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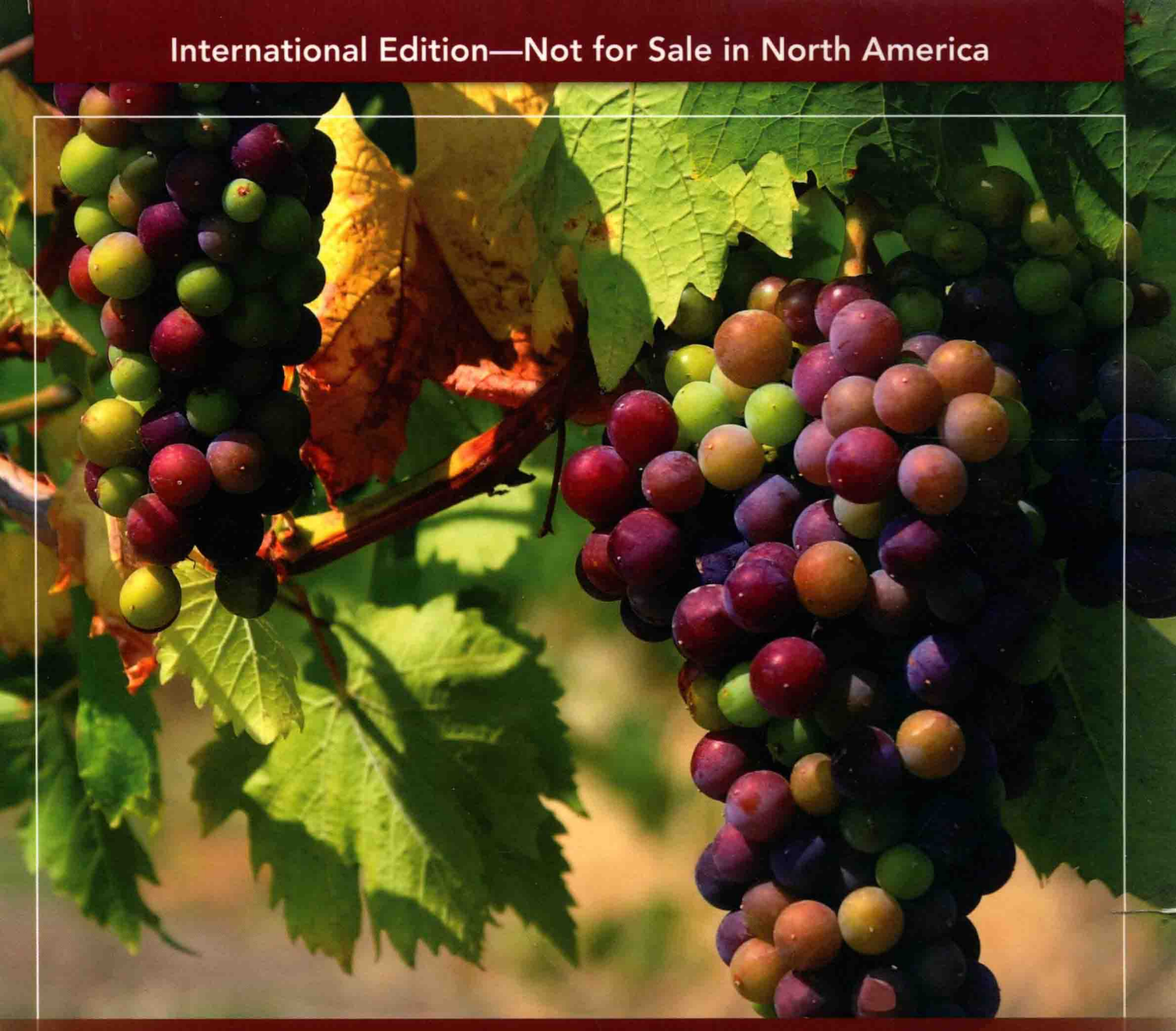
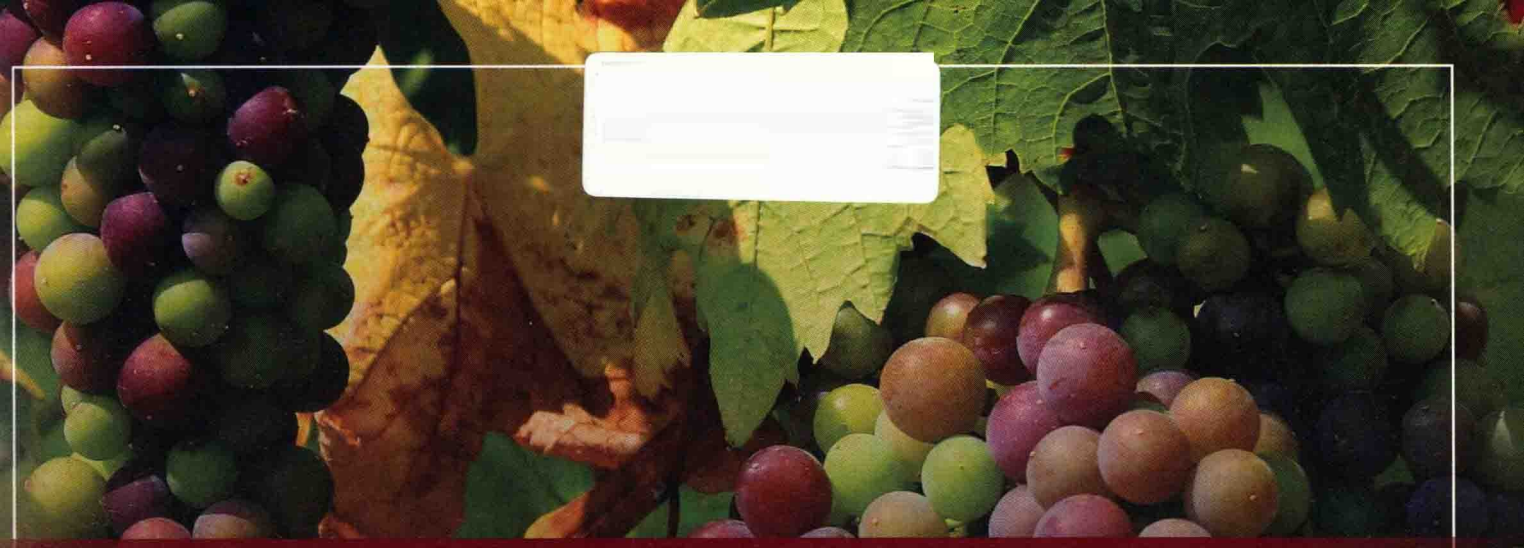


