

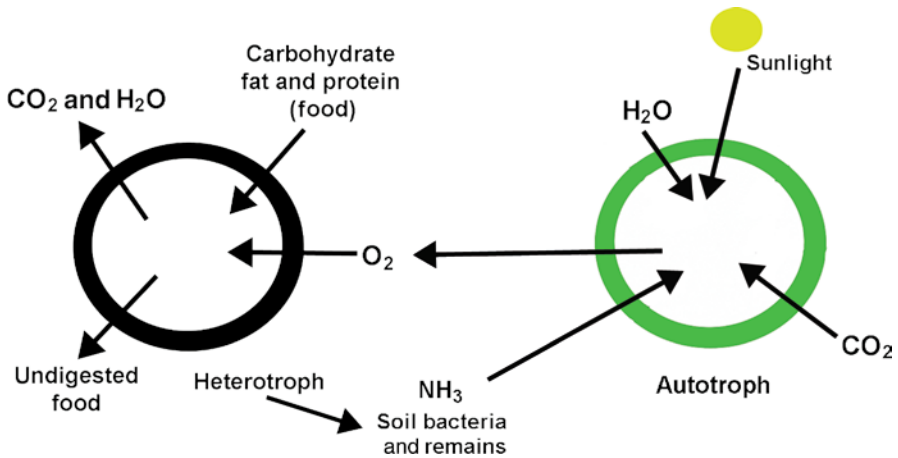
Starch and sucrose, key substrates for the development of dental caries, are exclusively synthesized by plants. They are made in plant leaves by a process called photosynthesis, which utilizes sunlight as the energy source. This chapter outlines the light and dark reactions of photosynthesis and compares the light reaction with mitochondrial electron transport (Sect. 1). The key dark reaction, the production of phosphoglycerate by the enzyme ribulose biphosphate carboxylase (rubisco), is described along with the production of fructose, sucrose, and starch (Sect. 2). The chapter concludes with a detailed discussion of the roles of starch and sucrose in plant metabolism (Sect. 3).

## 2.1.1.

### Role of Photosynthesis in Living Organisms

As discussed in Sect. 1.3.1, insects, animals, and bacteria respire by consuming oxygen gas and a complex mixture of organic material containing carbon–hydrogen bonds (proteins, fats, and carbohydrates) for energy, growth, and maintenance. By contrast, the photosynthetic organisms, plants and algae, consume carbon dioxide gas from which they make all their molecular carbon. Nitrogen-containing molecules (amino acids, nucleic acid bases, and various other compounds) require ammonia, which comes from decaying organisms in the soil, or from root-associated bacteria that produce it from nitrogen gas.

Photosynthesis splits water into hydrogen and oxygen atoms in a reaction that requires sunlight (light reaction). Oxygen is passed into the atmosphere and the hydrogen is used to assimilate carbon dioxide in a dark (non-photosynthetic) reaction that forms starch, sucrose, and another disaccharide called maltose. Metabolites such as  $\alpha$ -ketoglutarate are derived from starch and sucrose and incorporate (fix) the ammonia absorbed from the soil into the nitrogen-containing compounds. The cycle is summarized in Fig. 2.1.



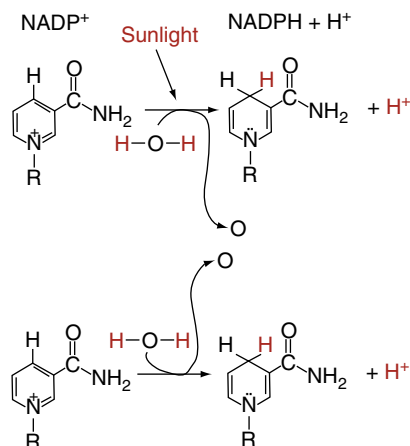
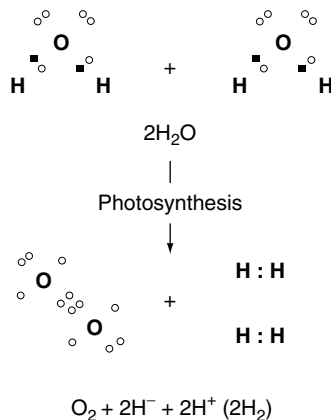
**Fig. 2.1** Photosynthesis and respiration. *Left side* is Fig. 1.6. *Right side* shows photosynthesis in which sunlight and water in the atmosphere are absorbed by plants and algae to generate ATP and NADPH, which make carbohydrates and other organic carbon products from carbon dioxide, which is absorbed from the atmosphere separately. All of the carbon in plants and algae is ultimately derived from a single source, carbon dioxide, and they are called autotrophs. Nitrogen is obtained mostly as ammonia from bacterial metabolism of proteins from dead organism in the soil

