



THE CHEMISTRY OF FOOD

JAN VELÍŠEK

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Contents

PREFACE vii

ABOUT THE COMPANION WEBSITE ix

CHAPTER 1 INTRODUCTION 1

CHAPTER 2 AMINO ACIDS, PEPTIDES AND PROTEINS 4

- 2.1 Introduction 4
- 2.2 Amino acids 4
- 2.3 Peptides 27
- 2.4 Proteins 35
- 2.5 Reactions 63

CHAPTER 3 FATS, OILS AND OTHER LIPIDS 87

- 3.1 Introduction 87
- 3.2 Classification 87
- 3.3 Fatty acids 88
- 3.4 Homolipids 108
- 3.5 Heterolipids 123
- 3.6 Miscellaneous simple and complex lipids 129
- 3.7 Substances accompanying lipids 132
- 3.8 Reactions 145

CHAPTER 4 SACCHARIDES 198

- 4.1 Introduction 198
- 4.2 Monosaccharides 199
- 4.3 Derivatives of monosaccharides 207
- 4.4 Oligosaccharides 217
- 4.5 Polysaccharides 230
- 4.6 Complex saccharides 278
- 4.7 Reactions 280

CHAPTER 5 VITAMINS 335

- 5.1 Introduction 335
- 5.2 Vitamin A 337
- 5.3 Vitamin D 345
- 5.4 Vitamin E 349
- 5.5 Vitamin K 356
- 5.6 Thiamine 359
- 5.7 Riboflavin 364
- 5.8 Niacin 367

- 5.9 Pantothenic acid 370
- 5.10 Pyridoxal, pyridoxol and pyridoxamine 372
- 5.11 Biotin 375
- 5.12 Folic acid 377
- 5.13 Corrinoids 380
- 5.14 Vitamin C 384
- 5.15 Other active substances 396

CHAPTER 6 MINERALS 402

- 6.1 Introduction 402
- 6.2 Chemistry of minerals 404
- 6.3 Essential elements 416
- 6.4 Non-essential elements 442
- 6.5 Toxic elements 444
- 6.6 Toxic inorganic anions 451
- 6.7 Radionuclides 454

CHAPTER 7 WATER 459

- 7.1 Introduction 459
- 7.2 Drinking water 459
- 7.3 Water in foods 463
- 7.4 Structure 464
- 7.5 Properties 466
- 7.6 Interactions 466
- 7.7 Phase interfaces 473
- 7.8 Food dispersed systems 477
- 7.9 Water activity 494

CHAPTER 8 FLAVOUR-ACTIVE COMPOUNDS 499

- 8.1 Introduction 499
- 8.2 Odour-active substances 500
- 8.3 Taste-active substances 621

CHAPTER 9 PIGMENTS AND OTHER COLORANTS 656

- 9.1 Introduction 656
- 9.2 Tetrapyrroles 657
- 9.3 Other nitrogen pigments 669
- 9.4 Flavonoids 677
- 9.5 Xanthenes 699
- 9.6 Curcuminoids 701
- 9.7 Isochromenes 701
- 9.8 Quinoid pigments 703

- 9.9 Carotenoids 713
- 9.10 Iridoids 730
- 9.11 Other terpenoid pigments 730
- 9.12 Enzymatic browning reactions 732

CHAPTER 10 ANTINUTRITIONAL, TOXIC AND OTHER BIOACTIVE COMPOUNDS 741

- 10.1 Introduction 741
- 10.2 Antinutritional compounds 743
- 10.3 Toxic compounds 747

CHAPTER 11 FOOD ADDITIVES 847

- 11.1 Introduction 847
- 11.2 Substances prolonging the shelf life of foods 848
- 11.3 Substances regulating odour and taste 863
- 11.4 Substances modifying colour 875
- 11.5 Substances modifying texture 882

- 11.6 Substances increasing biological value 888
- 11.7 Other food additives 888

CHAPTER 12 FOOD CONTAMINANTS 892

- 12.1 Introduction 892
- 12.2 Technological contaminants 894
- 12.3 Microbial toxins 942
- 12.4 Persistent organohalogen contaminants 963
- 12.5 Chlorinated aliphatic hydrocarbons 999
- 12.6 Pesticides 999
- 12.7 Veterinary drugs 1022
- 12.8 Contaminants from packaging materials 1031

BIBLIOGRAPHY 1041**INDEX 1079**

Preface

During the 15 years that have elapsed since the first Czech edition of the textbook *The Chemistry of Food* was published, many important monographs and scientific articles from various areas of food science have appeared in the literature, thanks to developments in analytical instrumentation and advances in the knowledge in the field of food technology. All these, plus the interest expressed by the readers, were the impetus that led to the third Czech edition of the book in 2009. This first English edition of *The Chemistry of Food* has remained essentially unchanged in terms of the basic structure of the 12 chapters and the majority of the text, tables, figures and formulae. Certain specific parts, however, have, necessarily, been revised, supplemented and updated.