# PLANT BIOCHEMISTRY

FLORENCE K. GLEASON
*with Raymond Chollet*



# PLANT BIOCHEMISTRY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WITH

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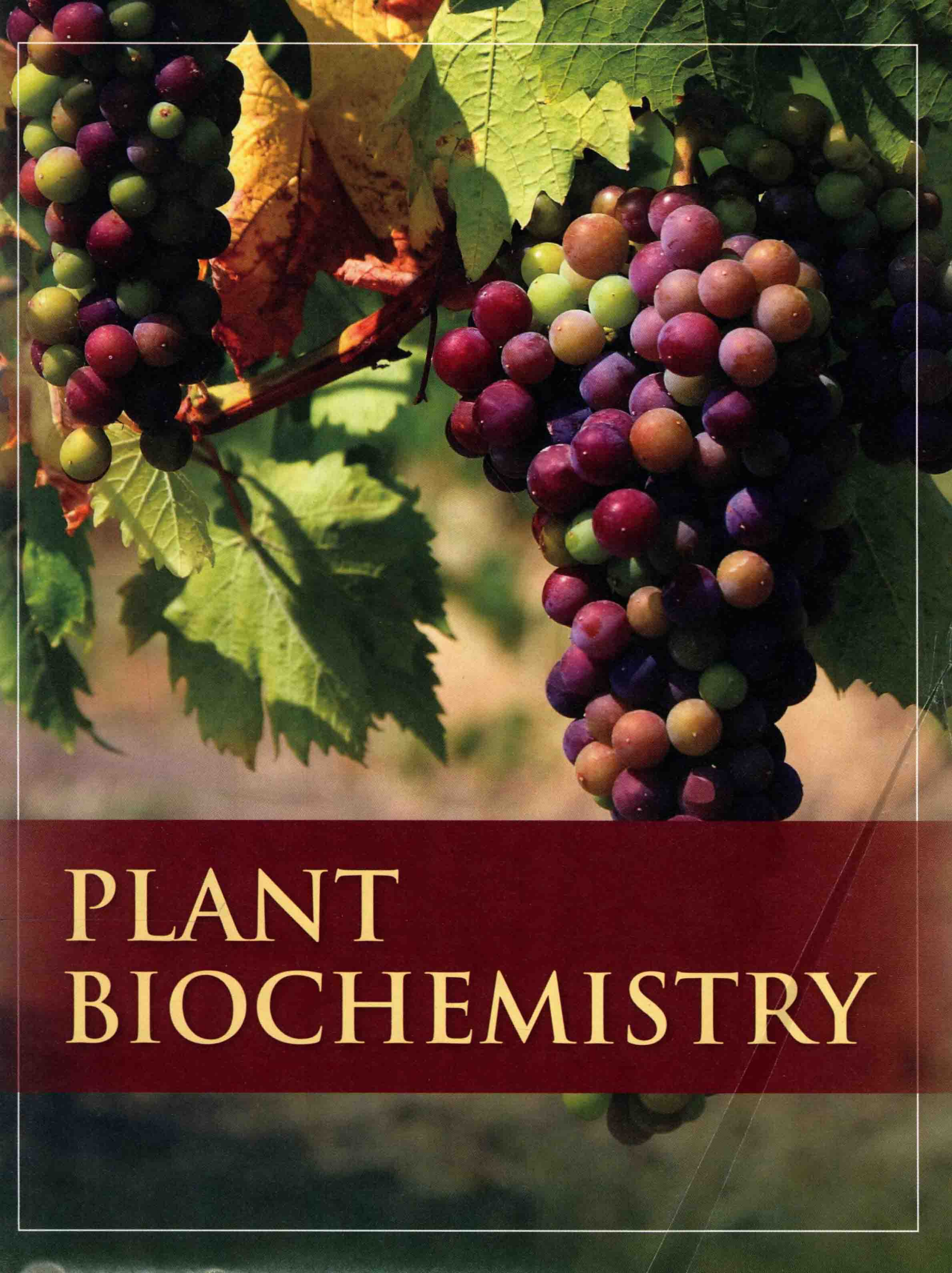

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# PREFACE

The seeds for this book were planted approximately 20 years ago when I taught my first course in plant biochemistry. Although there were several excellent texts on general biochemistry, I soon realized that none of them placed an emphasis on plant metabolism. Initially, I selected a group of reviews from the literature to use in class, but these usually assumed that the readers already had a good grasp of the subject, which many did not. The resolution was to generate my own series of lecture notes for the students, the initial outlines of which quickly grew into chapters and eventually into this book.

This text assumes that the students have a background in basic organic chemistry and cell biology. The fundamental concepts of biochemistry, such as energy transfer, are introduced, but from a plant perspective. Many of the same topics are covered here as in a general biochemistry text, but I also stress how these processes differ in photoautotrophs, including photosynthetic bacteria, cyanobacteria, and plants. This book also delves into specific plant-related topics such as cell wall and natural product synthesis. Each chapter can stand alone and some sections, and even entire chapters, can be omitted based on the plant biochemistry instructor's preferences without causing a major break in the development of a particular topic. When it is appropriate, the reader is referred to chapters and appendices where more details on a given subject can be found. Literature references are kept to a minimum and include recent reviews on the chapter topics. To ensure that these references remain relevant, they will be included and updated on the book's Student Companion Web site http://biology.jbpub.com/gleason/plantbiochemistry/.

