BASIC FOOD CHEMISTRY

Second Edition

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Dedicated to the memory of
Dr. Donald K. Tressler
and Prof. Dr. Reinhold Grau,
both respected friends and colleagues

Preface

Food chemistry has grown considerably since its early foundations were laid. This has been brought about not only by research in this field, but also, and more importantly, by advances in the basic sciences involved.

In this second edition, the chapters dealing with fundamentals have been rewritten and strengthened. Three new chapters have been added, Water and Solutions, Colloids, and Minerals. The chapter on Fruits and Vegetables has been expanded to cover texture.

Other chapters discuss flavor and colors, together with one on browning reactions. The last seven chapters give the student a background of the classes of food products and beverages encountered in everyday use. Each chapter includes a summary and a list of references and suggested readings to assist the student in study and to obtain further information.

Basic Food Chemistry is intended for college undergraduates and for use in food laboratories.

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Frank A. Lee

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1

Photosynthesis

INTRODUCTION

The basic source of energy in the world is photosynthesis. This is the result of a series of reactions by which the low energy substances, carbon dioxide and water, are converted into sugars, which are high energy substances. The conversion is accomplished with the addition of a minimal free energy which amounts to +686,000 calories per mole and is obtained from the oxidation of a mole of glucose.

ROLE OF CHLOROPHYLL

The agent for the conversion of carbon dioxide and water into sugars is chlorophyll, the green pigment in plants, and the energy is derived from sunlight. This involves two types of reactions. One takes place in the sunlight, the second takes place in the dark and results in the formation of sugars. Chlorophyll *a* is the agent for solar energy conversion in the primary process, the products of which are enzymatically converted to sugars in the subsequent dark reactions.

Many types of plants have the power to carry on photosynthesis. These include the higher green plants as well as the green, brown, and red algae and many unicellular organisms. Lower forms that carry on photosynthesis include the blue-green algae and purple and green bacteria. Many of these are anaerobes and require H_2S or other compounds of sulfur to complete their activities in this chain of reactions. In such cases the S takes the place of O_2 in the process. These lower forms of life are very important in the photosynthetic process, and it seems likely that a great deal of photosynthesis is carried on by them. It follows that photosynthetic products are produced in great quantities by unicellular forms of life. It is well to note, however, that all forms of life which carry on photosynthesis, except bacteria, make use of water as the hydrogen (electron) donor to reduce carbon dioxide which is the electron acceptor.

Chlorophyll and associated pigments are contained in the plants in bodies known as chloroplasts. Chloroplasts are rather complex structures. They vary in size, being about 1–2 μm in diameter and 4–10 μm long, and are composed of structures known as grana. These latter are composed of lamellae, which, in turn, are made up of sheets of membranes known as quantasomes (Table 1.1).

Chlorophyll is present in the chloroplasts as lipoprotein complexes. However, the physical state of the chlorophyll, which is photochemically active, is not yet understood. This combination is broken by nonpolar solvents, hence the extraction of chlorophyll from plant materials is by means of these solvents. Isolated spinach chloroplasts are often used to study the reactions involved in photosynthesis.

Blue-green algae, and bacteria that are capable of carrying on photosynthesis, do not have chloroplasts, although the blue-green algae have lamellae in the cytoplasm. The photosynthetic bacteria have another arrangement, which is attached to the cell membrane.

Chlorophyll is the important pigment in photosynthesis because of its part in the absorption of light, the energy of which permits the buildup of sugars. The presence of many conjugated double bonds in chlorophyll results in a particular structure resonating at the frequencies of the red and blue range of visible light. Actually, chlorophylls *a* and *b* are involved, usually about 3 parts of *a* to 1 part of *b*, in the higher plants. Chlorophyll *c* is found in brown algae, diatoms, and dinoflagellates. Chlorophyll *d* is found in red algae. Accessory pigments include the yellow carotenoids and the blue or red phycobilins. It is perhaps likely that these accessory pigments have an effect in the part of the solar spectrum that is not in the chlorophyll range. Chlorophyll, depending on its plant source, can utilize light wavelengths from about 400 to almost 900 nm to carry on photosynthesis. For chlorophyll *a*

TABLE 1.1. Approximate Composition of an Average Spinach Quantasome

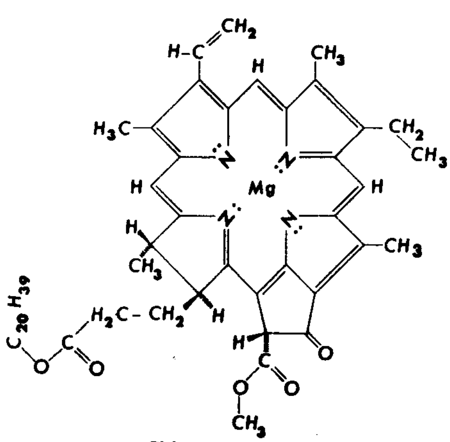
Component	Molecules per Quantasome	Component	Molecules per Quantasome
Chlorophyll *a*	160	Phospholipids (lecithin, phosphatidyl ethanolamine, phosphatidyl inositol, phosphatidyl glycerol)	116
Chlorophyll *b*	65		
Carotenoids	48		
Quinones			
Plastoquinone A	16	Sulfolipids	48
Plastoquinone B	8	Galactosylglycerides	500
Plastoquinone C	4	Cytochrome b_6	1
α-Tocopherol	10	Cytochrome *f*	1
α-Tocopherylquinone	4	Plastocyanin	5
Vitamin K_2	4	Ferredoxin	5

