FOOD CHEMISTRY

Second Edition, Revised and Expanded

edited by Owen R. Fennema

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SECOND EDITION, REVISED AND EXPANDED

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FOOD CHEMISTRY

PREFACE TO THE SECOND EDITION

Considerable time has passed since publication of the favorably received first edition so a new edition seems appropriate. The purpose of the book remains unchanged—it is intended to serve as a textbook for upper division undergraduates or beginning graduate students who have sound backgrounds in organic chemistry and biochemistry, and to provide insight to researchers interested in food chemistry. Although the book is most suitable for a two-semester course on food chemistry, it can be adapted to a one-semester course by specifying selective reading assignments. It should also be noted that several chapters are of sufficient length and depth to be useful as primary source materials for graduate-level speciality courses.

This edition has the same organization as the first, but differs substantially in other ways. The chapters on carbohydrates, lipids, proteins, flavors, and milk and the concluding chapter have new authors and are, therefore, entirely new. The chapter on food dispersions has been deleted and the material distributed at appropriate locations in other chapters. The remaining chapters, without exception, have been substantially modified, and the index has been greatly expanded, including the addition of a chemical index. Furthermore, this edition, in contrast to the first, is more heavily weighted in the direction of subject matter that is unique to food chemistry, i.e., there is less overlap with materials covered in standard biochemistry courses. Thus the book has undergone major remodeling and refinement, and I am indebted to the various authors for their fine contributions and for their tolerance of my sometimes severe editorial guidance.

This book, in my opinion, provides comprehensive coverage of the subject of food chemistry with the same depth and thoroughness that is characteristic of the better quality introductory textbooks on organic chemistry and biochemistry. This, I believe, is a significant achievement that reflects a desirable maturation of the field of food chemistry.

Owen R. Fennema

PREFACE TO THE FIRST EDITION

For many years, an acute need has existed for a food chemistry textbook that is suitable for food science students with backgrounds in organic chemistry and biochemistry. This book is designed primarily to fill the aforementioned need, and secondarily, to serve as a reference source for persons involved in food research, food product development, quality assurance, food processing, and in other activities related to the food industry.

Careful thought was given to the number of contributors selected for this work, and a decision was made to use different authors for almost every chapter. Although involvement of many authors results in potential hazards with respect to uneven coverage, differing philosophies, unwarranted duplication, and inadvertent omission of important materials, this approach was deemed necessary to enable the many facets of food chemistry to be covered at a depth adequate for the primary audience. Since I am acutely aware of the above pitfalls, care has been taken to minimize them, and I believe the end product, considering it is a first edition, is really quite satisfying—except perhaps for the somewhat generous length. If the readers concur with my judgment, I will be pleased but unsurprised, since a book prepared by such outstanding personnel can hardly fail, unless of course the editor mismanages the talent.

Organization of the book is quite simple and I hope appropriate. Covered in sequence are major constituents of food, minor constituents of food, food dispersions, edible animal tissues, edible fluids of animal origin, edible plant tissues and interactions among food constituents—the intent being to progress from simple to more complex systems. Complete coverage of all aspects of food chemistry, of course, has not been attempted. It is hoped, however, that the topics of greatest importance have been treated adequately. In order to help achieve this objective, emphasis has been given to broadly based principles that apply to many foods.

Figures and tables have been used liberally in the belief that this approach facilitates understanding of the subject matter presented. The number of references cited should be adequate to permit easy access to additional information.

To all readers I extend an invitation to report errors that no doubt have escaped my attention, and to offer suggestions for improvements that can be incorporated in future (hopefully) editions.

Since enjoyment is an unlikely reader response to this book, the best I can hope for is that readers will find it enlightening and well suited for its intended purpose.

Owen R. Fennema

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FOOD CHEMISTRY

FOOD SCIENCE AND TECHNOLOGY

A Series of Monographs and Textbooks

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INTRODUCTION TO FOOD CHEMISTRY

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I. WHAT IS FOOD CHEMISTRY?