When I generated a table of contents for the proposed textbook, I realized that the topics were a rather select group that faculty and students at the University of Minnesota felt were missing in their other courses. Some topics that could be included will not be found, such as light quality and perception by plants or techniques for genetic manipulation, which have been very influential in the development of modern biochemistry but are widely available in general biochemistry texts. A great deal of information is included on biosyntheses and enzyme structure and regulation. My goal is to illustrate how plants take sunlight and convert it into all the biochemical compounds needed to sustain life, reproduce, and interact with the other organisms and abiotic elements in their environment.

**Chapters 1** and **2** cover photosynthesis, the light reactions, and carbon dioxide fixation. These processes involve the transformation of light energy into chemical bond energy and form the core of plant function. Photosynthesis is arguably the most important biochemical process on this planet because it is the major pathway for taking carbon dioxide from the atmosphere and putting it into the biosphere. Research on photosynthesis has had a long and inspiring history. Some of the key historical discoveries are described, including the Hill reaction and the use of 14C to trace the path of carbon in $CO_2$ fixation. Major breakthroughs in photosynthesis research include the use of molecular techniques to isolate genes, to overproduce chloroplast proteins, and to determine the three-dimensional structure of the membrane-embedded proteins that facilitate the light reaction. Research in photosynthesis is still an active and vibrant field as we strive to find more ways of increasing plant productivity for food and fuel.

**Chapter 3** covers the catabolism of carbohydrates. The processes of glycolysis, the citric acid cycle, and electron transport in plants are similar to those found in nonphotosynthetic organisms. Some features, however, are unique to plant systems. In green tissues, the chloroplast is the ultimate source of fixed carbon compounds. In a leaf's cytoplasm, these compounds can be used to generate ATP or alternatively used to synthesize sucrose and other sugars for export to the nongreen tissues. In addition, the photosynthetic cell must maintain the pools of sugar-phosphates in the chloroplast at levels that are sufficient to sustain the C-3 cycle. The regulatory mechanisms for all these pathways in plants are governed by small molecules. Some of the regulatory mechanisms are similar to those found in animal cells, but, in many cases, light is the ultimate regulatory agent.

The catabolic pathways are generally thought of as transforming the chemical bond energy in small organic molecules to bond energy in the phosphoester bonds of ATP. However, these pathways also supply carbon intermediates for the biosyntheses of other metabolites, especially in autotrophs. These biosynthetic products are used for cell growth and reproduction, but, in plants, a large sink for sugars and other carbon compounds is cell wall synthesis. **Chapter 4** describes the synthesis of primary cell walls consisting mainly of cellulose fibrils embedded in a complex carbohydrate matrix. A wall may seem to be a rather static structure, but primary cell walls are surprisingly dynamic. They contain several types of proteins that are important in maintaining and restructuring the walls. The wall proteins facilitate wall loosening and rebuilding to accommodate cell expansion. Recent reports have described many additional cell wall proteins that function in defense and intercellular signal transduction.

Carbon dioxide, water, and sunlight are the major plant "nutrients," but other inorganic compounds are also required. A source of fixed nitrogen and sulfur is essential and must be available in the environment. **Chapter 5** deals with the uptake and metabolism of the fixed forms of nitrogen, nitrate, nitrite, and ammonia.

Molecular nitrogen ($N_2$) is abundant in the atmosphere, but only certain prokaryotes, including some photosynthetic microorganisms, are capable of catalyzing its reduction into these fixed forms. Many plants have taken advantage of these microorganisms and their ability to fix nitrogen by forming symbiotic relationships. These relations are especially intimate in the case of legumes and rhizobia. The process of nitrogen fixation presents plants with an especially complex challenge: how to maintain oxygen-evolving photosynthesis in the presence of the nitrogen-fixing enzymes, which are irreversibly inactivated by oxygen. Plants must provide their symbionts with carbon nutrients and maintain them in a compartment that excludes oxygen. Free-living organisms face a similar problem and have several methods to cope with what seem to be the incompatible processes of nitrogen fixation, photosynthesis, and aerobic respiration.

Nitrogen assimilation and fixation generally result in the synthesis of the amino acid, glutamate. This amino acid is the major amino donor for the synthesis of most of the other major amino acids. These pathways are discussed in Chapter 8 for aromatic amino acids and in Appendix 6. The two exceptions are the sulfur-containing amino acids, cysteine and methionine, which are covered in the second half of Chapter 5. The role of cysteine in plant metabolism is further explored by outlining the synthesis of glutathione. Its role in maintaining the redox state of the cytoplasm and binding and detoxification of heavy metals and xenobiotics are vital to cell survival. Chapter 5 ends with a description of the synthesis and action of the sulfur-containing natural products, in particular, the glucosinolates. These natural products are found mainly in the Brassica species, including vegetables that are a staple of the human diet such as cabbage and broccoli. The glucosinolates are produced by the plant as protection from herbivores. In some instances, insect herbivores have adapted and are attracted to glucosinolates. Some insects can even sequester the plant glucosinolates in their own cells to protect themselves from predators.

**Chapter 6** continues with the theme of carbon metabolism by outlining the synthesis of lipids. Lipid production in plants starts with fatty acid synthesis in plastids. Fatty acids are esterified to glycerol by enzymes associated with the endoplasmic reticulum and are often modified by addition of double bonds. The resulting lipids are then transferred back to plastids or to other organelles and extensively modified. Plants produce over 300 different types of lipids, such as the unique galacto- and sulfo-lipids, which maintain the fluidity of thylakoid membranes. The greatest lipid variety occurs in seeds. These lipids include oils such as the ricinoleic acid–containing triglyceride in castor beans. This unusual hydroxylated oil is used by humans to produce lubricants and paints and is only one of many seed oils in commercial use. Plants are also a possible source of the very long chain polyunsaturated fatty acids that are required in the human diet. Most of these compounds are found in fish oils, which are, in turn, derived from algae and fungi. Genetic engineering of plants to express the genes for very long-chain polyunsaturated fatty acids (VLC-PUFA) synthesis may one day provide an alternate source of these nutrients.