Source: White *et al.* (1973). Reproduced with permission of the McGraw-Hill Book Company.

from higher plants, the absorption maximum is in the neighborhood of 675 nm while that of chlorophyll *b* is about 650 nm. Accessory pigments such as the carotenoids and other chlorophylls absorb from 400 to about 550 nm.

Evidence has been collected that indicates that two light reactions are involved in the part of the photosynthetic process that evolves oxygen. It has been postulated by Duysens (1964) that photosystem I involves chlorophyll *a* and does not evolve oxygen. However, photosystem I is associated with photosystem II which contains chlorophyll *a* and chlorophyll *b* or another chlorophyll (*c* or *d*) according to the species involved and does evolve oxygen. Other pigments are involved also. There has been much speculation concerning the mechanisms of action of these two systems.

Chlorophylls *a* and *b* have a non-ionic magnesium atom in the structure, which is held by two coordinate and two covalent linkages. When chlorophyll is treated with weak acids, the magnesium is removed from the molecule and pheophytin, the olive green compound, is formed. This is especially important to food chemists because it is the cause of the particular green color found in canned green vegetables that have been processed under pressure.



Chlorophyll *a*

The basic structures for chlorophylls *a* and *b* were worked out by H. Fischer (1934, 1937). The structure for chlorophyll *b* is the same as chlorophyll *a* except that a —CHO (formyl) group takes the place of the methyl group at position 3.

CHEMISTRY OF PHOTOSYNTHESIS

For many years it was thought that the path for the conversion of carbon dioxide and water into sugars was through formaldehyde,

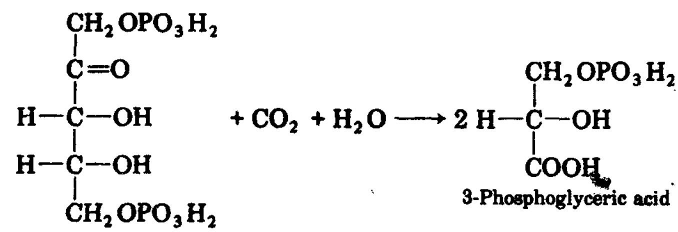
CH_2O, the simplest such compound. However, this compound could never be detected. Furthermore, it is toxic to plants if present in more than trace amounts. This theory was abandoned when the work of Calvin showed that a different and complex pathway is the actual course of events. The general equation for this synthesis is

$$6\ CO_2 + 6\ H_2O \longrightarrow C_6H_{12}O_6 + 6\ O_2$$

This may be written in the more general terms as follows:

$$x\ CO_2 + x\ H_2O \longrightarrow (CH_2O)x + O_2$$

These changes were investigated using CO_2 and water with labeled carbon atoms (^{14}C) and suspensions of green algae, followed by two-directional paper chromatography. Finally the spots were demonstrated by placing the chromatograms over photosensitive paper. The first compound to be formed was found to be a 3-carbon compound, 3-phosphoglyceric acid, with the labeled carbon appearing mainly in the carboxyl carbon atom. This compound was formed from a 5-carbon compound, ribulose-1,5-diphosphate rather than a 2-carbon compound. When CO_2 and H_2O react with this compound, two molecules of 3-phosphoglyceric acid result. The enzyme involved in this reaction is diphosphoribulose carboxylase.



Ribulose-1,5-diphosphate 3-Phosphoglyceric acid

Table 1.2 gives the steps involved in the production of sugars by photosynthesis together with regeneration of pentose, which is necessary to the continuation of the cycle. It should be noted that the carbohydrates actively engaged in this process are in the form of phosphoric acid esters. The transfer of energy is brought about by adenosine triphosphate (ATP), an extremely important compound. In reaction 2, the 3-phosphoglycerate from the first reaction is reduced to 3-phosphoglyceraldehyde. The molecules of this compound thus formed are used in 3 and 4 to make fructose-6-phosphate in the amount of five molecules of this compound. As the table shows, one of these molecules is the net gain or final product of the photosynthetic process. The others are changed into ribulose-1,5-diphosphate for use in the next cycle. This set of reactions has been demonstrated by the use of purified enzymes. It is believed that this set of reactions occurs in the chloroplasts. There are, however, reasons to believe the possible existence of other pathways for the production of sugars by photosynthesis.

