Chlorophyll

The generic name for the intensely green, blue, or purple tetrapyrrolic pigments found in higher plants, algae, and photosynthetic bacteria that serve as photoreceptors and transducers of light energy to chemical energy in photosynthesis. *See* PHOTOSYNTHESIS.

Occurrence and Distribution of Major Cholorophylls

Although only about 20 chlorophylls are discussed here, new chlorophylls are found every year, especially in marine microalgae and photosynthetic bacteria of lakes and tidal flats. Chlorophylls *a*, *b*, and *d* are found in oxygenic photosynthetic organisms. All members of the chlorophyll *c* group are found in oxygenic, marine microalgae. Bacteriochlorophylls *c*, *d*, *e*, and *g* are found in anoxygenic (non-oxygen-producing) photosynthetic bacteria. All members of the chlorophyll *c* group are found in oxygenic, marine microalgae.

Chlorophylls a and b. The principal chlorophylls of higher plants and green algae are chlorophylls *a* and *b*. Chlorophyll *a* is found in the light-harvesting pigment-protein complexes (also called antennae) and reaction-center complexes (where the chemistry takes place) of all oxygen-evolving organisms, while chlorophyll *b* is found only in the antennae.

In higher plants, chlorophylls *a* and *b* are contained in the chloroplast (a type of cell plastid). At the highest magnification of the light microscope, one may just see tiny grana in the plastids of higher plants. A granum is made up of 10–100 discs (known as thylakoids), which are the basic photosynthetic apparatus. Chlorophylls *a* and *b* are attached to specific proteins located in the thylakoid membrane. In addition to the outer light-harvesting antennae complexes, two functionally and structurally distinguishable groups of chlorophyll-protein complexes exist: photosystem I and photosystem II. Each photosystem, with the associated antenna, contains about 300 chlorophyll molecules (and a few carotenoid molecules). The majority of these chlorophylls serve as light-harvesting antennae and funnel the energy they absorb to the special reaction-center chlorophylls of photosystem I and II. These reaction-center chlorophylls are special as they are two chlorophyll *a* molecules held in close juxtaposition by a unique protein environment. *See* CAROTENOID; CELL PLASTIDS; PLANT CELL.

Chlorophyll c. The chlorophyll *c* group is a rapidly expanding group of at least eight antenna chlorophylls. All members of the chlorophyll *c* group are found in oxygenic marine microalgae and brown algae. *See* ALGAE.

Chlorophyll d. Chlorophyll *d* has been shown to be the major chlorophyll in the cyanobacterium *Acaryochloris marina* which is a free-living epiphytic bacterium growing in association with red algae. *See* CYANOBACTERIA.

Bacteriochlorophylls. Photoheterotrophic bacteria, which do not evolve O_2, contain bacteriochlorophyll *a* as their reaction-center pigment but may contain bacteriochlorophylls *a, b, c, d, e,* and *g* as antenna pigments. Purple photosynthetic bacteria contain bacteriochlorophylls *a, b,* and *g,* and the green bacteria contain bacteriochlorophylls *a, c, d,* and *e*. *See* BACTERIA; BACTERIAL PHYSIOLOGY AND METABOLISM.

Function

Chlorophyll molecules have three functions: (1) They serve as antennae to absorb light quanta. (2) They transfer this energy from one chlorophyll to another over distances usually of 1.5–2 nm by a process of resonance transfer, so that the energy finally comes to reside in the special chlorophyll molecules P700 or P680 (the number after P represents their long-wavelength absorption maxima) in the reaction centers of photosystem I or II. (3) The special reaction-center chlorophyll molecules P680 and P700, having in their excited states (symbolized as P680* and P700*) the energy of the photon, undergo chemical oxidation by transferring one of their electrons to a neighboring acceptor molecule. Specifically, P680* transfers one electron to a pheophytin molecule (in case of photosystem II) and P700* to another chlorophyll molecule (in the case of photosystem I). In this way the energy of the fleeting light quanta is converted into stable chemical energy.