**Chapter 7** describes isoprenoid or terpene synthesis in plants. The mevalonic acid pathway that produces sterols in animals is found in the plant cytoplasm. In addition, plants have a second synthetic pathway for isoprenoids located in plastids. This methyl-erythritol phosphate pathway is apparently a legacy of their cyanobacterial ancestors. The total isoprenoid synthesis is divided between these two pathways. The traditional mevalonic acid pathway produces sterols and inducible defense compounds called phytoalexins. The plastid pathway generates the carotenoids essential in photosynthesis, and the volatile monoterpenes that attract insect pollinators or deter herbivores. The monoterpenes are well known to most humans. They are some of the common flavoring agents in foods such as mint and menthol and the scents in perfumes. In addition, the plastid pathway generates the precursors for a wealth of plant hormones, the cytokinins, gibberellins, brassinosteroids, abscisic acid, and strigolactones. This division of labor between the two plant pathways seems to be absolute. Although they both produce similar precursors, mutations in genes for either pathway are usually lethal.

Phenolic compounds and their derivatives are the subject of **Chapter 8.** The chapter starts with the shikimic acid pathway and the synthesis of the aromatic amino acids. Phenylalanine is especially important; removal of the amino group yields cinnamic acid and leads to the vast number and complexity of the phenylpropanoids. There are two main branches; one produces monolignols, which are essential for lignin synthesis, and a second that leads to a variety of natural products. Lignin, a random polymer of monolignols, is the structural component of secondary cell walls. It provides protection, physical support for terrestrial plants, and a rigid vascular system for water transport. Its chemical intransigence presents a major problem for humans who want to use plant products for food for themselves and animals and for commercial processes such as plant-derived biofuels. Government agencies and private interests are actively supporting research to manipulate lignin synthesis and degradation.

The monolignols are also a source of natural products. Modified monolignols often serve the same purposes as monoterpenes. Volatiles such as eugenol and myristicin may deter herbivores but generally attract humans.

The second major branch of the phenylpropanoids leads to the polyketides. The best known of theses compounds are the flavonoids and derivatives. The anthocyanins enable plants to cope with abiotic stressors such as intense sunlight and UV radiation. They may also serve to lure pollinators by imparting attractive colors to flower petals or to lure seed dispersal agents by providing brightly colored fruits. Resveratrol, the polyketide found in grapes, seems to provide major health benefits to humans such as maintaining a healthy heart and preventing diabetes.

While phenylpropanoids provide the plant with both essential components and natural products, the alkaloids described in **Chapter 9** can all be considered secondary metabolites. They are produced as defensive compounds, but their occurrence is often limited to a small number of species. The human use of alkaloids has a long and colorful history and continues today with the discovery of new compounds and uses. Many alkaloids have chemical structures similar to mammalian neuroreceptors or neurotransmitters. These alkaloids, such as opiates and tropanes, are well known for their neurological effects. While multivolume series have been written on alkaloids, this chapter explores only a few of the compounds that are of major use to humans. This includes synthesis and action of the opiates and vinca alkaloids used in modern medicine. Because of their complex structures and intricate biosynthesis, these compounds are still obtained from the producing plants rather than chemical synthesis. Research using plant tissue cultures and semisynthesis, where the precursor made by the plant is further modified by a chemist, has provided additional sources of alkaloids and analogs.

The final chapter covers proteins and peptides that are unique to plants. These include the well-characterized seed storage proteins important in human nutrition. Recent research on gene expression has shown that these proteins are often synthesized in tissues other than seeds and have functions in plant development and defense. The germins are a good example; they were once considered simply a food source for germinating embryos. Many germins and similar proteins also have enzymatic activity and most likely act to remodel primary cell walls in both embryos and developing organs. The seed proteases and protease inhibitors have well-defined defensive functions. The ribosome-inactivating proteins (RIPs) also seem to be designed to kill herbivores. Their ability to enter cells, however, is often incompatible with this role. They may actually be a defense against viral invasion.

Genomic analyses of several plants have produced a long list of peptides labeled defensins. These peptides are synthesized as large precursor proteins that are subsequently cleaved and modified usually by the formation of disulfide bonds. Their small size and stability have facilitated determination of their tertiary structures. Defensins have a variety of tertiary structures, and some of them are rather unusual, such as the cyclic, knotted cyclotides. These peptides can disrupt bacterial cell membranes and, thus, protect against microbial invaders. Recent reports, however, show that not all defensins are for defense. Some of these peptides are actually plant hormones or other signaling molecules. At this point, we have reached a frontier in plant biology.

## Ancillaries

### For the Student

A student companion website, hosting study quiz questions, an interactive glossary, crossword puzzles, interactive flashcards, and research and reference links, has been developed to accompany Plant Biochemistry and is available at http://biology.jbpub.com/gleason/plantBiochemistry/.

### For Instructors

An Instructor's Media CD-Rom containing PowerPoint® Lecture Outlines and an Image Bank are available to instructors using Plant Biochemistry in their course instruction.