### 2.1.2. The Light Reaction

Photosynthesis is the sunlight-mediated splitting of water into oxygen and energy. It occurs within a special membrane, the thylakoid membrane, which contains chlorophyll and surrounds a lumen. This membrane resembles the thick inner membrane of mitochondria or oxygen-utilizing bacteria. The thylakoid membrane lies within an organelle called a chloroplast, which is exclusive to leaf cells and algae where photosynthesis occurs. Central to the process of photosynthesis is the light-mediated loss of two electrons and two hydrogen atoms from a molecule of water (Fig. 2.2). Both electrons and one of the two hydrogen atoms pass to NADPH, the equivalent of NADH in mitochondria or bacteria; the other hydrogen atom becomes a hydrogen ion ( $H^+$ ), a proton. When two molecules of water are split by chlorophyll, a molecule of oxygen ( $O_2$ ) is released. For each molecule of oxygen, two molecules of NADPH and two protons ( $H^+$ ) are made (Fig. 2.3).

Figure 2.4 illustrates electron and proton transport processes. Electrons are initially energized by sunlight hitting *photosystem II* (*PSII*; see figure legend) and transported to *photosystem I* (*PSI*). In *PSI*, sunlight energy is again imparted and the electrons are transferred by ferredoxin, another electron carrier, to NADPH. Electron transport from *PSII* to *PSI* is via *plastoquinone* (*PQ*), cytochrome b6/cytochrome f complex, and plastocyanin (blue arrows in Fig. 2.4). During electron transport, protons are taken up by plastoquinone (similar to

**Fig. 2.2** In plants, light mediates the loss of two electrons and two hydrogen atoms from a molecule of water. See text for discussion of this process

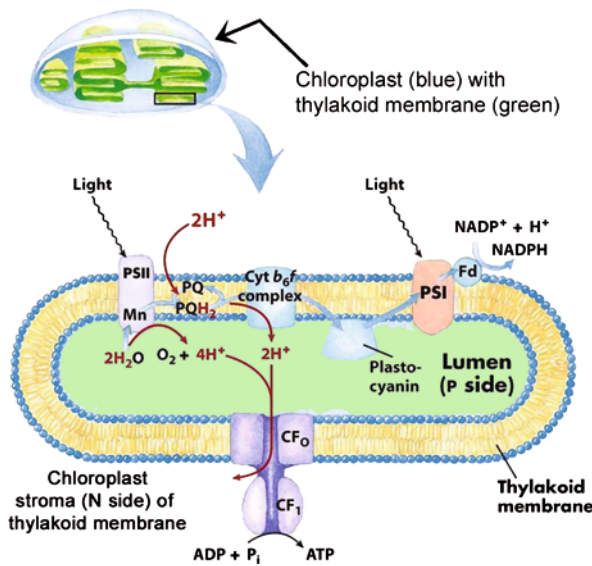


**Fig. 2.3** The electrons are passed from water to NADPH. See text

ubiquinone in mitochondria) and released into the lumen (see legend to Fig. 2.4). As they accumulate, the protons start diffusing across the thylakoid membrane through an ATP synthase  $F_0/F_1$  complex identical to that of mitochondria (red arrows in Fig. 2.4). Electrons that reach PSI are re-energized by sunlight and reduce  $\text{NADP}^+$  by transport through ferredoxin (blue arrows in Fig. 2.4). The ATP, NADPH, and protons accumulate in the stroma of the chloroplast where they assist in the synthesis of triose phosphate and starch.