The Chemistry of Food is the result of many years of experience by workers at the Department of Food Chemistry and Analysis (now Department of Food Analysis and Nutrition), Institute of Chemical Technology in Prague, through the teaching of this subject, plus other related topics taught in the Faculty of Food and Biochemical Technology. The reader will first be introduced to the chemical composition of foods, the important properties of food components and their functions. After these set descriptions, subsequent sections deal with the changes and reactions that occur, or may occur, in foods under certain conditions. It is necessary for the reader to be able to understand the context and complexity of all the processes taking place in foods. As in the previous Czech editions, the authors have tried to reduce to a minimum the amount of text, as is typical for textbooks on biochemistry, microbiology, organic, inorganic and physical chemistry, so that it should not be necessary to consult other specialised textbooks too often, but, at the same time, ensuring the text is clear to both students and professionals.

The textbook contains an introductory chapter and then 11 chapters dealing with the main and accessory nutrients that determine the nutritional and energy value of food raw materials and foods. There is a chapter describing amino acids, peptides and proteins, a chapter dealing with fats, oils and other lipids, as well as chapters on carbohydrates, vitamins, mineral substances and water. Another chapter considers compounds responsible for the aroma, taste and colour attributes that determine the sensory quality of food raw materials and foods. The remaining chapters discuss substances that affect, or may affect, the hygienic–toxicological quality of food raw materials and foods, including antinutritional, toxic

and other biologically active food components, food additives and food contaminants.

The third Czech edition featured the work of many workers from the Department of Food Chemistry and Analysis, along with colleagues from other departments of the Faculty of Food and Biochemical Technology and also external authors. Jan Pánek acted as a co-author of the chapters dealing with the main nutrients, and Helena Čížková and Michal Voldřich participated in these and other chapters. Co-authors of the chapter on amino acids, peptides and proteins were Karel Cejpek and Roman Kubec, of the chapter on fats, oils and other lipids Jana Dostálová and Vladimír Filip, of the chapter on carbohydrates Karel Cejpek and Kamila Míková, of the chapter on minerals Richard Koplík, of the chapter on flavour-active substances Jan Šavel, of the chapter on pigments and other colourants Jana Dostálová, of the chapter of antinutritional and toxic substances Pavel Kalač and Přemysl Slanina, and of the chapter on contaminants Jaroslav Dobiáš, Marek Doležal and Jana Hajšlová. The co-authors of the sections dealing with food legislation were Vladimír Kocourek and Kamila Míková. Most of these co-authors were also involved in the first and second Czech editions of this publication. In addition, co-authors of the first and second Czech editions included Jan Pokorný (the chapter on fats, oils and other lipids), Jiří Davídek (the chapter on vitamins and contaminants), Tomáš Davídek (the chapter on carbohydrates), Karel Hrnčířík (chapters on vitamins and antinutritional and toxic compounds) and Helena Valentová (the chapter on pigments and other colourants). I would like to take this opportunity to thank all of my co-authors and other colleagues for their thorough work. Considerable thanks are also due to the reviewers of the first Czech edition, Prof. Ing. Alexander Příbela, DSc. (Slovak University of Technology in Bratislava, Slovak Republic) and Ass. Prof. RNDr Jan Staněk, PhD, who also did a great deal of hard work on the project.

The co-authors of the Czech editions were Ass. Prof. Ing. Karel Cejpek, Ing. Helena Čížková, PhD, Prof. Ing. Jiří Davídek, DSc., Ass. Prof. Ing. Jaroslav Dobiáš, PhD, Ass. Prof. Ing. Marek Doležal, Prof. Ing. Jana Dostálová, PhD, Prof. Ing. Vladimír Filip, PhD, Prof. Ing. Jana Hajšlová, PhD, Prof. Ing. Vladimír Kocourek, PhD, Prof. Dr Ing. Richard Koplík, Ass. Prof. Ing. Kamila Míková, PhD, Ass. Prof. Ing. Jan Panek, PhD, Prof. Ing. Jan Pokorný, DSc., Ass. Prof. Dr Ing. Kateřina Riddelová and Prof. Ing. Michal

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Jan Velíšek
Prague, February 2013

About the Companion Website

This book is accompanied by a companion website:

www.wiley.com/go/velisek/foodchemistry

The website includes:

- Powerpoints of all figures from the book for downloading
- PDFs of tables from the book
- Powerpoints of all formulae from the book

1

Introduction

The term **food** means material (eaten or drunk) that contains or consists of nutrients (proteins, fats, carbohydrates, vitamins and minerals) and many other chemical substances. Food is usually of plant or animal origin but, to a lesser extent, it may come from other sources, such as algae or microorganisms. Organisms use food to perform one or more of the four essential functions: to supply energy, to build, repair and maintain body tissues, to supply chemical substances that regulate body processes and to supply chemical substances that protect the organism. Traditionally food was provided through agriculture, but today most of the food consumed by the world's population is either supplied by the food industry or home-grown.