Light-induced oxidation of reaction-center chlorophyll molecules leads to photobleaching, which is detected spectroscopically by an absorbance decrease. Loss of an electron oxidizes the reaction-center chlorophyll molecules. P680 is transformed to $P680^+$ and P700 to $P700^+$. Analogous bacteriochlorophyll species, P840+ or P890+, is produced in nonoxygenic photosynthetic bacteria. These cationic species are detected both optically as well as by the electron spin resonance technique, because each has an unpaired electron. *See* SPECTROSCOPY.

Chemical Structure

Chlorophylls contain up to four pyrrole rings that are joined by four methine ($—CH\!\!=\!\!$) bridges at C5, C10, C15, and C20. However, all chlorophylls also contain a fifth cyclopentanone ring, designated E. Chlorophylls with four pyrrole rings are called phytoporphyrins, and the chlorophylls of the *c* group belong to this family, the members of which are emerald green in color. Chlorophyll *a* contains three pyrrole rings (rings A, B, and C) and one dihydropyrrole ring (ring D) with a hydrogen atom at C17 and C18 (**Fig. 1**). Such chlorophylls are called chlorins, and chlorophylls *a*, *b*, and *d*, and bacteriochlorophylls *c*, *d*, and *e* belong to this family: chlorophyll *a* is blue and the other five are green. Some chlorophylls contain two dihydropyrrole rings (rings B and D) with hydrogen atoms at C7, C8, C17 and C18. These chlorophylls are called bacteriochlorins. Bacteriochlorophylls *a*, *b*, and *g* belong to the bacteriochlorin family and they are purple. These different-colored chlorophylls allow the organisms that possess them to efficiently use (as photosynthetically active radiation) those parts of the visible and near-infrared spectrum of solar radiation that permeate their environment.
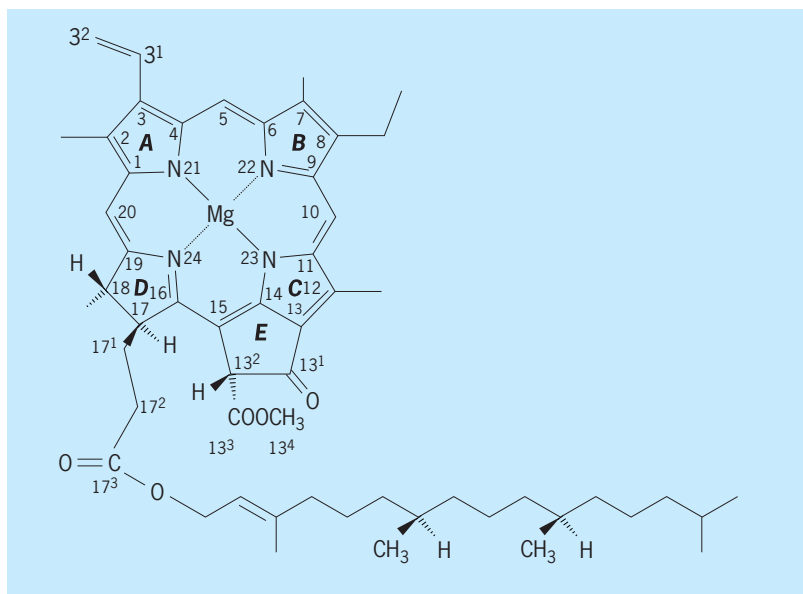
Fig. 1. Structure of chlorophyll *a* ($C_{55}H_{72}O_5N_4Mg$).

Central metal atom. Chlorophyll molcecules contain a central magnesium (Mg) atom that binds extra ligands (besides the four pyrrolic nitrogens) so strongly that it seldom exists only as a four-coordinate metal: one or both of the axial positions are occupied by an electron donor (nucleophile) group so that the Mg is generally a six-coordinate metal, but also sometimes exists as a five-coordinate metal. Axial coordination to the central Mg atom is important for understanding the ligation of chlorophyll to histidine, glutamine, or asparagine residues of chlorophyll apoproteins. Due to the greater than 4 coordination number of Mg, chlorophyll can exist as a monomer, dimer, trimer, tetramer, and as an aggregate of *n* number of chlorophyll molecules. The monomers absorb red light maximally in the 660–670-nm region, whereas the aggregates absorb (darker) red light in the 680–700-nm region. On the other hand, the chlorophyll-H_2O-chlorophyll adduct is suggested to absorb as far as 740 nm; the (chlorophyll·$H_2O)_2$ adduct may absorb around 700 nm.

