Second Edition

Second Edition

Frank A. Lee, Ph.D.

Professor of Chemistry, Emeritus New York State Agricultural Experiment Station Cornell University Geneva, New York



THE AVI PUBLISHING COMPANY, INC.
Westport, Connecticut

Copyright 1975, 1983 by THE AVI PUBLISHING COMPANY, INC. Westport, Connecticut

All rights reserved. No part of this work covered by the copyright hereon may be reproduced or used in any form or by any means—graphic, electronic, or mechanical, including photocopying, recording, taping, or information storage and retrieval systems—without written permission of the publisher

Library of Congress Cataloging in Publication Data

Lee, Frank A
Basic food chemistry.

Includes bibliographies and index
1. Food. 2 Food—Composition I. Title
TX354.L43 1983 641 3'007454 83-946

ISBN 0-87055-416-6 Printed in the United States of America

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.

The author wishes to express his appreciation to the following people, who reviewed the chapters on their respective specialties: Doctors L.R. Hackler, M. Keeney, B. Love, L.M. Massey, Jr., L.R. Mattick, W.B. Robinson, R.S. Shallenberger, D.F. Splittstoesser, E. Stotz, W.L. Sulzbacher, and J. Van Buren.

In addition, the author wishes to express his appreciation to Dr. H.O. Hultin and Dr. F.W. Knapp for their reviews of the entire original

manuscript and for their helpful comments.

The author welcomes notices of errors and omissions as well as suggestions and constructive criticism.

Frank A. Lee

## Contents

Pre	face	хi
1.	Photosynthesis	1
	Introduction	1
	Role of Chlorophyll	1
	Chemistry of Photosynthesis	3
	Summary	6 7
3	Bibliography	•
2.	Water and Solutions	9
	The Structure of Water	9
	Solutions	19
	Summary	22
	Bibliography	23
3.	Colloids	25
	What Are Colloids?	25
	Behavior of Colloids in an Electric Field	26
	Syneresis	27
	Imbibition	28
	Emulsions	28
	Breaking of Emulsions	29
	Foams	29
	Viscosity	30
	Summary	31
	Bibliography	32
4.	Carbohydrates	33
	Introduction	-00
		33
	Monosaccharides	34
	Structure of Carbohydrates	39
	Carbohydrate Reactions	44
	Oligosaccharides	53
	Polysaccharides	56
	Digestion of Carbohydrates	76
	Qualitative Tests	76
	Quantitative Tests	78
		wii

viii	CONTENTS
* ***	

	Summary	79
	Bibliography	80
_	** **	
5.	Lipids	87
	Simple Lipids	88
	Composite Lipids	102
	Derived Lipids	107
	Oxidation of Lipids	108
	Summary	124
•	Bibliography	126
6.	Proteins	133
	A 1 A 13	
	Amino Acids	133
	Classification of Proteins	144
	Properties of Proteins.	146 152
	Protein Synthesis	152
	Proteins in Foods.	165
	Summary	172
	Bibliography	173
~	Ramman	
7.	Enzymes	177
	Classification	178
	Enzyme Composition	182
	Properties of Enzymes	182
	Enzyme Reactions	190
	Some Enzyme Applications in Food	193
	Bibliography	195 197
		101
8.	The Vitamins	199
	The Water-Soluble Vitamins	199
	The Fat-Soluble Vitamins.	212
	Vitamins and Malnutrition	217
	Summary	218
	Bibliography	220
_	Not	
9.	Minerals	225
	Occurrence of Minerals	228
	Anionic Minerals	231
	Minerals in Canned Foods	232
	Summary	233
	Bibliography	234
10.	Flavor	237
		<b>43</b> /
	The Basic Tastes	237
	Flavors and Volatiles	241
	Flavor Enhancement	253 254

	CONTENTS	ix
	Summary	256 257
11.	Natural Colors	261
	Chemistry of Natural Coloring Matters  Caramels and Melanoidins	262 272
	Color Determination	273 274 278
12.	Browning Reactions	283
	Enzymatic Browning Non-enzymatic Browning The Formation of Brown Pigments Inhibition of Browning. Summary Bibliography	283 288 297 300 301 302
13.	Food Colorings	307
	Color Safety and Regulations.  Colors Exempt from Certification  Color Analysis and Desired Properties  Summary  Bibliography	307 317 320 321 322
14.	Alcoholic Fermentation	323
	Wine Beer and Brewing Distilled Products Vinegar Summary Bibliography	326 336 337 337 338 339
15.	Baked Products	343
	Flour Leavening Summary Bibliography	343 354 357 358
16.	Milk and Milk Products	363
	Milk Composition Rancidity and Off-Flavor in Milk Cheese and Cheese Chemistry Fermentation in Milk Milk Products Other than Cheese Determination of Fat in Dairy Products Total Solids Analysis Summary Riblicorraphy	363 373 375 384 385 387 388 388