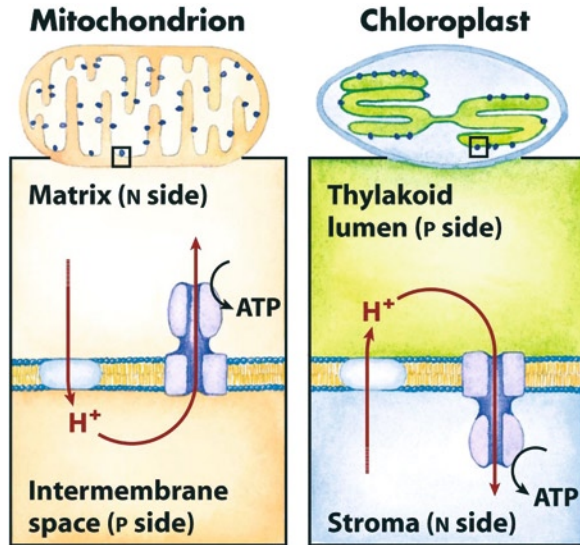
Figure 2.5 compares the orientation of the ATP synthase  $F_0/F_1$  complex in mitochondria with that in chloroplasts. The lumen enclosed by the thylakoid membrane is slightly acidic; it corresponds to the mitochondrial intermembrane space where electron transport first pumps protons ( $\text{H}^+$ ). In chloroplasts, ATP is made as protons diffuse from the thylakoid lumen through the membrane to the chloroplast stroma (Fig. 2.4). In mitochondria, ATP is made as protons diffuse from the mitochondrial intermembrane space through the inner mitochondrial membrane to the mitochondrial “lumen” or matrix.

**Photophosphorylation due to electron flow (blue)  
and proton flow (red)  
in chloroplast thylakoid membranes**



**Fig. 2.4** Phosphorylation and electron transport in chloroplasts. Electron flow is shown in *blue* and the proton flow in *red*. The thylakoid membrane is colored *yellow* and the lumen is colored *green*. Light activates photosynthesis site II (*photosystem II* [*PSII*]) within chlorophyll whose manganese ions bind water molecules. Light rays attack a bound water molecule, breaking it up into oxygen atoms that combine to form oxygen gas, and hydrogen atoms that split into protons and electrons. Each two molecules of water give two pairs of electrons that are transported along with four protons to *plastoquinone* ( $2PQH_2$ ). The protons are released into the thylakoid lumen (*red arrows*) as  $PQH_2$  is reoxidized to PQ by the cytochrome complex (*blue arrows*). Protons accumulate in the lumen (P side of thylakoid membrane) and diffuse into the chloroplast stroma through carriers that synthesize ATP ( $CF_0$  and  $CF_1$ ; *purple* at the foot of figure). ATP is made from ADP and phosphate ( $P_i$ ) in the chloroplast stroma (N side of thylakoid membrane). As detailed in the text, electrons are transported from PSII to photosystem I ([PSI], *pink*) where they are activated by light to reduce  $NADP^+$  (*top right* of figure). Extra protons are taken back into the thylakoid lumen by plastoquinone. The plant partitions its electron flow and protons so that the ratio of ATP to NADPH matches its need for assimilation of carbon dioxide into carbohydrates, the primary product of photosynthesis (Adapted from Fig. 19-57 in Lehninger Principles of Biochemistry. D.L. Nelson & M.M. Cox, 4th Ed. 2005. W.H. Freeman & Co., New York)

**Fig. 2.5** ATPase orientation in mitochondria and chloroplasts. *Blue dots* indicate the ATP synthetase in mitochondria (*top left*) and *green dots* in chloroplasts (*top right*). See text for further description (Adapted from Fig. 19-58 in Lehninger Principles of Biochemistry, D.L. Nelson & M.M. Cox, 4th Ed. 2005. W.H. Freeman & Co., New York)