Chlorins. The structure of chlorophyll *a*, which is a 3-monovinyl compound, is shown in Fig. 1. This molecule has now been synthesized in the laboratory. The characteristic feature of chlorophyll *a* is that it is a Mg-chlorin. Because rings A, B, C, and D are linked through methine bridges at C5, C10, C15, and C20 (Fig. 1), a large resonating 16-membered inner ring of carbon and nitrogen atoms attached to each other through alternating single and double bonds is formed. Closely related derivatives of chlorophyll *a* (the monovinyl pigment shown in Fig. 1) include [3,8-divinyl]-chlorophyll *a* which sometimes has long-chain alcohols other than phytol esterified at $C17^3$. Some widely dispersed marine phytoplanktonic *Prochlorococcus* strains contain 3,8-divinyl derivatives of chlorophylls *a* and *b*: it has been calculated that these divinyl pigments are responsible for approximately 25% of global photosynthesis.

Other chlorophylls closely related to chlorophyll *a* possess formyl (—CH=O) groups. Chlorophyll *b* is [7-formyl]-chlorophyll *a* and chlorophyll *d* is [3-formyl]-chlorophyll *a*.

Bacteriochlorophylls *c* and *d*, like chlorophyll *a*, belong to the chlorin family. The common features include a hydroxyethyl (—CHOHCH₃) group at C3, while the carboxymethyl (—COOCH₃) group at $C13^2$ of chlorophyll *a* is replaced by a H atom and the long-chain alcohol esterified at $C17^3$ is frequently farnesol ($C_{15}H_{25}OH$) of chlorophyll *a*, which replaces the phytol ($C_{20}H_{39}OH$). Bacteriochlorophylls *c* and *e* in addition have a C20 methyl (—CH₃) substituent.

Phytoporphyrins. The chlorophyll *c* group is a diverse group of Mg-phytoporphyrins including [3,8-divinyl]-protochlorophyllide *a*, which is also shown as a biosynthetic intermediate in the biosynthesis of chlorophyll *a* (**Fig. 2**). Most chlorophylls *c* have a free $C17^3$ carboxyl group, but two recently discovered nonpolar chlorophylls *c* are esterified at $C17^3$ to the sugar residue of a monogalactosyldiacylglycerol (MGDG) moiety. Frequently, the propionate group at C17 is replaced by an acrylic acid (—CH=CH—COOH) side chain.

Bacteriochlorins. Bacteriochlorophylls *a, b*, and *g* belong to the bacteriochlorin family of chlorophylls. There are several forms of bacteriochlorophyll *a*: one is esterified at $C17^3$ with phytol and the other is esterified with geranyl-geranol. Both forms have an acetyl (—CO—CH₃) group at C3 and an ethyl (—C₂H₅) group at C8. Bacteriochlorophylls *b* and *g* have an ethylidene (=CH—CH₃) group at C8 but bacteriochlorophyll *b* has an acetyl group at C3 where bacteriochlorophyll *g* has a vinyl (—CH=CH₂) group. In *Acidiphilium rubrum* the central Mg of bacteriochlorophyll *a* is replaced by a zinc (Zn) atom.

Chlorophyll derivatives. Pheophytins are chlorophyll derivatives lacking the central Mg atom; they occur naturally as electron acceptors in photosystem II. Bacteriopheophytin *a* is a derivative of bacteriochlorophyll *a* and serves as an electron acceptor in bacterial reaction centers. Pheophorbides are chlorophyll derivatives that have lost the central Mg atom and the long-chain alcohol ester moiety.