Concern about food exists throughout the world, but the aspects of concern differ with location. In underdeveloped regions of the world, the bulk of the population is involved in food production, yet attainment of adequate amounts and kinds of basic nutrients remains an ever-present problem. In developed regions of the world, food production is highly mechanized and efficient, a small portion of the population is involved in food production, food is available in abundance, and much of it is processed or has been altered by the addition of chemicals. In these localities, concern is directed mainly to the cost of food, its quality, its variety, and its ease of preparation, and to the effects of processing and added chemicals on its wholesomeness and nutritive value. All these concerns are important, and they fall within the realm of food science–the science that deals with the nature of food and the principles underlying its spoilage, preservation, and modification.

Food science is an interdisciplinary subject involving primarily bacteriology, chemistry, biology, and engineering. Food chemistry, a major aspect of food science, is the science that deals with the composition and properties of food and the chemical changes it undergoes. Food chemistry is intimately related to chemistry, biochemistry, physiological chemistry, botany, zoology, and molecular biology. The food chemist relies heavily on knowledge of the aforementioned sciences to effectively study and control biological substances as sources of human food. Knowledge of the innate properties of biological substances and mastery of the means of studying them are common interests of both food chemists and other biological scientists. It is important to note, however, that food chemists have specific interests distinct from those of other biological scientists. The primary interests of biological scientists include reproduction, growth, and changes biological substances undergo under environmental conditions that are compatible or almost compatible with life. On the other hand, food chemists are concerned primarily with biological substances that are dead or dying (postharvest physiology of plants and postmortem physiology of muscle) and are exposed to a wide range of environmental conditions. For example, conditions suitable for sustaining residual life processes are of concern to food chemists during the marketing of fresh fruits and vegetables, whereas conditions incompatible with life processes are of major interest when long-term preservation of food is attempted, that is, during thermal processing, freezing, concentration, dehydration, and irradiation and during the addition of chemical preservatives. In addition, food chemists are concerned with the chemical properties of disrupted food tissues (flour, fruit and vegetable juices, isolated and modified constituents, and manufactured foods), single-cell sources of food (eggs and microorganisms), and one major biological fluid (milk). In summary, food chemists have much in common with other biological scientists, yet they also have interests that are distinctive and of the utmost importance to humankind.

II. HISTORY OF FOOD CHEMISTRY

The origins of food chemistry are obscure, and its general history has not yet been properly analyzed and recorded. This is not surprising, since food chemistry did not acquire an identity until the twentieth century and its history is deeply entangled with that of agricultural chemistry for which historical documentation is not considered exhaustive (5,17). Thus, the following brief excursion into the history of food chemistry is incomplete and somewhat selective. Nonetheless, the available information is sufficient to impart needed perspectives with regard to when, where, and why certain notable food-related events transpired, and with regard to changes that have occurred in the quality of the food supply since the early 1800s.

Although the origin of food chemistry, in a sense, extends to antiquity, the most significant discoveries, as we judge them today, began in the late 1700s. The best accounts of developments during this period are those of Filby (15) and Browne (5), and the authors are indebted to these sources for much of the information presented here.

During the period of 1780-1850 a number of famous chemists made important discoveries, many of which related directly or indirectly to the chemistry of food. In the writings of Scheele, Lavoisier, de Saussure, Gay-Lussac, Thenard, Davy, Berzelius, Thomson, Beaumont, and Liebig lie the origins of modern food chemistry. Some may question whether these scientists, whose most famous discoveries bear little relationship to food chemistry, were in fact involved to a significant degree with the origins of modern food chemistry. Whereas it is admittedly difficult to categorize early scientists as chemists, bacteriologists, or food chemists, for example, it is relatively easy to determine whether a given scientist made substantial contributions to a given field of science. From the following brief examples it is clearly evident that many of these scientists did in fact study foods intensively and did make discoveries of such fundamental importance to food chemistry that their inclusion in any historical account of food chemistry cannot be questioned.

Carl Wilhelm Scheele (1742-1786), a Swedish pharmacist, was one of the greatest chemists of all time. In addition to his more famous discoveries of chlorine, glycerol, and oxygen (3 years before Priestly, but unpublished) he isolated and studied the properties of lactic acid (1780), prepared mucic acid by oxidation of lactic acid (1780), devised a means of preserving vinegar by means of heat (1782, well in advance of Appert's "discovery"), isolated citric acid from lemon juice (1784) and gooseberries (1785), isolated malic acid from apples (1785), and tested twenty common fruits for citric, malic, and tartaric acids (1785). His isolation of various new chemical compounds from plant and animal substances is considered the beginning of accurate analytical research in agricultural and food chemistry.