Human food, including such items as meat, poultry, fish, milk, vegetables, fruit and beer for example, is chemically very complex. According to rough estimates, fresh foods contain about half a million different chemical compounds. A much larger number of compounds are the result of biochemical (enzymatic) and chemical (non-enzymatic) reactions that occur during the storage of raw materials and foods and during their industrial and culinary processing.

Food science – the scientific study of food – is one of the major branches of the life sciences. Every aspect of food is covered, integrating and incorporating concepts and information from many different fields, including natural, technical and social sciences. It draws primarily on the knowledge of chemical science (biochemistry, organic, inorganic, physical and analytical chemistry), some areas of physics (such as the mechanics of solids and liquids), biology (especially microbiology), biotechnology, some of the branches of medical science (human nutrition, human physiology, pharmacology, toxicology) and agricultural science (e.g., crop and livestock production, post-harvest plant physiology and *post-mortem* muscle physiology). It also uses a range of experiences from technical engineering disciplines, such as agricultural and food engineering, particularly in the form of genetic food engineering. Food science may also call upon some experience of economics, sociology, psychology and other branches of social science.

The most important building blocks of food science are **food chemistry** and **food technology**. Food chemistry deals not only with the composition of food raw materials and end food products, but also with the behaviour, interactions and reactions of food components and the changes occurring in these food raw materials and end food products under various conditions during production, storage, processing, preparing and cooking. Food technology covers the entire gamut from procuring food raw materials to processing them into food products to preserving, packaging and delivering the food products to the consumer market. The common interest of both disciplines is examination of the possibilities of enhancing the positive changes and preventing the unwanted ones, elimination of antinutritive and toxic food components, and prevention of possible contamination with substances that can pose health risks and guarantee food safety. Producing safe and nutritious food for human and animal consumption is one of the principal aims of both food chemistry and food technology.

The most important natural constituents of foods are the **nutrients** that all organisms need in order to live and grow. The **main** (primary or basic) **nutrients** are **proteins**, **fats** (mainly triacylglycerols and phospholipids, but also numerous other lipids) and **carbohydrates** (such as some poly-, oligo- and monosaccharides) that determine the **nutritional** (nutritive) **value** of food, as they provide structural material (e.g., proteinogenic amino acids used for protein synthesis and lipids from which cell membranes are built) and energy. They may also have other functions. Nutrients are said to be essential if they must be obtained from an external source, either because the organism cannot synthesise them or it cannot produce them in sufficient quantities. Essential main nutrients include not only essential amino acids, but also lipids that are precursors of biologically active substances (such as essential fatty acids and some signalling molecules) and thus have protective functions. Also, some oligosaccharides are biologically active substances (e.g., breast milk oligosaccharides that act as receptor analogues to inhibit the adhesion of pathogens on the epithelial surface).

The energy value of consumed food depends on the content of nutrients and on such factors as their digestibility, utility, content of some other substances, dietary regime, mental health status and other factors. Energy value is mainly related to proteins, fats and carbohydrates.

Organic nutrients also include **vitamins**. Inorganic chemical compounds, such as dietary **minerals, water** (and oxygen), may also be considered nutrients. Vitamins and dietary minerals are collectively known as **accessory (additive) nutrients** and are often referred to as **essential nutritional factors**. With the exception of some vitamins that humans cannot synthesise, these accessory nutrients must be obtained from foods. They are therefore known as **exogenous factors**. Another essential nutrient is water, which is obtained in small amounts by oxidation of primary nutrients, but in much larger quantities from foods, and especially from beverages. Most foods contain a mixture of some or all of the nutrient classes, together with many other substances. Some nutrients can be stored internally (such as the fat soluble vitamins), while others are required more or less continuously. Poor health may be caused by a lack of required nutrients or, in extreme cases, too much of a required nutrient.

Some nutrients, such as proteins, peptides and amino acids, lipids, carbohydrates, vitamins and minerals, are also sensorially active substances (e.g., sweet or bitter). The main nutrients along with other substances (certain organic acids, such as acetic and citric acids, and sugar alcohols, such as glucitol, known as sorbitol) can simultaneously also be a source of energy, for example, ethanol has a relatively high energy value.