Biosynthesis

The two major plant tetrapyrrole pigments, chlorophylls and hemes, are both synthesized from ALA (5-aminolevulinic acid). ALA is converted to protoporphyrin in a series of enzymatic steps, which are identical in plants and animals. Thereafter, the pathway branches to form hemes text are porphyrins chelated with iron (Fe^{2+}), which are present in many respiratory hemoproteins including cytochromes. In the other branch, porphyrins are chelated with Mg^{2+} to form precursors of chlorophyll (Fig. 2). *See* HEMOGLOBIN; PORPHYRIN.

ALA is formed by the condensation of succinyl coenzyme A and glycine by ALA-synthase in non-plastid-containing eukaryotes (animals, yeasts and fungi) and in the *α* subgroup of proteobacteria (which includes the well-known genera of photosynthetic bacteria *Rhodopseudomonas,*

Rhodobacter, and *Rhodospirillum*). However, in plants, algae, Archaea, and most bacteria (excluding the α-proteobacteria), ALA is formed from glutamate, a 5-carbon amino acid, by the C_5 pathway. This is the more ubiquitous pathway of ALA formation in nature. All of the enzymes necessary for converting glutamate to ALA (and further to chlorophyll) are contained in the chloroplasts of higher plants and green algae. The $C13^1$, $C13^2$, and $C13^3$ of ring E (Fig. 1) arise from the propionic acid (—CH_2—CH_2—COOH) group of Mg-protoporphyrin. An oxygen is introduced to form a 13^1-oxo-propionic acid (—CO—CH_2—COOH) moiety and spontaneous bonding then occurs between $C13^2$ and C15, thus forming ring E with a $C13^3$ carboxymethyl ($CHOOCH_3$) substituent. In higher plants and green algae, the oxygen for the 13^1-oxo-group comes from molecular oxygen (O_2), by activity of an oxygenase-type enzyme; in anaerobic photosynthetic bacteria, it comes from water (H_2O), by a hydratase enzyme activity.

In higher plants, a light-dependent and reduced nicotinamide adenine dinucleotide phosphate (NADPH)-dependent protochlorophyllide reductase (LPOR) introduces a hydrogen atom at both C17 and C18, thus converting protochlorophyllide to chlorophyllide. Cyanobacteria, green algae, mosses, ferns, and gymnosperms contain both LPOR and a dark (that is, light-independent) DPOR enzyme so that these organisms can synthesize chlorophyllide in light or dark. The esterification of a geranylgeranyl pyrophosphate forms chlorophyll *a* with a geranyl-geranyl ester, which is followed by reduction to a phytyl ester: the esterification and reduction are both catalyzed by chlorophyll synthase, thus completing chlorophyll *a* formation. Among additional cofactors required for chlorophyll formation are Fe^{2+}, Mg^{2+}, adenosine triphosphate (ATP), nicotinamide adenine dinucleotide (NAD), and O_2. Concomitant with chlorophyll synthesis, the disk, or thylakoid, membranes are also synthesized. The possible origins of the phycobilin pigments, chlorophylls *b*, *c*, and *d*, and the bacteriochlorophylls are shown in Fig. 2.

Fluorescence

Chlorophylls reemit a fraction of the light energy they absorb as fluorescence. Regardless of the wavelength of the absorbed light, the emitted fluorescence is always on the long-wavelength side of the lowest energy absorption band, in the red or infrared region of the spectrum. The fluorescent properties of a particular chlorophyll are functions of the structure of the molecule and its immediate environment. Thus, the fluorescence spectrum of chlorophyll in the living plant is always shifted to longer wavelengths (peak at 685 nm) relative to the fluorescence spectrum of a solution of the same pigment (peak at approximately 660 nm). This red shift is characteristic of chlorophyll-protein complexes.