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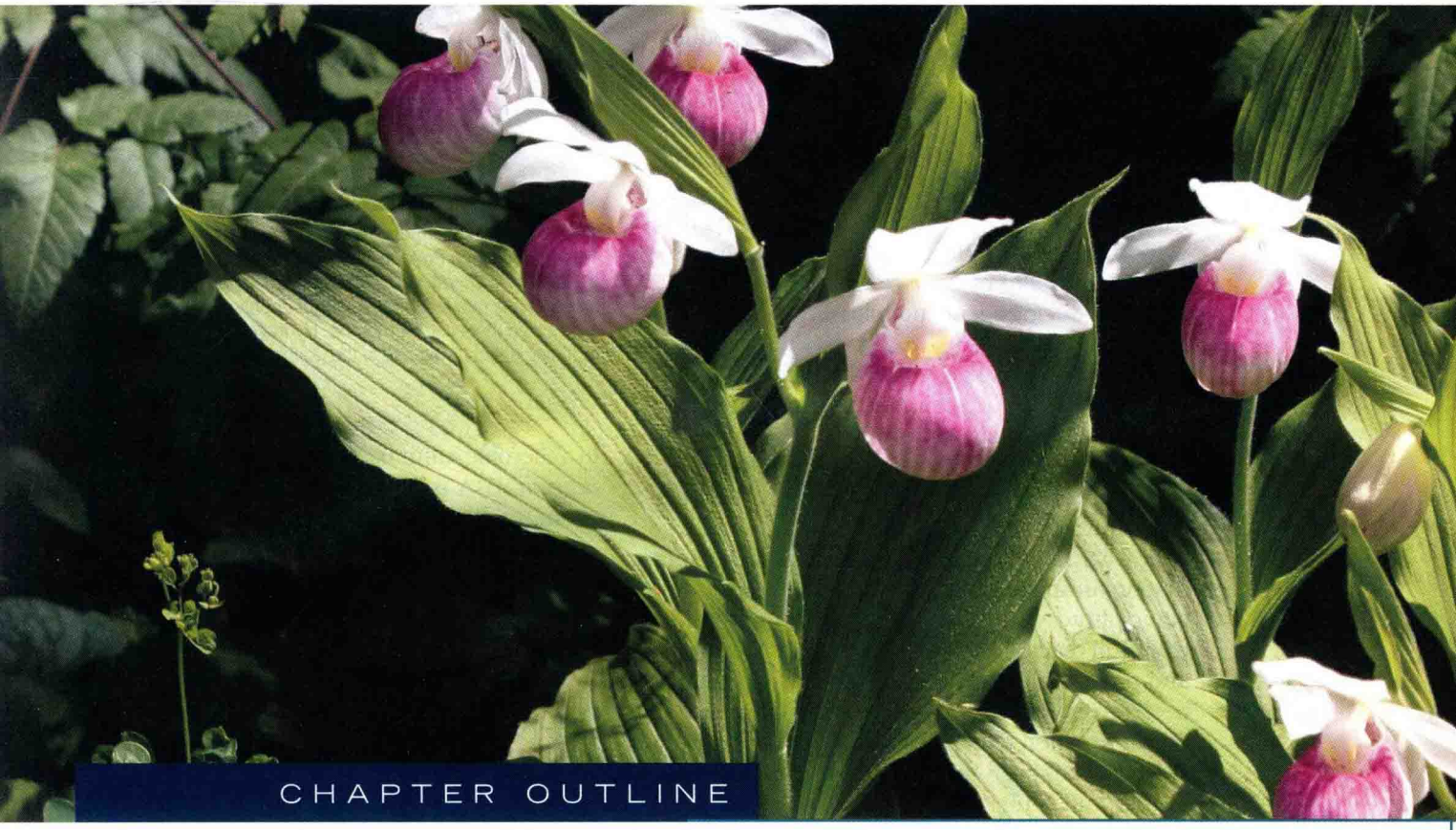
# CHAPTER 1

# Photosynthesis: The Light Reaction



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**1.12 Photosynthesis Inhibitors: Herbicides**

## 1.1 Overview

Life on Earth runs on solar energy. The biological solar age started 3.5 to 3.0 billion years before the present when ancient microorganisms first evolved the ability to convert light energy from the sun into chemical bond energy of organic molecules. These ancient microorganisms lived in an anoxic world and used sunlight to produce adenosine triphosphate (ATP). Using this photochemically derived energy, they were thus able to take advantage of the various reduced compounds, such as $H_2S$, on the primitive Earth and subsequently reduce atmospheric $CO_2$ to sugars. About 0.5 billion years later, cyanobacteria developed a slightly different process, replacing reduced sulfur and organic compounds with $H_2O$ as their reducing agent and releasing oxygen into the primitive atmosphere. The oxygen released from this oxygenic photosynthesis slowly built up in the Earth's atmosphere, reaching a partial pressure of 1 kPa approximately 1.5 billion years ago. At this time the oxygen concentration was sufficient for formation of ozone ($O_3$) in the stratosphere that screened out the more energetic solar radiation and made it possible for the first organisms to colonize the land. Today, oxygenic photosynthesis is the most common biochemical reaction on our planet, both in aquatic and terrestrial systems, and sustains almost all heterotrophic life forms. This complex series of reactions, often referred to as green plant photosynthesis, has been conserved throughout Earth's history and is the mechanism for energy transduction in cyanobacteria, algae, and nonvascular and vascular plants.

The overall chemical process of green plant photosynthesis was first described in the nineteenth century by the following equation:

$$6CO_2 + 6H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2$$

A large amount of energy is required to drive this reaction; the standard free energy change ($\Delta G^\circ$) is calculated to be 2,880 kJ $mol^{-1}$. This energy is provided by visible light with wavelengths of 400 to 700 nm. The equation, as written, describes an oxidation-reduction (redox) reaction. Historically, the reaction was not recognized as a redox reaction because water does not readily release electrons and thus is not an effective reducing agent. However, in the 1930s Cornelis van Niel and his coworkers demonstrated that anaerobic photosynthetic bacteria perform the following reaction:

$$nCO_2 + nH_2A \xrightarrow{\text{Light}} (CH_2O)_n + nA$$

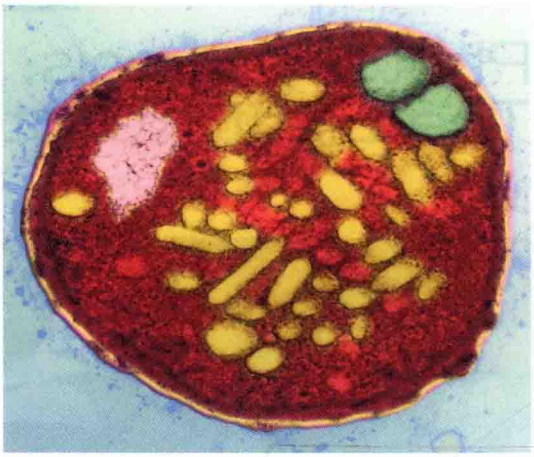


**FIGURE 1.1** Light micrograph of a purple sulfur bacterium. This example of a Proteobacterium photosynthesizes only under anoxic conditions. Bacteriochlorophylls, other pigments, and proteins needed to harvest light energy and produce ATP are located in its cell membrane. Hydrogen sulfide ($H_2S$) is the reducing agent giving rise to the grains of elemental sulfur.