In human nutrition, nutrients are often inaccurately classified in a way that reflects the amount that the body requires. These nutrient classes can be categorised as either **macronutrients** (required in relatively large amounts) or **micronutrients** (required in smaller amounts). The macronutrients include proteins, fats, carbohydrates and water; the micronutrients are minerals and vitamins. A third class of dietary material, known as fibre (such as non-digestible polysaccharide cellulose), is also necessary, for both mechanical and biochemical reasons. Other micronutrients include antioxidants and various phytochemicals, which are said to influence or protect some body systems. Their necessity is not well established.

Besides nutrients, foods contain many substances that influence the food sensory impression and its **organoleptic properties**. These food constituents are known as **sensorially active compounds**. They determine the **sensory value** (quality) of foods, inducing an **olfactory** sensation (perception), which is described as the aroma, odour and smell, **gustative** perception, which is the taste, **visual** perception, which is the colour, **haptic (tactile)** perception, which is the touch and feel, and **auditorial** perception, which is the sound. The olfactory sensation is derived from odour-active compounds and the gustative perception from taste-active compounds. Flavour is the sensory impression determined by the chemical senses of both taste and smell and is caused by flavour-active food components. Haptic sensation is the **texture**, which is affected mainly by high molecular weight compounds, such as proteins and polysaccharides, often referred to collectively as hydrocolloids. Geometric aspects of texture that evoke both haptic and visual sensations symbolise the terms **appearance** and **shape**.

Aspects of texture related to mechanical properties of food are called **consistency**. Auditorial sensations are associated with a range of textural characteristics (such as crispiness).

Food also contains a range of substances with beneficial or, vice versa, with a negative impact on human health. There is now increasing evidence to support the hypothesis that some foods and food components have beneficial physiological and psychological effects over and above the provision of the basic nutrients. Food that does not have a significant history of consumption or is produced by a method that has not previously been used for food is called **novel food**. This was first termed by the European Union (EU) in Regulation (EC) No. 258/97 of the European Parliament and of the Council of 27 January 1997 concerning novel foods and novel food ingredients. An example of a novel food is margarine containing phytosterols that help to reduce the blood cholesterol level. Other examples include canola oil produced from rapeseed with low levels of both erucic acid and glucosinolates and exotic fruits and vegetables, which have a long history of safe use. **Functional foods** are defined as foods (beverages) having disease preventing and/or health promoting benefits in addition to their nutritive or processing value. A food can be regarded as functional if it is satisfactorily demonstrated to affect beneficially one or more target functions in a body, beyond adequate nutritional effects. Functional food can be a natural food, a food to which an existing ingredient has been added, or a food from which a harmful component has been removed by technological or biotechnological processes. The term functional food (officially not used by the EU) was first used in Japan in the 1980s. (FOSHU, Ministry of Health, Labor and Welfare, Japan. Available at: <http://www.mhlw.go.jp/english/topics/foodsafety/fhc/02.html>.) Examples of functional foods with a long history are table salt fortified with iodine or margarine fortified with vitamin D. Another example is yoghurts with live microorganisms beneficial to the host organism (bacteria of the genus *Bifidobacterium*), which have advantageous effects on health and are called **probiotics**. **Prebiotics** are non-digestible food ingredients (usually oligosaccharides and other substances classified as soluble dietary fibre) that stimulate the growth and/or activity of beneficial bacteria in the small intestine. **Symbiotics** contain both prebiotics and probiotics. **Nutraceuticals** are foods and food products, in some countries physiologically active compounds isolated from foods, which reportedly have a physiological benefit or provide protection against chronic diseases. Such products may range from nutrients (essential amino acids, essential fatty acids, vitamins and minerals), to **dietary supplements** (also known as food supplements or nutritional supplements) and specific diets, to genetically modified foods and other products. Dietary supplements provide nutrients, fibre and various biologically active substances from foods, usually classified according to their effects as antioxidants and anticarcinogens, which may be missing or may not be consumed in sufficient amounts in food. Some countries define dietary supplements as foods, while in others they are defined as drugs or natural health products. Supplements containing vitamins or dietary minerals are included as a category of food in the 'Codex Alimentarius', a collection of internationally recognised standards, codes of practice, guidelines and other recommendations relating to foods, food production and

food safety. **Organic food** is food that is produced using methods that do not involve modern synthetic inputs, such as synthetic pesticides and chemical fertilisers, and does not contain genetically modified organisms or food additives and is not processed using irradiation.

