelles.

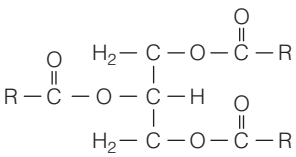


Fig. 3. The structure of a triacylglycerol.

Sucrose, polysaccharides and starch

Plant cells produce a range of **monosaccharides**, from 3-carbon triose sugars such as dihydroxyacetone and glyceraldehyde to 6-carbon hexoses such as D-glucose, D-fructose, D-mannose and D-galactose (*Fig. 4*). **Sucrose** is a disaccharide, made of glucose and fructose. Polysaccharides are large polymers of these monosaccharides. By far the most important of these as a storage product is starch, made up of α-(1–4) and α-(1–6) branched D-glucose residues (*Fig. 4*). Cellulose, a major structural component of cell walls, is another polysaccharide, made up of β-D glucose (*Fig. 4*).

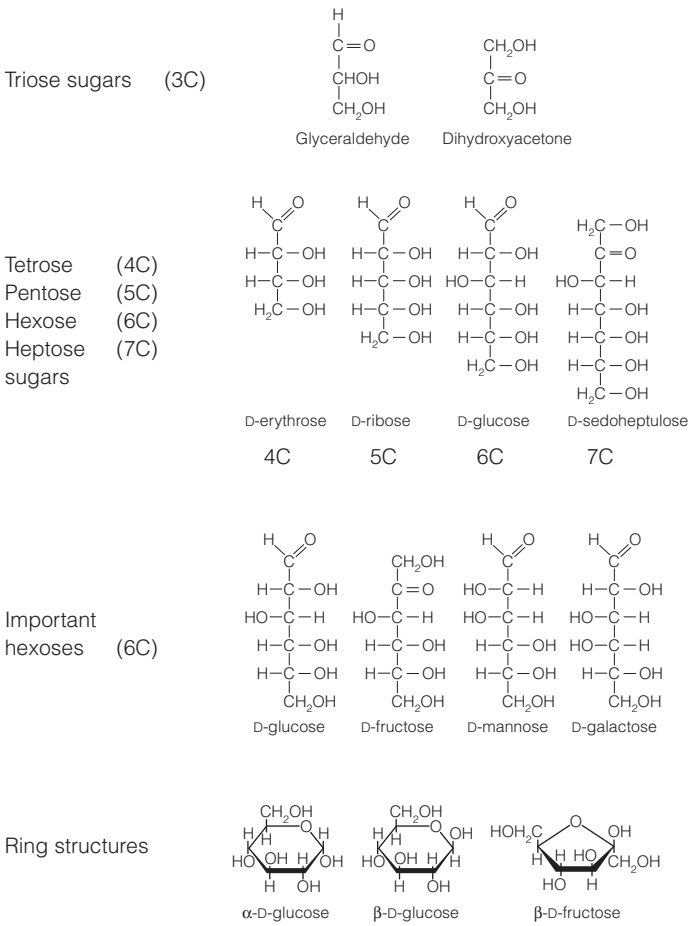


Fig. 4. Structures of major sugars. Note that for ring structures, α or β depends on the position of the hydroxyl (OH) groups adjacent to the oxygen which closes the ring.

Sucrose synthesis occurs in the cytoplasm by one of two routes as a result of the activity of two enzymes, **sucrose phosphate synthase** and **sucrose phosphate phosphatase**:

$$\text{UDP-glucose + fructose-6-phosphate} \xrightarrow[\text{synthase}]{\text{sucrose phosphate}} \text{sucrose-6-phosphate + UDP}$$

$$\text{sucrose -6-phosphate + } H_2O \xrightarrow[\text{phosphatase}]{\text{sucrose phosphate}} \text{sucrose + } P_i$$

or by a single enzyme, **sucrose synthase**:

$$\text{UDP-glucose + fructose} \xrightarrow{\text{sucrose synthase}} \text{UDP + sucrose}$$

In leaves, **starch synthesis** occurs primarily in chloroplasts, commencing with **fructose-6-P**.

$$\text{Fructose-6-P} \xrightarrow{\text{hexose phosphate isomerase}} \text{glucose-6-P}$$

$$\text{Glucose-6-P} \xrightarrow{\text{phosphoglucomutase}} \text{glucose-1-P}$$

$$\text{Glucose-1-P + ATP} \xrightarrow{\text{ADP glucose phosphorylase}} \text{ADP-glucose + } PP_i$$

$$\text{ADP-glucose + } \alpha\text{ (1-4) glucan} \xrightarrow{\text{starch synthase}} \alpha\text{-(1–4)glucosyl-glucan + ADP}$$

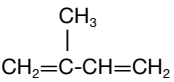
Cellulose is synthesized by **cellulose synthase**, an enzyme located in rosettes in the plasma membrane (Topic B2). Other polysaccharide complexes inserted in the cell wall are synthesized in the Golgi apparatus and secreted in vesicles, which fuse with the plasma membrane.

Regulating both the rates of sucrose and starch synthesis is important. If too much sucrose is produced, the chloroplast becomes depleted in the intermediates of the citric acid cycle, and photosynthesis will be inhibited. If too little starch is produced, the cell will not have sufficient reserves of carbohydrate for respiration during the night. Photosynthetic tissues also export assimilated carbon to other tissues and so regulation of the whole process must allow for this.

Plant secondary products

Plant **secondary products** are compounds generated by **secondary pathways** and not from primary metabolism. Many are toxic or give the plant an unpleasant taste and it is likely they give a selective advantage as anti-herbivory agents. Numerous plant secondary products have been used over many hundreds of years for a wide array of purposes (Topics N2 to N4). They are generally produced in specialized tissues, with highly developed multi-enzyme pathways for their production. *Table 1* summarizes major secondary products, with their origins and uses.

Table 1. Plant secondary products

Family of compounds	Biosynthesis	Examples	Examples of key producers
Terpenoids, isoprenoids; based on isoprene: 	Mevalonic acid pathway (originating from acetyl CoA)	Carotenoid pigments; Sterols and steroid derivatives (e.g. cardiac glycosides like digitoxin); Hormones (abscisic acid, gibberellins);	*Digitalis purpurea* (foxglove)
		Latex	*Hevea brasiliensis* (rubber tree)
		Flavors (e.g. menthol); Odors	*Mentha palustris* (mint)
Phenolics based on phenol: 	Shikimic acid pathway (originating from aromatic amino acids tryptophan, tyrosine, phenylalanine)	Many defence and anti-herbivory compounds including: phenolic monomers; tannins (also flavor wine and tea); lignins (also wood); flavonoids (pigments like anthocyanins)	
Alkaloids (diverse group, containing a N-group and water soluble)	Diverse origins. Name derived from slight alkalinity in solution. May be aromatic (heterocyclic) or aliphatic	Stimulants	
		Caffeine	*Coffea arabica* (coffee)
		Nicotine	*Nicotiana tabacum* (tobacco)
		Sedatives	
		Morphine	*Papaver somniferum* (opium poppy)
		Codeine	
		Poisons	
		Atropine	*Atropa belladonna* (deadly nightshade)
		Chemo-therapy agents	
		Vinblastine	*Catharanthus roseus* (rosy periwinkle)
		Vincristine	
		Narcotics	
		Cocaine	*Erythroxylum coca* (coca)