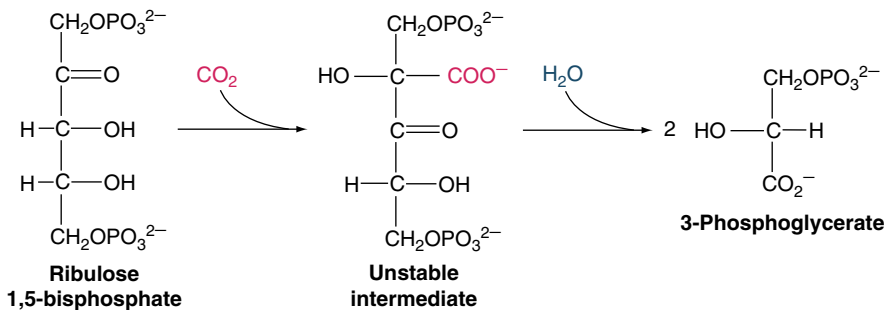
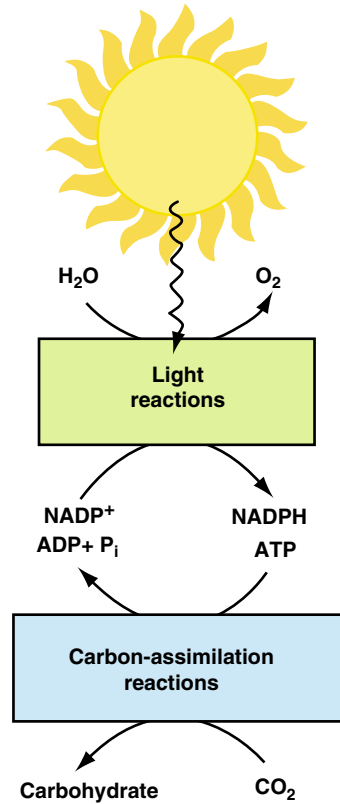


Animals and bacteria are heterotrophs; they obtain carbon in various forms as food and metabolize many forms of it to provide energy and body structure. Plants are autotrophs; all their carbon comes from  $CO_2$  powered by photosynthesis. Photosynthesis occurs within the thylakoid membranes of chloroplasts in plant leaves, and it is mediated by chlorophyll. The light reaction splits water into  $O_2$ , electrons, and protons ( $H^+$ ). NADPH is produced by electron transport and ATP synthesis by associated proton transport.

### 2.2.1. The Dark Reaction

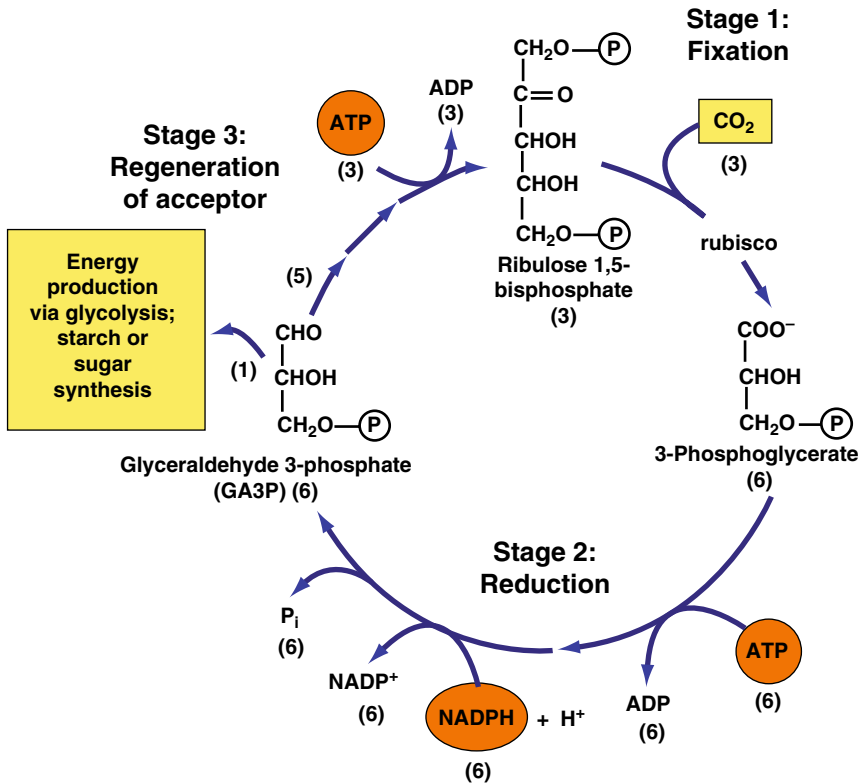
The utilization of carbon dioxide by ATP and NADPH occurs in the chloroplast matrix, (outside the thylakoid lumen). A series of reactions assimilates carbon dioxide (Fig. 2.6), the Calvin cycle or dark reaction, and generates fructose 6-phosphate. Fructose 6-phosphate is the immediate precursor of glucose 6-phosphate for the synthesis of starch in the