The food components that impair utilisation of nutrients (proteins, lipids, carbohydrates, vitamins and minerals) by biochemical mechanisms are called **antinutritional substances**. An example of such an antinutritional substance is oxalic acid, found in spinach and rhubarb, and which binds up calcium to insoluble calcium oxalate and prevents its absorption. Many foods (especially foods of plant origin) contain various natural toxic substances. These may be toxic only to certain individuals causing an **allergy**, which is related to the immune system response of the organism, or a **food intolerance**, which occurs when food irritates a person's digestive system or when a person is unable to properly digest or breakdown the food. The most common food allergies are peanuts, tree nuts (such as walnuts, pecans and almonds), fish and shellfish, milk, eggs, soy products and wheat. Intolerance to lactose in milk and other dairy products is the most common food intolerance.

Substances toxic to all individuals are called **toxic substances** or **toxins**. Once a toxic substance has contacted the body it may have either acute (immediate) or chronic (long term) effects. Most of food-borne toxins are substances with low acute toxicity (such as the pungent alkaloid piperine in black pepper), although some may present chronic effects, such as hepatotoxic pyrrolizidine alkaloids in plants (such as comfrey and coltsfoot species) or cause pathological changes to the respiratory system (e.g., tobacco smoke).

Many chemical compounds in foods (as well as in feeds for livestock) are added intentionally as food **additives**. The purpose is to protect foods against spoilage, oxidation and increase some aspects of the food quality (e.g., nutritional value, aroma, taste, colour or texture). Preservatives, colours and flavours are the best-known additives, but there are in fact many categories of additives, each tailored to a specific purpose.

Contaminants are harmful chemical substances (chemical contamination) and toxic microorganisms (microbiological contamination) that have not been intentionally added to food but may be present there as a result of human activities in agriculture or industry. They may enter food at various stages of its production, packaging, transport or storage. A separate issue is genetically modified food or the presence in food of ingredients from genetically modified organisms, which is sometimes referred to as a form of food contamination. In relation to food, contaminants are sometimes differentiated into primary or exogenous contaminants that come from the external environment (e.g., residues of agrochemicals such as pesticides) and secondary or endogenous contaminants, which are, under certain circumstances, generated during food processing (e.g., by heating and fermentation) from

natural food components (nutrients and other constituents). These contaminants are often called technological, processing or process-induced contaminants. They are absent in the raw materials, and are formed by chemical reactions between natural and/or added food constituents during processing. Typical examples are acrylamide formed in potato chips from asparagine, methanol produced in fruit alcoholic beverages by hydrolysis of pectin and chloropropanols formed from fats and hydrochloric acid in hydrolysed vegetable proteins.

Food contaminants and some additives used inappropriately, and sometimes even natural toxic substances, are collectively termed **xenobiotics**. The term is primarily understood to describe artificial substances that do not exist in nature and also covers substances that are present in much higher concentrations than are usual. Their presence in foods is related to the **hygienic–toxicological quality**.

As food chemistry is a dynamic discipline, it also deals with the biochemical and chemical reactions, interactions and physical processes that occur during food processing and storage. Knowledge of these processes is a prerequisite for their eventual regulation and also allows the optimisation of production processes, so that it is possible to produce high value foods in all aspects of quality, foods with high nutritional, sensory and hygienic–toxicological value (healthy foods), while satisfying all the requirements and demands of the consumers. In addition, knowledge of these processes can be applied in ordinary culinary experiences. Finally, food chemistry examines the ways in which to enhance positive changes and to prevent the unwanted ones, eliminate the antinutritive and toxic substances, and prevent possible contamination with substances that can pose health risks to guarantee food safety. Producing safe and nutritious food for human and animal consumption is one of the principal aims of both food chemistry and food technology.

This book takes you on a tour of food chemistry, an incredibly fascinating field of study that will provide you with a constant sense of discovery. For better or for worse, food chemistry is all around us every day and everything in food is chemistry, as chemistry is essential to meet our basic needs of food, energy, health, water and air. Food plays a role in everyone's lives and touches almost every aspect of our existence in some way. Therefore, the magic of food composition and its changes has attracted inquisitive minds for centuries. The understanding of the nature of chemicals and pivotal chemical processes occurring in foods, which the reader will gain, has been divided into 11 chapters, each of which provides insights into different classes of food constituents and related reactions, including proteins, peptides and amino acids, fats and other lipids, saccharides and their derivatives, vitamins, mineral compounds, water, odour- and taste-active substances, colours, beneficial, antinutritive and toxic components, food additives and contaminants and covering all aspects of the subject that are necessary for a comprehensive understanding about how things work. Let us wade into this information soup.