The French chemist *Antoine Laurent Lavoisier* (1743-1794) was instrumental in the final rejection of the phlogiston principle and in formulating the principles of modern chemistry. With respect to food chemistry, he established the fundamental principles of combustion organic analysis, he was the first to show that the process of fermentation could be expressed as a balanced equation, he made the first attempt to determine the elemental composition of alcohol (1784), and he presented one of the first papers (1786) on organic acids of various fruits.

(Nicolas) Théodore de Saussure (1767-1845), a French chemist, did much to formalize and clarify the principles of agricultural and food chemistry provided by Lavoisier. He also studied CO_2 and O_2 changes during plant respiration (1804), studied the mineral contents of plants by ashing, and made the first accurate elemental analysis of alcohol (1807, by the combusion technique).

Joseph Louis Gay-Lussac (1778-1850) and *Louis-Jacques Thenard* (1777-1857) devised in 1811 the first method for quantitatively determining the percentages of carbon, hydrogen, and nitrogen in dry vegetable substances. Their oxidative combusion technique did not, however, provide a procedure for estimating the quantity of water formed.

The English chemist *Sir Humphry Davy* (1778-1829) in the years 1807 and 1808 isolated the elements K, Na, Ba, Sr, Ca, and Mg. His contributions to agricultural and food chemistry came largely through his books on agricultural chemistry, of which the first edition (1813) was *Elements of Agricultural Chemistry, in a Course of Lectures for the Board of Agriculture* (11). His books served to organize and clarify knowledge existing at that time. In the first edition he stated, "all the different parts of plants are capable of being decomposed into a few elements. Their uses as food, or for the purpose of the arts, depend upon compound arrangements of these elements, which are capable of being produced either from their organized parts, or from the juices they contain; and the examination of the nature of these substances is an essential part of agricultural chemistry" (p. 64). In the fifth edition (Ref. 12, p. 121) he stated that plants are usually composed of only seven or eight elements, and that "the most essential vegetable substances consist of hydrogen, carbon, and oxygen in different proportion, generally alone, but in some few cases combined with azote [nitrogen]."

The works of the Swedish chemist *Jons Jacob Berzelius* (1779-1848) and the Scottish chemist *Thomas Thomson* (1773-1852) resulted in the beginnings of organic formulas, "without which organic analysis would be a trackless desert and food analysis an endless task" (Ref. 15, p. 189). Berzelius determined by analysis the elemental components of about 2000 compounds, thereby verifying the law of definite proportions. He also devised a means of accurately determining the water content of organic substances, a deficiency in the method of Gay-Lussac and Thenard. Moreover, Thomson showed that the laws governing the composition of inorganic substances apply equally well to organic substances, a point of immense importance.

In a book entitled *Considérations générales sur l'analyse organique et sur ses applications* (6), *Michel Eugene Chevreul* (1786-1889), a French chemist, listed the elements known at that time to exist in organic substances (O, Cl, I, N, S, P, C, Si, H, Al, Mg, Ca, Na, K, Mn, Fe) and cited the processes then available for organic analysis: (a) extraction with a neutral solvent, such as water, alcohol, or aqueous ether, (b) slow distillation, or fractional distillation, (c) steam distillation, (d) passing the substance through a tube heated to incandescence, and (e) analysis with oxygen.

Chevreul was a pioneer in the analysis of organic substances, and his classic research on the composition of animal fat led to the discovery and naming of stearic and oleic acids.

Dr. William Beaumont (1785-1853), an American Army surgeon stationed at Fort Mackinac, Michigan, performed classic experiments on gastric digestion that destroyed the concept existing from the time of Hippocrates that food contained a single nutritive component. His experiments were performed during the period 1825-1833 (4) on a Canadian, Alexis St. Martin, whose musket wound afforded direct access to the stomach interior, thereby enabling food to be introduced and subsequently examined for digestive changes.