#### x CONTENTS

17.	Coffee	397
	Composition of the Green Coffee Bean	398
	Changes During Roasting	401
	Roasted Coffee	403
	Coffee Products	413
	Summary	414
	Bibliography	415
18.	Tea	419
	Methods of Preparation	419
	Chemical Components of Tea	422
	Amino Acids	425
	Chemistry of Tea Manufacture	428
	Tea Aroma	433
	Summary	435
	Bibliography	435
19.	Cocoa and Chocolate	441
	Introduction	441
	Manufacture of Cocoa and Chocolate	442
	Chemical Composition	444
	Changes During Manufacture of Cocoa and Chocolate	447
	Volatiles and Chocolate Flavor	456
	Chocolate and Cocoa Products	457
	Summary	458
	Bibliography	459
20.	Meat and Meat Products	463
	Muscle Composition	463
	Changes in Muscle After Slaughter and During Processing	476
	Effect of Ionizing Radiation	
	Summary	492
	Bibliography	495
21.	Fruits and Vegetables	505
	Ripening and Post Harvest Changes	505
	Storage	518
	Chemistry Involved in the Texture of Fruits and Vegetables	520
	Summary	538
	Bibliography	535
Inde	3X	5 <b>46</b>

### Photosynthesis

Introduction
Role of Chlorophyll
Chemistry of Photosynthesis
Summary
Bibliography

#### 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  $1-2 \,\mu\mathrm{m}$  in diameter and  $4-10 \,\mu\mathrm{m}$  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,	116
Chlorophyll b	65	phosphatidyl ethanol-	
Carotenoids	48	amine, phosphatidyl	
Quinones		inositol, phosphatidyl glycerol)	
Plastoquinone A	16	Sulfolipids	48
Plastoquinone B	8	Galactosylglycerides	500
Plastoquinone C	4	Cytochrome b	1
a-Tocopherol	10	Cytochrome f	1
a-Tocopherylquinone	4	Plastocyanin	5
Vitamin K.	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.

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<sub>2</sub>O, 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

$$6 \text{ CO}_2 + 6 \text{ H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2$$

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

$$x CO_{\bullet} + x H_{\bullet}O \longrightarrow (CH_{\bullet}O)x + O_{\bullet}$$

These changes were investigated using CO<sub>2</sub> and water with labeled carbon atoms (<sup>14</sup>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<sub>2</sub> and H<sub>2</sub>O react with this compound, two molecules of 3-phosphoglyceric acid result. The enzyme involved in this reaction is diphosphoribulose carboxylase.

$$CH_2 OPO_3 H_2$$
 $C=O$ 
 $CH_2 OPO_3 H_2$ 
 $H-C-OH$ 
 $COOH$ 
 $CH_2 OPO_3 H_3$ 
 $CH_2 OPO_3 H_3$ 
 $CH_2 OPO_3 H_3$ 
 $CH_2 OPO_3 H_3$ 

Ribulose-1.5-diphosphate

ġ

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 passible existence of other pathways for the production of sugars by photosynthesis.

TABLE 1.2. Hexose Accumulation and Pentose Regeneration in Photosynthesis

S. A. K.

Step	Enzyme	Reaction*	Carbon Balance
1. 2.	Carboxylation enzyme Phosphoglyceric acid Finase	6 Ribulose-1,5-diphosphate $\rightarrow$ 12 3-phosphoglyceric acid 12 3-Phosphoglyceric acid + 12 ATP $\rightarrow$ 12 1,3-diphosphoglyceric acid + 12 ATP $\rightarrow$ 12 1,3-diphosphoglyceric acid +	$6(5) + 6(1) \rightarrow 12(3)$
co	Phosphoglyceraldehyde dehydrogenase Triose isomeraldelase	12 1.3-Diphosphoglyceric acid + 12 DPNH + 12 H $^+$ $\rightarrow$ 12 3-phosphoglyceraldehyde + 12 DPN $^+$ + 12 P <sub>1</sub> 5 2-Phosphoglyceraldehyde - $^+$ 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	$12(3) \rightarrow 12(3)$ $12(3) \rightarrow 12(3)$ $12(3) \rightarrow 12(3)$
;		5 3-Phosphogyceraldehyde + 5-dihydroxyacetone phosphate — 5-fructose-1,6-diphosphate	y(s) + y(s) 5(3) + 5(3) → 5(6)
<b>4</b> i 1	Phosphatase	5 Fructose-1,6-diphosphate $\rightarrow$ 5 fructose-6-phosphate + 5 P <sub>1</sub>	5(6) → 5(6)
ıci	Transketolase	2 Fructose-6-phosphate + 2 3-phosphoglyceraldehyde $\rightarrow$ 2 xylulose-5-phosphate + 2 erythrose-4-phosphate	2(6) + 2(3) → 2(5) + 2(4)
9	Transaldolase	2 Fructose-S-phosphate $+2$ exythrose-4-phosphate $\rightarrow 2$ sedoheptulose-7-phosphate $+2$ 3-phosphoclyceraldehyde	2(6) + 2(4) → 2(7) + 2(3)
.7	Transketolase	2 Sedoheptulose-7-phosphate + 2 3-phosphoglyceraldehyde → 4 xylulose-5-phosphate	9(7) + 9(3) -+ 4(6)
øj.	Epimerase	6 Xylulosp-5-phosphate → 6 ribulose-5-phosphate	6(5) → 6(5) 1 ±(3)
ග්	Phosphoribulokinase	6 Ribulose-5-phosphate + 6 ATP -> 6 ribulose-1,5-diphosphate + 6 ADP	$6(5) \to 6(5)$
	Net: 6 Kibulose-1,5-diphospi	Neg. 6 Kibulose-1,5-diphosphate + 6 CO <sub>2</sub> + 18 ATP + 12 DPNH + 12 H + → 6 ribulose-1,5 diphos-	6(5) + 6(1) +
	pnate + 1-tructose-6-	phace + i-iructose-o-phosphate + i'l $P_i$ + 18 ADP + 12 DPN +	6(5) + 1(6)