2

Amino Acids, Peptides and Proteins

2.1 Introduction

Aminocarboxylic acids (see p. 5) occurring in nature have vital functions in living organisms. Many of these amino acids are found as free substances or higher molecular weight compounds, where the amino acid building units are connected to each other by amide bonds, $-\text{CO}-\text{NH}-$, termed **peptide bonds**. Depending on the size of the molecule (the number of bound amino acids), these compounds are divided into two large main groups, which are:

- **peptides**, usually composed of 2–100 monomers
- **proteins**, which contain more than 100 monomers, but also hundreds or even thousands of amino acids.

Proteins and peptides may even contain some further compounds in addition to amino acids. Proteins are undoubtedly the most important amino acid derivatives: they are the basic chemical components of all living cells and therefore are also part of almost all food raw materials and foods of plant, animal and microbial origin. In organisms, proteins perform a number of unique and extraordinary functions. Along with ribonucleic acids (RNA) and deoxyribonucleic acids (DNA), polysaccharides, some lipids and other macromolecules (such as polyisoprene, the major component of rubber tree latex), peptides and proteins are often known as biological polymers or biopolymers. Nucleic acids (RNA and DNA) have almost no significance as food components in human and animal nutrition, although they play fundamental roles in living systems. Plants and some microorganisms are capable of synthesising proteins from basic substrates such as carbon dioxide, water and inorganic nitrogen compounds, but animals rely on getting their necessary vegetable or animal protein from their food. In the process of digestion, the food proteins are enzymatically broken down (hydrolysed) to their building blocks, from which animals may synthesise their own proteins

or use them (along with carbohydrates and lipids) as a source of energy. Therefore, proteins, together with carbohydrates and lipids, belong to the category of **main (primary) nutrients**. In human and animal nutrition, proteins are irreplaceable because they cannot be substituted by other nutrients over a long period of time.

The following sections deal with important amino acids, peptides and proteins, their structure, occurrence, properties, fate in the human organism, nutritional aspects and important interactions and reactions that fundamentally affect the nutritional value, organoleptic properties (odour, taste, colour and texture) and the hygienic–toxicological quality of food commodities.

2.2 Amino acids

Amino acids are found in foods – they are the building units of proteins, peptides and many other compounds – but they also occur as free compounds. Plants, animals and other organisms have been shown to contain more than 700 different amino acids. Some of these are spread quite generally throughout nature, while others occur only in certain species of plants, animals or in other organisms. According to their origins, therefore, the following two groups of amino acids are recognised:

- amino acids found in all living organisms (bound in proteins, peptides or occurring as free amino acids)
- amino acids found only in some organisms (bound in peptides or present as free compounds) that are not protein constituents.

The amino acids bound in proteins (22 compounds) are called proteinogenic, encoded, basic, standard or primary amino acids; 21 of them are constituents of proteins, food raw materials and foods. Of the 22 proteinogenic amino acids, 20 are encoded by the

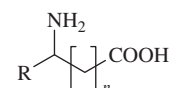
universal genetic code. The remaining two amino acids (selenocysteine and pyrrolysine) are incorporated into proteins by unique synthetic mechanisms. For each of the encoded amino acids, specific transfer RNA molecules exist, and proteins of each organism arise as products of protein synthesis controlled by the genetic code. Amino acids bound in peptides or free amino acids have the same nutritional value as proteins, but their importance in nutrition is usually negligible due to the small amounts in which free amino acids and peptides commonly occur in foods. An example of an amino acid occurring only in some organisms is pyrrolysine, which occurs as a component of enzymes involved in the production of methane in some methanogens, members of a group of single-celled microorganisms of a relatively new domain, Archaea, in the classification of life.

The process of protein biosynthesis is called translation. Post-translational oxidation, alkylation and esterification of some amino acids that are bound in proteins yield modified proteinogenic amino acids (see Section 2.2.1.1.2). Non-proteinogenic (non-encoded, non-standard or secondary) amino acids do not function as building blocks of proteins, as they have other roles in organisms. Amino acids also have an influence on the organoleptic properties of food, especially on their taste. Products of reactions of amino acids are often important compounds influencing odour, taste and colour of foods.

2.2.1 Structure, terminology, classification and occurrence

Amino acids are organic compounds, containing at least one primary amino group, $-\text{NH}_2$, together with at least one carboxyl group, $-\text{COOH}$, and various side groups in the molecule. They can be also defined as amino group substituted carboxylic acids. According to the distance of the amino group from the carboxylic group, amino acids (2-1) are generally divided into:

- **2-aminocarboxylic acids** (α -aminocarboxylic acids) that have the amino and carboxyl groups attached to the same carbon atom (such as α -alanine);
- **3-aminocarboxylic acids** (β -aminocarboxylic acids) that have the amino and carboxylic groups attached to adjacent carbon atoms (such as β -alanine);
- **4-aminocarboxylic acids** (γ -aminocarboxylic acids) that have one carbon atom (group) between the amino and carboxylic groups (such as γ -aminobutyric acid);
- **5-aminocarboxylic acids** (δ -aminocarboxylic acids) that have two carbon atoms (groups) between the amino and carboxylic groups (such as 5-aminolaevulinic acid, the precursor of the biosynthetic pathway that leads to haem in mammals and chlorophyll in plants);
- **6-aminocarboxylic acids** (ϵ -aminocarboxylic acids) that have three carbon atoms (groups) between the amino and carboxylic groups (such as lysine).