**Fig. 2.6** Overall design of photosynthesis. The light reactions make ATP and NADPH to be used in the carbon dioxide assimilation reactions that form fructose and glucose (Modified from Fig. 19-37 in Lehninger Principles of Biochemistry. D.L. Nelson & M.M. Cox, 4th Ed. 2005. W.H. Freeman & Co., New York)



**Fig. 2.7** Assimilation of carbon dioxide. The key reaction of the dark reaction is the assimilation of carbon dioxide by ribulose 1:5-bisphosphate carboxylase (Simplified from Fig. 26-31 in Biochemistry. L. Stryer, 4th Ed. 1995. W.H. Freeman & Co., New York)

chloroplast matrix and sucrose in the leaf cell cytosol. The substrate for carbon dioxide is ribulose 1:5-bisphosphate, and the reaction is mediated by a substrate-specific carboxylase, *rubisco* (Fig. 2.7). The products are two molecules of 3-phosphoglycerate, each of



**Fig. 2.8** Summary of the Calvin cycle. The cycle consists of three stages, culminating in the regeneration of ribulose 1:5-bisphosphate and a net increase in glyceraldehyde 3-phosphate. *Numbers in parenthesis* reveal the fate of carbon atoms entering and leaving the cycle (Modified from Fig. 20-04 in Lehninger Principles of Biochemistry. D.L. Nelson & M.M. Cox, 4th Ed. 2005. W.H. Freeman & Co., New York)

which reacts with an ATP molecule to make 1:3-bisphosphoglycerate, and then with NADPH to be reduced to glyceraldehyde 3-phosphate. For every six molecules of glyceraldehyde 3-phosphate obtained from three molecules of ribulose 1:3-bisphosphate, one is used for energy via glycolysis, or to synthesize monosaccharides or starch (Fig. 2.8). The other five interact to make three molecules of ribulose 5-phosphate, each of which utilizes three ATP molecules to regenerate three ribulose 1:5-bisphosphate molecules.

The enzymes that regenerate ribulose 5-phosphate from glyceraldehyde 3-phosphate are the same as those of the pentose phosphate path in non-photosynthetic organisms. The three stages of the Calvin cycle are (1) fixation of carbon dioxide by rubisco, which utilizes ATP; (2) reduction of the 1:3-bisphosphoglycerate to 3-bisglyceraldehyde, which utilizes ATP and NADPH; and, finally, the formation of ribulose 5-phosphate, which reacts with ATP to regenerate the rubisco substrate, ribulose 1:3-bisphosphate.

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### 2.2.2.

#### **Starch and Sucrose Provide the Carbon Skeletons of All Plant Compounds**

During photosynthesis, starch is synthesized and stored in the chloroplast matrix and sucrose is synthesized in the leaf cytosol from which it diffuses to the rest of the plant. Starch resembles glycogen, but it has few or no  $\alpha$ -1:6 glycosidic linkages, the glucose residues are little branched (amylopectin) or not branched (amylose). Amylose and amylopectin are substrates for salivary amylase, and their structures are illustrated in Fig. 12.10. The substrate for starch synthase is ADP-glucose, whereas the substrate for glycogen and sucrose synthases is UDP-glucose.

Sucrose is a highly soluble disaccharide that provides a mobile energy source for all the plant cells. Sugar cane stores large amounts of sucrose in its leaves and stalk, whereas sugar beet stores it in roots. *All plants make sucrose from two molecules of fructose 6-phosphate.* One molecule is activated with UDP and isomerized to UDP-glucose. Sucrose 6-phosphate synthase reacts with UDP-glucose and fructose 6-phosphate to make sucrose 6-phosphate. The latter then reacts with a phosphatase to produce sucrose (Fig. 2.9).

The amount of sucrose is regulated by a kinase that inhibits sucrose synthase by phosphorylating a serine residue on its polypeptide and a phosphatase that activates the synthase by dephosphorylating the serine residue. This mode of regulation resembles that of glycogen synthase in the mammalian liver. Both enzymes make enzyme energy storage compounds: sucrose for the plant as a whole and glycogen specifically for liver or muscles.