Even in dilute solutions, the capacity of chlorophyll to fluoresce depends on the nature of the solvent. In solvents that can combine with the central Mg atom of chlorophyll by donating a pair of elec-
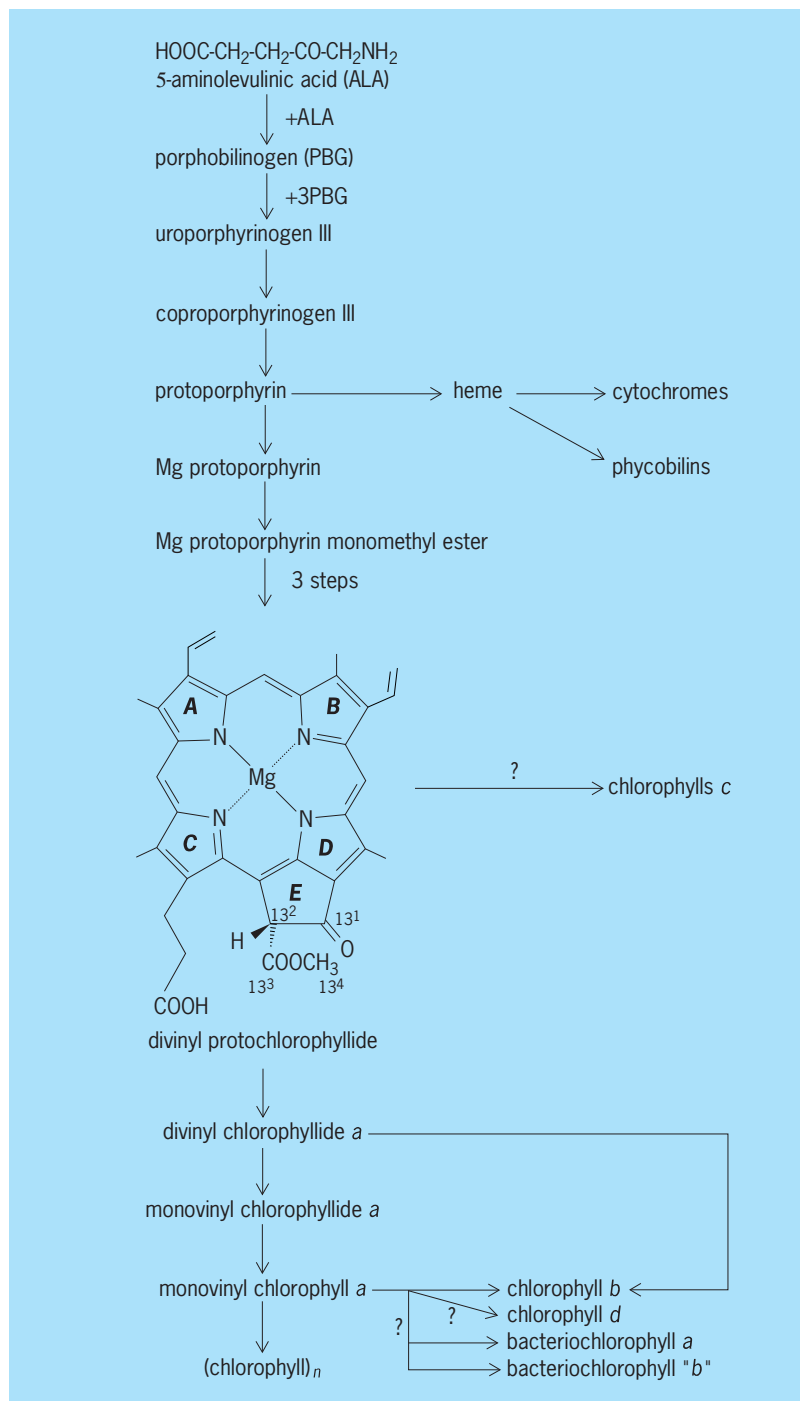

Fig. 2. Simple biosynthetic route for chlorophyll *a* and some related compounds. (In reality most of the pathways are much more complex and are often branched.) The tetrapyrrole structure shown above is Mg 3,8-divinyl protochlorophyllide.

trons to it, chlorophyll is fluorescent. In solvents that lack this property, chlorophyll is dimeric or polymeric and nonfluorescent at room temperature. The aggregates are formed by combining the carbonyl group of one molecule with the Mg atom of the neighboring molecule.

An excited chlorophyll *a* in diethyl ether has a mean lifetime of 5×10^{-9} s (5 nanoseconds), whereas in the living plant this is reduced to $0.5–2 \times 10^{-9}$ s (0.5–2 ns). A long-lived excited state of chlorophyll *a* (the triplet state) has been observed under

special conditions, such as illumination of concentrated solutions in dry hydrocarbon solvents at low temperatures. Under these conditions, chlorophyll *a* emits phosphorescence at a spectral maximum of 750 nm. Weak phosphorescence of chlorophyll *a* has been recently observed in living cells.