Among his many notable accomplishments, *Justus von Liebig* (1803-1873) studied vinegar fermentation (1837) and showed that acetaldehyde was an intermediate between alcohol and acetic acid. In 1842 he classified foods as either nitrogenous (vegetable fibrin, albumin, casein, and animal flesh and blood) and nonnitrogenous (fats, carbohydrates, and alcoholic beverages). Although this classification was not correct in detail, it served to distinguish differences among various foods. He also perfected methods for the quantitative analysis of organic substances, especially by combustion, and he published in 1847 what is apparently the first book on food chemistry, entitled *Researches on the Chemistry of Food* (22). Included in this book are accounts of his research on the water soluble constituents of muscle (creatine, creatinine, sarcosine, inosinic acid, lactic acid, and so on).

It is interesting that the developments just reviewed paralleled the beginning of serious and widespread adulteration of food, and it is no exaggeration to state that the need to detect impurities in food was a major stimulus for the development of analytical chemistry in general and analytical food chemistry in particular. Unfortunately, it was also true that advances in chemistry contributed somewhat to the adulteration of food since unscrupulous purveyors of food were able to profit from the availability of chemical literature, including formulas for adulterated food, and could replace older and less effective empirical approaches to food adulteration by more efficient approaches based on scientific principles. Thus, the history of food chemistry and the history of food adulteration are closely interwoven by the threads of several causative relationships (Ref. 15, pp. 18-19), and it is therefore appropriate to consider the matter of food adulteration.

The history of food adulteration in the more developed countries of the world falls into three distinct phases. From ancient times to about 1820 food adulteration was not a serious problem and there was little need for methods of detection. The most obvious explanation for this situation was that food was procured from small businesses or individuals, and the transactions involved a large measure of personal accountability. The second phase began in the early 1800s, when intentional food adulteration increased greatly in both frequency and seriousness. This development can be attributed primarily to increased centralization of food processing and distribution, with a corresponding decline in personal accountability, and partly to the rise of modern chemistry, as already mentioned. Intentional adulteration of food remained a serious problem until about 1920, which marks the end of phase two and the beginning of phase three. At this point regulatory pressures and effective methods of detection reduced the frequency and seriousness of intentional food adulteration to respectable levels, and the situation has gradually improved up to the present time.

Some would argue that a fourth phase of food adulteration began about 1950, when foods containing legal chemical additives became increasingly prevalent, when the use of highly processed foods increased to a point where they represented a major part of the diet of persons in most industrialized countries, and when contamination of some foods with uncontrolled by-products of industrialization, such as mercury and pesticides, became a threat to food safety. The validity of this contention is hotly debated and a consensus is not possible at this time. Nevertheless the course of action in the next few years seems clear. Public concern over the safety of the food supply has already led to some remedial actions, both voluntary and enforced, and more such actions can be anticipated.

The early 1800s also were a period of public concern over the quality of the food supply. Public concern, or more properly public indignation, was aroused in England by Frederick Accum's publication *A Treatise on Adulterations of Food* (1) and by an anonymous publication entitled *Death in the Pot* (3). Accum claimed that, "Indeed, it would be difficult to mention a single article of food which is not to be met with in an adulterated state; and there are some substances which are scarcely ever to be procured genuine" (p. 14). He further remarked, "It is not less lamentable that the extensive application of chemistry to the useful purposes of life, should have been perverted into an auxiliary to this nefarious traffic" (p. 20). Although Filby (15) asserted that Accum's accusations were somewhat overstated, the seriousness of intentional adulteration of food that prevailed in the early 1800s is clearly exemplified by the following not uncommon adulterants cited by Accum and Filby:

Annatto. Adulterants included turmeric, rye, barley, wheat flour, calcium sulfate and carbonate, salt, and Venetian red (ferric oxide, which in turn was sometimes adulterated with red lead and copper).

Pepper, black. This important product was commonly adulterated with gravel, leaves, twigs, stalks, pepper dust, linseed meal, and ground parts of plants other than pepper (e.g., wheat flour, mustard husks, pea flour, sago, and rice flour).

Pepper, cayenne. Substances such as vermilion (α-mercury sulfide), ocher (native earthy mixtures of metallic oxides and clay), and turmeric were commonly added to overcome bleaching that resulted from exposure to light.

Essential oils. Oil of turpentine, other oils, and alcohol.