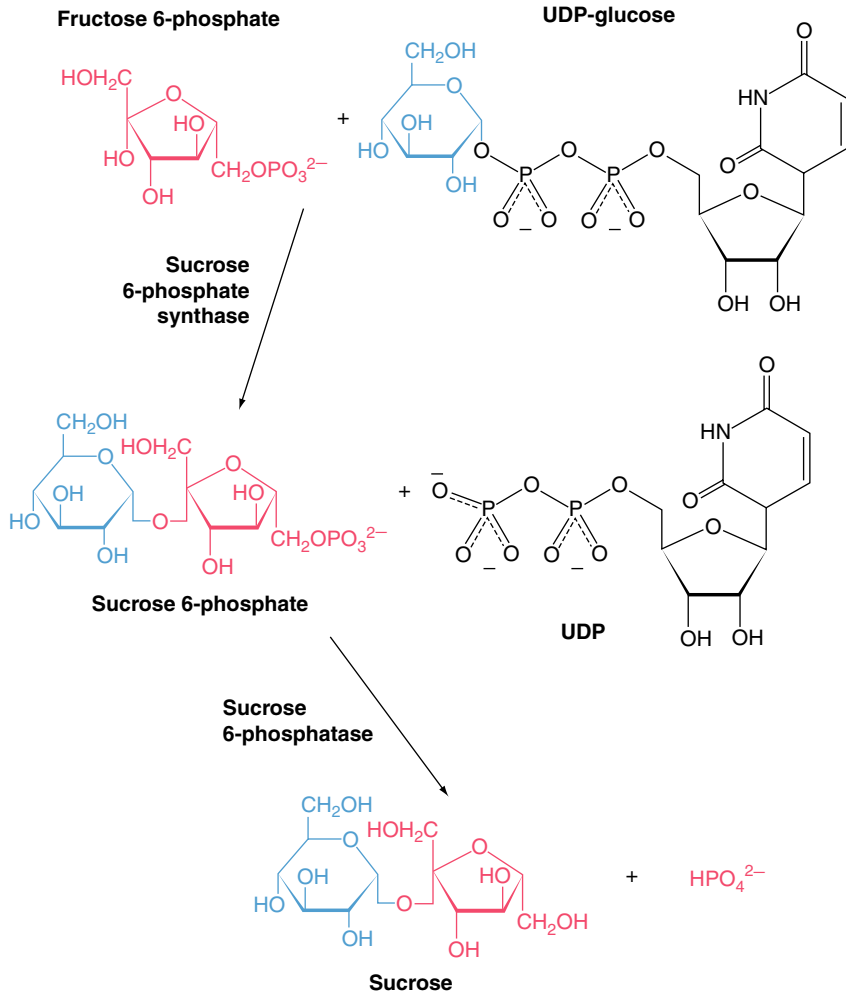
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### 2.2.3.

#### **Plants Are Autotrophs**

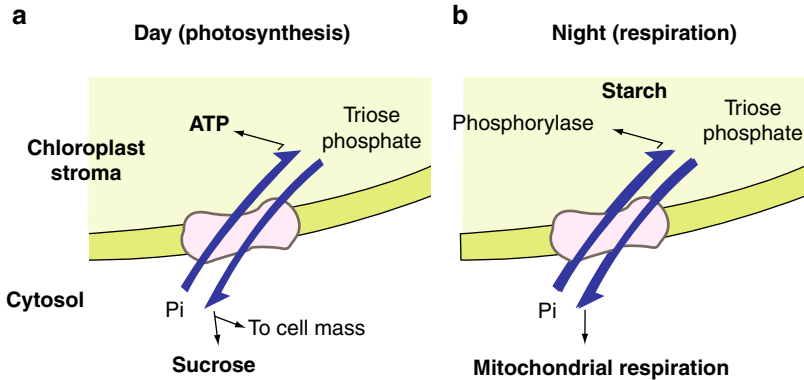
The light-powered incorporation of carbon dioxide into ribulose biphosphate by the Calvin cycle enzymes synthesizes starch, which remains in the chloroplast stroma. Once the space for starch in the chloroplast stroma is exhausted, the 3-phosphoglycerate intermediate is converted by triosephosphate isomerase to *dihydroxyacetone phosphate (DHAP)*. DHAP is the only metabolite allowed to leave the chloroplast, and it does so in exchange for *phosphate (Pi)* from the cytosol (Fig. 2.10). The incoming Pi reacts with ADP to form ATP in the chloroplast, and it eventually ends up in a new molecule of triosephosphate. The exchange of DHAP for Pi is mediated by a protein transporter called an antiport that allows the two metabolites to pass in opposite directions through the membrane and down their respective concentration gradients. Similar antiport transport gradients are required for bone metabolism (Sects. 9.3.5, and 10.1.4). Once in the leaf cytosol, the DHAP is converted back to 3-phosphoglycerate, which is metabolized to various compounds, especially sucrose.