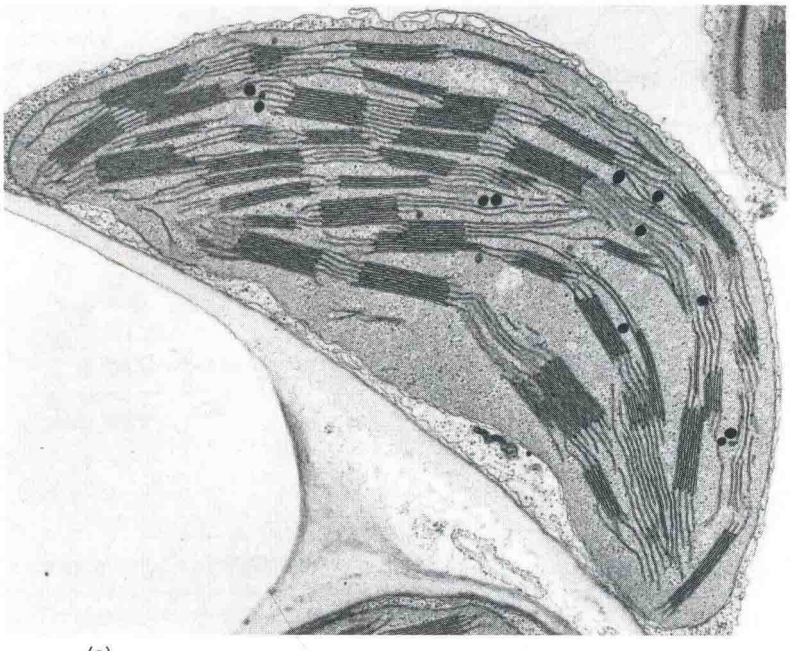
In anaerobic sulfur bacteria such as *Rhodospirillum rubrum*, $H_2A$ is $H_2S$, which is a good reducing agent, and elemental sulfur is excreted to the outside of the cell (**FIGURE 1.1**) or oxidized to other compounds. By analogy, $H_2A$ in green plant photosynthesis is $H_2O$ and oxygen is released. Subsequent experiments by Ruben and Kamen in 1941 using $^{18}O$-labeled water clearly showed that the oxygen generated in green plant photosynthesis is derived from the oxidation of water. Unlike anaerobic bacteria, plants absorb sufficient light energy to remove electrons from water. Subsequent research in the past 67 years has sought to elucidate the mechanisms behind this deceptively simple redox reaction.

## 1.2 The Hill Reaction

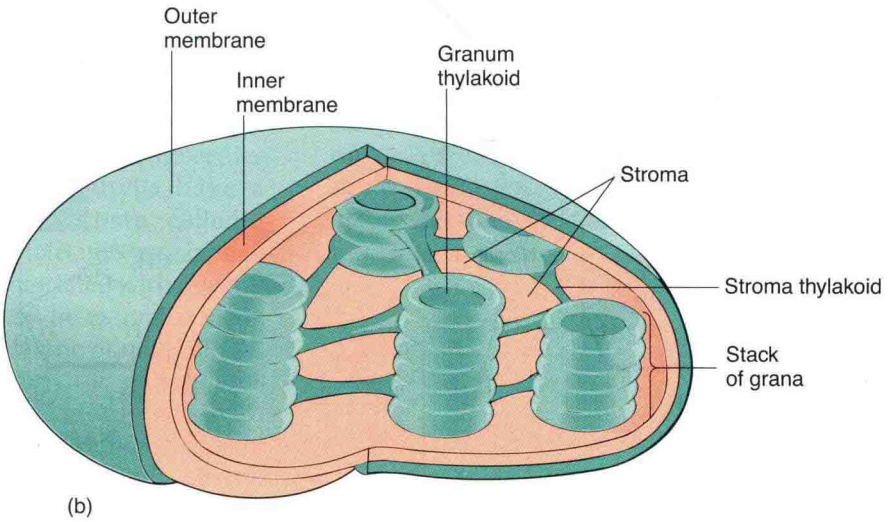
Photosynthesis occurs in the chloroplasts of eukaryotic algae and plants and in the cytoplasm of cyanobacteria. The chloroplast is an organelle with two or more outer membranes and a set of internal membranes called thylakoids. The soluble portion of the organelle is called the stroma (**FIGURE 1.2**).

Although the chloroplast is clearly the site of photosynthesis in plants, experiments with isolated chloroplasts in the early twentieth century were disappointing. When removed from the plant cell, these organelles were inactive. However, in 1937 Robin Hill showed that isolated chloroplasts evolve oxygen when supplied with an artificial electron acceptor such as ferricyanide:

$$4Fe^{3+} + 2H_2O \xrightarrow{\text{Light}} 4Fe^{2+} + 4H^+ + O_2$$



(a)




(b)