The most widespread chlorophylls in nature, chlorophylls *a* and *b*, fluoresce with a quantum efficiency of 0.33 and 0.16, respectively, in dilute solution in diethyl ether. In the living cell the quantum efficiency drops to 0.03 for chlorophyll *a* and to zero for chlorophyll *b*. This is due to the property of chlorophyll *b* to transfer all its excitation energy to chlorophyll *a*, which, in turn, channels most of its excitation to photosynthesis, allowing only a small fraction to escape as fluorescence.

Measurements of chlorophyll *a* fluorescence are of great practical use as these have been shown to be a probe of the efficiency of photosynthesis. Applications of fluorescence are numerous and include measurements of the photosynthetic efficiency of plants under field conditions; advance estimations of the impact of abiotic and biotic environmental stresses on anticipated crop and biomass and yields; and, the assessment of the photosynthetic efficiency and productivity of plant communities in terrestrial, inland water, and marine ecosystems by remote sensing of chlorophyll *a* fluorescence. *See* FLUORESCENCE.

Govindjee; Robert J. Porra; George C. Papageorgiou

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Choanoflagellida

An order of the class Zoomastigophorea, superclass Mastigophora, subphylum Sarcomastigophora, in the phylum Protozoa. They are principally small, single-celled or colonial, structurally simple, colorless flagellates distinguished by having the anterior end surrounded by a thin protoplasmic collar, within which is an ingestive area for particulate matter, for ex-
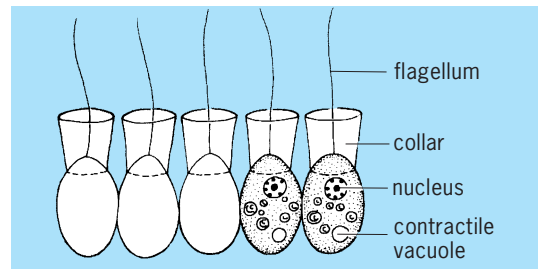
A linear colony of the choanoflagellate, *Desmarella moniliformis.*

ample, bacteria. A single flagellum arises from the center of this collar. The genus *Monosiga* is single, sometimes with a stalk, sometimes free in the plankton. *Desmarella* is a linear colony (see **illus.**), and *Astrosiga* and *Sphaerosiga* are colonies radiating from a center. *Proterospongia* cells arise in a common jelly, the zooids being organically connected. *Diploeca* lives in an attached lorica. *Stelexomonas* and *Aulomonas* inhabit tubular loricae. *Diplosiga* has a double colony. *Sportelloeca* and *Pleurasiga* live in complex loricae. *See* PROTOZOA; SARCOMASTIGOPHORA; ZOOMASTIGOPHOREA.

The botanist P. Bourrelly puts these organisms in the order Monosigales. It is generally agreed, however, that the group shows relationships to the sponges. They are widespread in fresh and salt water and are common in inshore waters.   James B. Lackey

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Choke (electricity)

An inductor that is used to prevent electric signals and energy from being transmitted along undesired paths or into inappropriate parts of an electric circuit or system. Power-supply chokes prevent alternating-current components, inherent to a power supply, from entering the electronic equipment. Radio-frequency chokes (RFCs) prevent radio-frequency signals from entering audio-frequency circuits. The printed circuit boards used in virtually all electronic equipment such as computers, television sets, and high-fidelity audio systems typically have one or more chokes. The purposes of these chokes are the (1) attenuation of spurious signals generated in the equipment itself so that these signals will not be transmitted to other parts of the circuit or beyond the overall system to other electronic devices; (2) prevention of undesired signals or electrical noise generated in other parts of the system from adversely affecting circuit performance; and (3) prevention of ripple from the power supply from degrading system behavior. Waveguide chokes keep microwave energy from being transmitted to the wrong part of a waveguide system. *See* ELECTRICAL