TABLE 1.2. Hexose Accumulation and Pentose Regeneration in Photosynthesis

Step	Enzyme	Reaction[a]	Carbon Balance
1.	Carboxylation enzyme	6 Ribulose-1,5-diphosphate → 12 3-phosphoglyceric acid	6(5) + 6(1) → 12(3)
2.	Phosphoglyceric acid kinase	12 3-Phosphoglyceric acid + 12 ATP → 12 1,3-diphosphoglyceric acid + 12 ADP	12(3) → 12(3)
	Phosphoglyceraldehyde dehydrogenase	12 1,3-Diphosphoglyceric acid + 12 DPNH + 12 H^+ → 12 3-phosphoglyceraldehyde + 12 DPN^+ + 12 P_i	12(3) → 12(3)
3.	Triose isomeraldelase	5 3-Phosphoglyceraldehyde → 5-dihydroxyacetone phosphate	5(3) → 5(3)
		5 3-Phosphoglyceraldehyde + 5-dihydroxyacetone phosphate → 5-fructose-1,6-diphosphate	5(3) + 5(3) → 5(6)
4.	Phosphatase	5 Fructose-1,6-diphosphate → 5 fructose-6-phosphate + 5 P_i	5(6) → 5(6)
5.	Transketolase	2 Fructose-6-phosphate + 2 3-phosphoglyceraldehyde → 2 xylulose-5-phosphate + 2 erythrose-4-phosphate	2(6) + 2(3) → 2(5) + 2(4)
6.	Transaldolase	2 Fructose-6-phosphate + 2 erythrose-4-phosphate → 2 sedoheptulose-7-phosphate + 2 3-phosphoglyceraldehyde	2(6) + 2(4) → 2(7) + 2(3)
7.	Transketolase	2 Sedoheptulose-7-phosphate + 2 3-phosphoglyceraldehyde → 4 xylulose-5-phosphate	2(7) + 2(3) → 4(5)
8.	Epimerase	6 Xylulose-5-phosphate → 6 ribulose-5-phosphate	6(5) → 6(5)
9.	Phosphoribulokinase	6 Ribulose-5-phosphate + 6 ATP → 6 ribulose-1,5-diphosphate + 6 ADP	6(5) → 6(5)
	Net: 6 Ribulose-1,5-diphosphate + 6 CO_2 + 18 ATP + 12 DPNH + 12 H^+ → 6 ribulose-1,5 diphosphate + 1-fructose-6-phosphate + 17 P_i + 18 ADP + 12 DPN^+		6(5) + 6(1) → 6(5) + 1(6)

Source: White *et al.* (1973). Reproduced with permission of the McGraw-Hill Book Company.

[a] Key to abbreviations: ATP = Adenosine triphosphate. ADP = Adenosine diphosphate. P_i = Inorganic orthophosphate. DPNH = Reduced diphosphopyridine nucleotide. DPN = Diphosphopyridine nucleotide.

It has been shown by the use of ^{18}O-labeled water and carbon dioxide that the oxygen formed during the process of photosynthesis comes from the water and not from the carbon dioxide (Kok and Jagendorf 1963). The great force that affects the conversion of light energy is demonstrated in this reaction by the fact that the electrons flow in the direction of the more energy-rich state, which is against the usual flow of electrons. Only a very powerful force could accomplish this.

It was suspected for a long time that two types of reactions were involved in photosynthesis. One of these reactions was thought to require the presence of sunlight to supply the necessary energy, the other could take place in the dark; that is, light was not required. Experimental support for this supposition was first obtained by Hill in 1937. The results of subsequent research have increased the fundamental knowledge of this phase of the photosynthetic process. It was found that a suspension of chloroplasts illuminated in the absence of CO_2 and then placed in the dark with CO_2 added permitted, briefly, the formation of sugars. This indicates that key compounds that can react with CO_2 were formed during the exposure to light.

Further, it was shown that the first step in the photosynthetic process, the one using sunlight as the energy source, reduces $NADP^+$ (nicotinamide adenine dinucleotide phosphate) and phosphorylates ADP, which results in the formation of NADPH and ATP. This first step releases oxygen, but oxygen is not released in the second step. This emphasizes the fact that the oxygen released during photosynthesis comes from water and not from the CO_2. Water, therefore, is the only electron donor necessary. NADPH and ATP are used in the dark reaction to reduce CO_2 to hexoses and other products.

$$2\,H_2O + 2\,NADP^+ \longrightarrow 2\,NADPH + 2\,H^+ + O_2$$

Photosynthetic bacteria use H_2S and other compounds in the first step of photosynthesis, and, therefore, do not release oxygen. However, if H_2S is used by them in this stage of the process, sulfur is released instead of oxygen. In short, the process is fundamentally similar.

Although a great deal has been learned in recent years about the process of photosynthesis and its intricacies, many problems are still unsolved.

SUMMARY

The basic source of energy in the world is the process known as photosynthesis. In this process, carbon dioxide and water are converted into sugars. It is, however, a rather complex process. The agent for the conversion of carbon dioxide and water into sugars is chlorophyll, the green pigment in plants. Chlorophyll is important in photosynthesis because of the part it plays in the absorption of light. The energy thus absorbed permits the buildup of sugars. Calvin (1956; Wilson and

Calvin 1955) showed the complex pathway that is the actual course of events in photosynthesis.

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