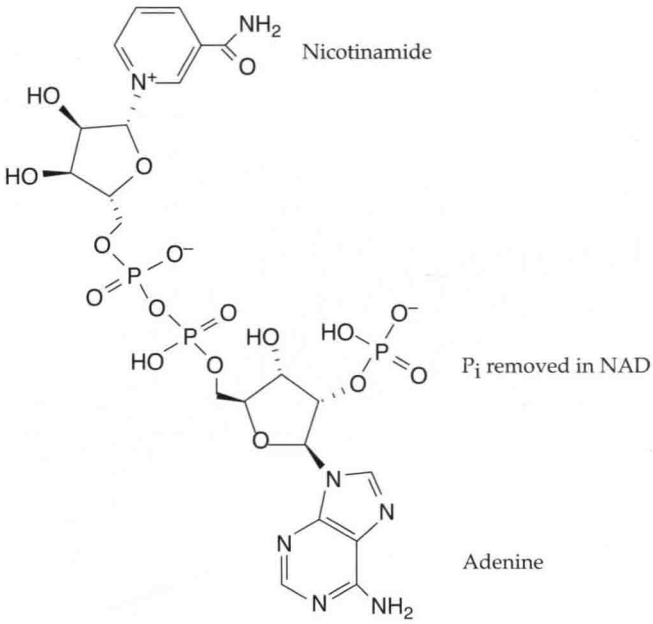
**FIGURE 1.2** Electron micrograph (a) and diagram (b) of a chloroplast from maize. Chloroplasts in eukaryotic algae and plants have two or more outer membranes. In addition, the organelle has an extensive array of interior membranes called thylakoids. In angiosperms (flowering plants), these are arranged in stacks called grana (singular, granum). The thylakoid membranes are the site of the light reaction. These membranes are small sacs with an internal space or lumen. The soluble portion of the chloroplast is the stroma. It contains enzymes and cofactors needed for $CO_2$ fixation.

He concluded that the biological electron acceptor must be a water-soluble compound that is leached out of the organelle during the isolation procedure. In the most commonly used methods for chloroplast isolation, the outer membranes are damaged and soluble components of the stroma can be lost. The membranes, including thylakoid membranes, remain associated with each other and can be separated by centrifugation into a pellet. The components of the stroma are present in the supernatant fraction, usually in a highly dilute form. Isolated chloroplasts evolve $O_2$ (oxidize $H_2O$) but cannot produce carbohydrates (reduce $CO_2$). Gentle procedures for chloroplast isolation that preserved intact organelles capable of the complete photosynthetic process were not devised until the 1960s.

However, Hill's work was a major breakthrough in the study of photosynthesis. He clearly showed that photosynthesis is basically two oxidation-reduction reactions. The light reaction involves the oxidation of water, release of oxygen, and reduction of a soluble component. This occurs in thylakoid membranes. The second redox reaction, the reduction of carbon dioxide and oxidation of the soluble component, occurs in the water-soluble portion (i.e., the stroma) of the chloroplast. The Hill reaction can be written as follows:

$$2H_2O + 2A \xrightarrow{\text{Light}} 2AH_2 + O_2$$

where A is a redox dye such as dichloroindophenol, methyl viologen, or ferricyanide. Hill's



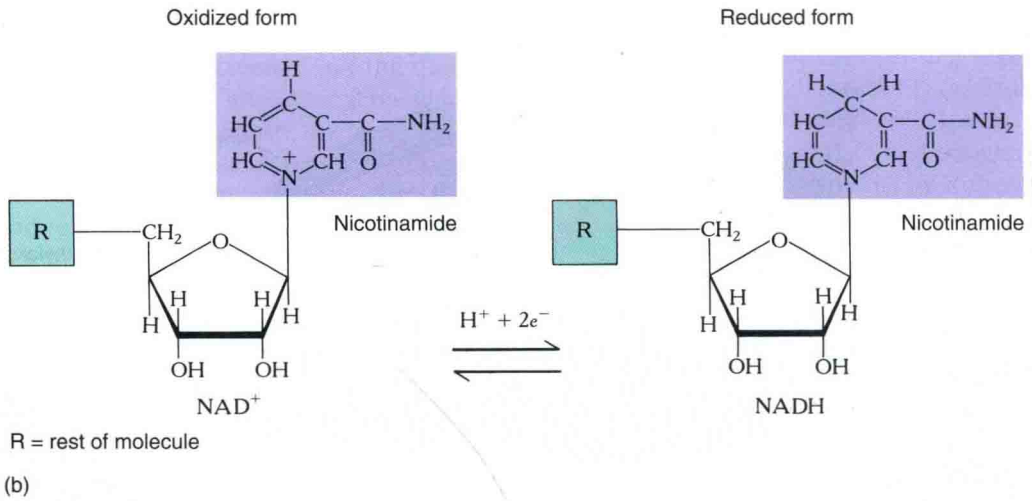




**FIGURE 1.3** Nicotinamide adenine dinucleotide phosphate (NADP). (a) NADP consists of two nucleotides connected by a phosphodiester bond. A similar redox cofactor, NAD, lacks the second phosphate group on the adenine ribose. (b) The nicotinamide ring accepts two electrons and one proton (hydride, $H^-$ ion) to produce the reduced cofactor, NADPH.

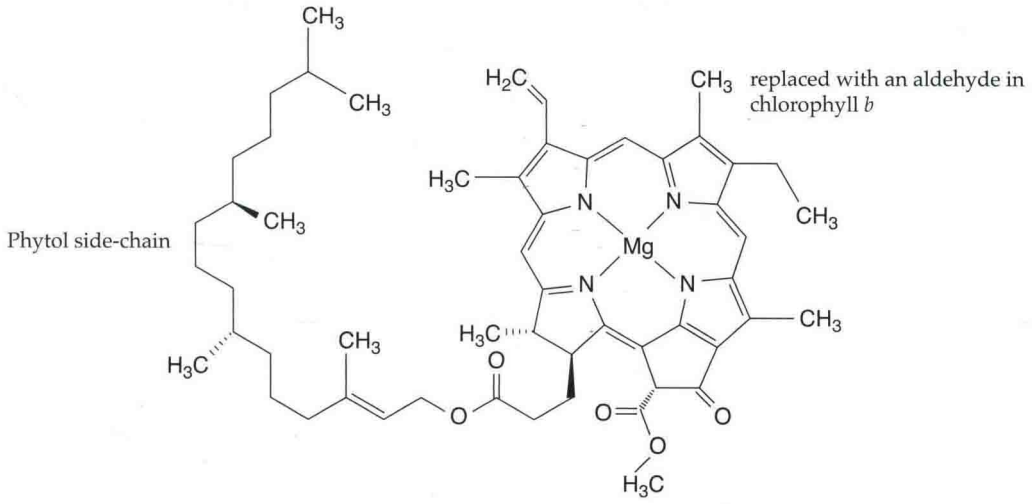
contribution made it possible to study the light reaction in isolated organelles either spectrophotometrically or polarographically by monitoring the evolution of oxygen. In the 1950s Daniel Arnon and coworkers demonstrated that the soluble cofactor, NADP (nicotinamide adenine dinucleotide phosphate; **FIGURE 1.3**), is the physiological electron acceptor. This research group also showed that isolated chloroplasts produce ATP when adenosine diphosphate (ADP) and $PO_4^{3-}$ (inorganic phosphate, Pi) are added to the incubation mixture. The light reaction could now be written in its complete form:

$$2\text{NADP} + \text{Pi} + \text{ADP} + 2\text{H}_2\text{O} \xrightarrow{\text{Light}} 2\text{NADPH} + 2\text{H}^+ + \text{ATP} + \text{O}_2$$

## 1.3 Photosynthetic Pigments

### ■ Chlorophyll *a*

This basic energy conversion, light energy to chemical bond energy, occurs in the thylakoid membranes. Visible light supplies the energy for the oxidation of water and the transfer of electrons to NADP. Electron transfer also provides the energy for the synthesis of ATP. Light energy is captured by photosynthetic pigments. All organisms that perform oxygenic photosynthesis use a pigment called chlorophyll *a* (**FIGURE 1.4**). The basic structural element of all chlorophylls is a tetrapyrrole ring that is also found in related molecules containing heme groups such as cytochromes. In the chlorophyll ring the four nitrogens are coordinated to a Mg ion, as opposed




Chlorophyll *a*

**FIGURE 1.4** Structure of chlorophyll *a*. The tetrapyrrole ring is a conjugated system, making this portion of the molecule rigid and planar. The four nitrogens of the tetrapyrrole ring are conjugated to a Mg ion. Various substitutions can be made to the groups on the ring to produce other types of chlorophylls. For example, in chlorophyll *b* a methyl group is substituted with an aldehyde. The 20-carbon long phytol side chain makes the entire molecule very hydrophobic.

to an Fe in heme groups. The ring is a conjugated system (i.e., alternating double and single bonds), which means that it has a rigid, planar structure because of the overlap of the hybrid molecular orbitals. In addition, chlorophylls have a 20-carbon hydrocarbon side chain, called a phytol unit, making these molecules very hydrophobic. Chlorophylls are associated with integral membrane proteins and can be extracted using organic solvents such as acetone or ethanol.

In addition to chlorophyll *a*, most plants also contain other types of chlorophylls with different chemical groups on the side chains of the tetrapyrrole ring. Chlorophylls absorb visible light in the blue and red regions of the visible spectrum (**FIGURE 1.5**; **see Appendix 7 for discussion of spectrophotometry**). The absorption spectrum is influenced by the chemical environment (e.g., the solvent in which the molecules are dissolved). Figure 1.5 shows the spectrum of isolated chlorophyll *a* and associated carotenoid pigments dissolved in ethanol. The major absorption peak at approximately 430 nm is characteristic of all tetrapyrrole rings and is called the Soret band. The absorption bands in the red region of the spectrum (approximately 630 and 660 nm) are characteristic of chlorophyll *a* and are called the Q bands. Most photosynthetic organisms also synthesize some accessory pigments that absorb light in other regions of the visible spectrum. In chlorophyll *b*, a common accessory pigment in angiosperms, an aldehyde replaces a methyl group in the tetrapyrrole ring (Figure 1.4). This substitution shifts the Soret band toward the red end of the spectrum and the Q bands toward the blue end of the spectrum compared with chlorophyll *a*, thus providing a wider range of light absorption (**FIGURE 1.6**). "Green" light, at approximately 500 to 600 nm, is not absorbed but is

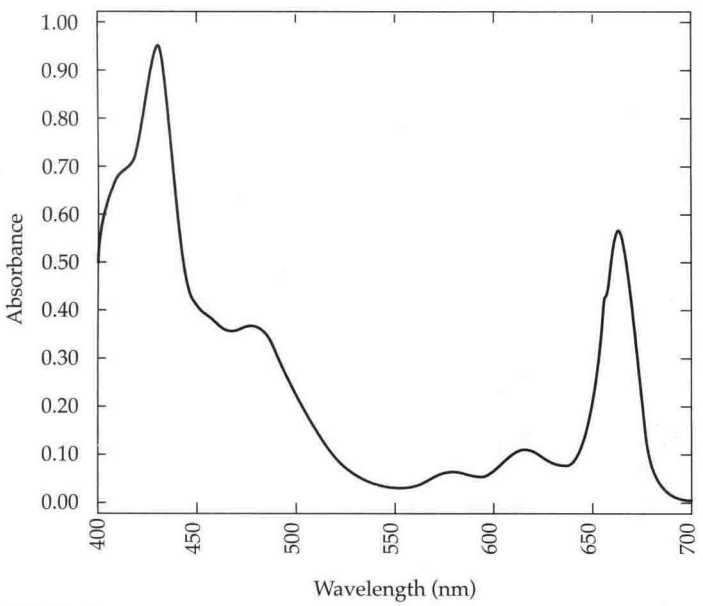



**FIGURE 1.5** The visible absorption spectrum of photosynthetic pigments from a cyanobacterium, *Gloeocapsa alpicola*. The photosynthetic pigments were extracted from the cells with ethanol. The major peak at 430 nm is called the Soret band and is characteristic of most cyclic tetrapyrroles. The bands at 630 and 660 nm, Q bands, are characteristic of chlorophyll *a*. The shoulder at approximately 470 nm is due to absorption of light by accessory carotenoid pigments.



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