- 2-1, 2-amino acid ($n = 0$)
 3-amino acid ($n = 1$)
 4-amino acid ($n = 2$)
 5-amino acid ($n = 3$)
 6-amino acid ($n = 4$)

The amino acids also include carboxylic acids that contain a secondary amino group $-\text{NH}-$ in the molecule that is a part of three-, four-, five- or six-membered rings. These amino acids are actually derivatives of the saturated nitrogen heterocycles aziridine, azetidine, azolidine (pyrrolidine) and azinane (piperidine) or of other more complex heterocyclic compounds. For example, the only proteinogenic amino acid with a pyrrolidine ring is proline, which in biochemical literature is sometimes incorrectly classified as an imino acid, but imino acids contain imino $-\text{C}(=\text{NH})-$ functional groups instead of secondary amino groups.

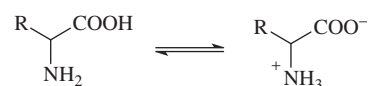
In most foods, about 99% of amino acids are bound in proteins and peptides. The rest (about 1%) are free amino acids. There is a larger amount of free amino acids in foods in which proteolytic enzymes or chemical agents have hydrolysed proteins during manufacture or storage. Larger amounts of free amino acids can be found in some cheeses, beer and wine. The enzymatic hydrolysates of proteins (such as soy sauce) or acidic protein hydrolysates (used as soup condiments) contain only free amino acids with small amounts of peptides, but no protein.

2.2.1.1 Amino acids of proteins

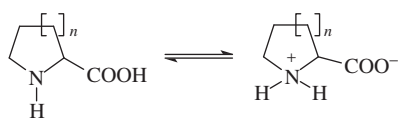
2.2.1.1.1 Proteinogenic amino acids

Proteinogenic amino acids bound in all proteins are exclusively 2-amino (α -amino) acids that have the primary or secondary amino and carboxyl groups attached to the same carbon atom in position 2 (α) to the carboxyl group. In other words, the amino groups are attached to the carbon adjacent to the carboxyl groups. The carbon atom in position 2 (α) is commonly referred to as C_α carbon in biochemical literature.

The proteins in most organisms contain only 21 basic amino acids, of which 20 amino acids have the primary amino group (2-2), while one amino acid is an alicyclic amino acid with a secondary amino group (2-3). All amino acids except glycine (which is achiral) are optically active (chiral) compounds that contain an asymmetric centre (chiral atom) and thus can occur in two non-superimposable mirror-image forms, D- and L-forms (optical isomers or enantiomers) that are the mirror images of each other. Proteinogenous amino acids almost exclusively belong to the L-series, thus have the L-configuration (see Section 2.2.3.2).



2-2, aliphatic α -amino acid

2-3, alicyclic α -amino acid

One or more hydrogen atoms of the substituent R of L- α -amino acids, known as a side chain, specific to each amino acid (2-2), may be substituted by a carboxyl group (called a distal carboxyl group), an amino group (or distal amino group) or other functional groups, such as a hydroxyl group $-\text{OH}$, a sulfhydryl (mercapto) group $-\text{SH}$, a sulfide group $-\text{S}-\text{CH}_3$, a guanidino group $-\text{NH}-\text{C}(=\text{NH})-\text{NH}_2$ or a phenyl group $-\text{C}_6\text{H}_5$. The methylene group or nitrogen atom of the secondary amino group of α -amino acids can also be substituted (2-3).

The proteinogenic amino acids are often known by their trivial names, which are derived from their properties or the source from which they were first isolated. Systematic names of the

proteinogenic amino acids are rarely used, but are more frequent in the non-protein amino acids. Each amino acid has both a three-letter code (mostly the first three letters of the trivial name) and a single-letter code that is used for the registration of long sequences of amino acids in proteins (Table 2.1).