At night, there is no photosynthesis and respiratory energy becomes as important in plants as in other organisms. The starch that accumulated during the day is metabolized by the activation of phosphorylase and some glycolytic enzymes to triose phosphate (Fig. 1.7),



**Fig. 2.9** Synthesis of sucrose. See text (Modified from Fig. 20-13 in Berg JM, Tymoczko JL and Stryer L. Biochemistry, 5th Ed. 2002. W.H. Freeman & Co., New York to also show the phosphatase step). Note: The diagram of fructose in this figure (*red*) is rotated so that its anomeric carbon atom (C2) lies to the right of the ring structure instead of the left as in a conventional diagram. Because of the rotation, it is not obvious that the fructose bond in sucrose is in the  $\beta$ -anomeric configuration. Only the glucose bond is in the  $\alpha$ -anomeric configuration. The conventional diagrams of glucose and fructose alone and in sucrose are illustrated in Fig. 15.6.

which passes through the antiport as DHAP in exchange for  $\text{P}_i$  (Fig. 2.10). In the cytosol, DHAP moves to the mitochondria as a source of ATP. The  $\text{P}_i$  enters the chloroplast where it is a co-substrate for phosphorylase for starch breakdown.



**Fig. 2.10** Phosphoglycerate utilization. **(a)** *During the day.* Photosynthesis in the chloroplast makes starch until there is no more room. The Calvin cycle continues to make triose phosphate, which exits the chloroplast in exchange for organic phosphate (Pi) entering the chloroplast and converting ADP to ATP. In the cytosol, the triose phosphate is mostly converted to sucrose but also to small amounts of other compounds such as amino acids for transport throughout the plant. **(b)** *During the night.* Phosphorylase is activated and it breaks up the starch to glucose 6-phosphate from which triose phosphate is made. The triose phosphate is exchanged for Pi. The Pi is a substrate for phosphorylase and keeps it active. Once in the cytosol, the triose phosphate is transferred mostly to mitochondria for respiration

The dark reaction (Calvin cycle) uses the NADPH and ATP to make glyceraldehyde 3-phosphate (triose phosphate), which is metabolized initially to starch, sucrose, and cellulose. Starch and sucrose are the major plant storage products. Starch is synthesized from ADP-glucose in the chloroplast, sucrose from fructose 6-phosphate and UDP-glucose in the leaf cytosol.

### 2.3.1.

#### Sucrose Is the Primary Transport Sugar and Plays a Central Role in Plant Growth and Development

The availability of metabolites for sucrose synthesis and the need for products of sucrose degradation regulate gene expression. For respiration, sucrose is hydrolyzed by *invertase* to free glucose and fructose, which are phosphorylated and undergo glycolysis to pyruvate. The pyruvate is then either metabolized by mitochondrial electron transport to ATP and NADH (respiration), or metabolized to provide starting products for amino acid, lipid, and nucleotide syntheses.

Cellulose helps protect plants from their environment and to access sunlight by providing a firm structure. Cellulose is  $\beta 1 \rightarrow 4$  glucose, whereas starch is  $\alpha 1 \rightarrow 4$  glucose. Both are derived from sucrose outside of chloroplasts. The sucrose synthase reaction (Fig. 2.9) is reversed: sucrose is phosphorylated with ATP to make sucrose 6-phosphate, an excess of which reverses the reaction. The products are UDP-glucose and fructose 6-phosphate. Cellulose is synthesized from UDP-glucose by cellulose synthase. Additional UDP-glucose reacts with ATP to form ADP-glucose, the precursor of starch. The fructose 6-phosphate is metabolized to provide the necessary energy (ATP and NADPH) by respiration.

Sucrose plays a central role in plant growth and development. Invertase-catalyzed hydrolysis of sucrose is associated with the respiration required for plant growth, whereas sucrose synthase-catalyzed hydrolysis is linked to cell wall or other storage product biosynthesis. Cellulose is synthesized from UDP-glucose using cellulose synthase in membranes. Cellulose protects plant cells from the environment and provides them with a firm structure to access sunlight.



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