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

<sup>a</sup> 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 <sup>18</sup>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<sub>2</sub> and then placed in the dark with CO<sub>2</sub> added permitted, briefly, the formation of sugars. This indicates that key compounds that can react with CO<sub>2</sub> 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<sub>2</sub>. Water, therefore, is the only electron donor necessary. NADPH and ATP are used in the dark reaction to reduce CO<sub>2</sub> 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.

#### BIBLIOGRAPHY

ARNON, D. I., TSIJIMOTO, H. Y., and McSWAIN, B. D. 1965. Photosynthetic phosphorylation and electron transport. Nature 207, 1367-1372.

BISHOP, N. I. 1971. Photosynthesis: The electron transport system of green plants. Annu. Rev. Biochem. 40, 197-226.

CALVIN, M. 1956. The photosynthetic carbon cycle. J. Chem. Soc. 1895-1915.

DUYSENS, L. N. M. 1964. The subcellular localization of the lysosomal enzyme and its biological significance. In Progress in Biophysics and Molecular Biology, Vol. 14, J. A. V. Butler and H. E. Huxley (Editors). Pergamon Press, Oxford, England.

FISCHER, H. 1934. Chlorophyll A. J. Chem. Soc. 245-256.

FISCHER, H. 1937. Chlorophyll. Chem. Rev. 20, 41-68.

GIBBS, M. 1967. Photosynthesis. Annu. Rev. Biochem. 36, 757-784.

HILL, R. 1965. The biochemists' green mansions: The photosynthetic electron transport chain in plants. In Essays in Biochemistry, Vol. 1. P. N. Campbell and G. D. Greville (Editors). Academic Press. New York.

KATZ, J. J. 1972. Chlorophyll function in photosynthesis. In Advances in the Chemistry of Plant Pigments, C. O. Chichester (Editor). Academic Press, New York.

KOK, B. 1965. Photosynthesis: the path of energy. In Plant Biochemistry, J. Bonner and J. E. Varner (Editors). Academic Press, New York.

KOK, B., and JAGENDORF, A. T. 1963. Photosynthetic Mechanisms in Green Plants. National Academy of Sciences, Washington, DC.

OCHOA, S., and VISHNIAC, W. 1952. Carboxylation reactions and photosynthesis. Science 115, 297-301.

RUBIN, S., RANDALL, M., KAMEN, M. D., and HYDE, J. L. 1941. Heavy oxygen (18O) as a tracer in the study of photosynthesis. J. Am. Chem. Soc. 63, 877-879.

SAN PIETRO, A., GREER, F. A., and ARMY, T. J. 1967. Harvesting the Sun. Academic Press, New York.

VERNON, L. P., and AVRON, M. 1965. Photosynthesis. Annu. Rev. Biochem. 34, 262-296.

VERNON, L. P., and SEELY, G. R. 1966. The Chlorophylls. Academic Press, New York.

WALKER, D. A., and CROFTS, A. R. 1970. Photosynthesis. Annu. Rev. Biochem. 39, 389-428.

WHITE, A., HANDLER, P., and SMITH, E. C. 1973. Principles of Biochemistry, 5th Edition. McGraw-Hill Book Co., New York.

WILSON, A., and CALVIN, M. 1955. The photosynthetic cycle. CO<sub>2</sub> dependent transients. J. Am. Chem. Soc. 77, 5948-5957.