Each classification of amino acids is somewhat imprecise and conforms to certain purposes. The most common way of sorting the proteinogenic amino acids in food chemistry is classification according to the structure of their side chain and functional groups present therein. This will distinguish the following groups of amino acids:

- aliphatic amino acids (monoaminomonocarboxylic acids) with an unsubstituted side chain, which include the simplest amino acid **glycine** (sometimes also classified as the only amino acid without a side chain), its higher homologue **alanine** (known as α -alanine) and branched chain amino acids **valine**, **leucine** and **isoleucine**;

Table 2.1 Trivial and systematic names of proteinogenic amino acids and their codes.

Trivial name	Systematic name	Three-letter code	One-letter code
Glycine	Aminoacetic acid	Gly	G
L-Alanine	L-2-Aminopropionic acid	Ala	A
L-Valine	L-2-Amino-3-methylbutanoic acid	Val	V
L-Leucine ^a	L-2-Amino-4-methylpentanoic acid	Leu	L
L-Isoleucine ^a	L-2-Amino-3-methylpentanoic acid	Ile	I
L-Serine	L-2-Amino-3-hydroxypropanoic acid	Ser	S
L-Threonine	L-2-Amino-3-hydroxybutanoic acid	Thr	T
L-Cysteine	L-2-Amino-3-mercaptopropanoic acid	Cys	C
L-Selenocysteine	L-2-Amino-3-selanylpropanoic acid	Sec	U
L-Methionine	L-2-Amino-4-methylthiobutanoic acid	Met	M
L-Aspartic acid ^a	L-Aminosuccinic acid	Asp	D
L-Glutamic acid ^a	L-2-Aminoglutaric acid	Glu	E
L-Asparagine ^a	L-2-Amino-4-carbamoylbutanoic acid	Asn	N
L-Glutamine ^a	L-2-Amino-5-carbamoylpentanoic acid	Gln	Q
L-Lysine	L-2,6-Diaminohexanoic acid	Lys	K
L-Pyrrolysine	(2R,3R)-N6-[3-Methyl-3,4-dihydro-2H-pyrrole-2-ylcarbonyl]-L-lysine	Pyl	O
L-Arginine	L-2-Amino-5-guanidylpentanoic acid	Arg	R
L-Histidine	L-2-Amino-3-(4-imidazolyl)propionic acid	His	H
L-Phenylalanine	L-2-Amino-3-phenylpropionic acid	Phe	F
L-Tyrosine	L-2-Amino-3-(4-hydroxyphenyl)propionic acid	Tyr	Y
L-Tryptophan	L-2-Amino-3-(3-indolyl)propionic acid	Trp	W
L-Proline	L-Pyrrolidine-2-carboxylic acid	Pro	P

^aIn addition to the specific amino acid codes, three-letter code and one letter-code placeholders are used for ambiguous amino acids, i.e. Asx and B for aspartic acid or asparagine, Glx and Z for glutamic acid and glutamine, Xle and J for leucine or isoleucine and Xaa (Unk) and X for unspecified (unknown) amino acid.

- aliphatic hydroxyamino acids, which include **serine** and **threonine**;
- aliphatic sulfur-containing amino acids **cysteine** and **methionine**;
- selenoanalogue of cysteine called **selenocysteine**;
- amino acids with carboxyl groups in the side chain (monoaminodicarboxylic acids), such as **aspartic acid** and **glutamic acid**;
- their monoamides (amino acids with carboxamide groups in the side chains): **asparagine** and **glutamine**;
- amino acids with basic functional groups in the side chain, that is, diaminomono-carboxylic acid **lysine**, lysine derivative with a 1-pyrroline ring known as **pyrrolysine**, **arginine** with a guanidino group in the side chain and the derivative of 1*H*-isomer of imidazole called **histidine**;
- amino acids with aromatic and heterocyclic side chains, which include **phenylalanine**, its hydroxyl derivative **tyrosine** and **tryptophan** with an indole ring;
- **proline** is the amino acid, in which the functional group is involved in the ring structure.

For clarity, formulae of amino acids are shown in the non-ionised form. Non-ionised molecules are, however, virtually absent in aqueous solutions and in animal and plant tissues. Amino acids are ionised and form inner salts (2-2 and 2-3), and carboxyl groups exist as -COO^- anions and amino groups as -NH_3^+ cations. The amino acid molecule simultaneously carries positive and negative charges. Because the resulting amino acid contains one positive and one negative charge, it is a neutral molecule called a **zwitterion**. These forms are the predominant ionic forms of amino acids under neutral conditions (about pH 7 in solution). Under these conditions, the distal carboxyl groups of aspartic and glutamic acids, distal amino group of lysine, guanidine group of arginine and imidazole cycle of histidine are also more or less ionised. The nitrogen atoms of the imidazole ring of histidine are denoted by *pros* ('near', abbreviated π) and *tele* ('far', abbreviated τ) to show their position relative to the side chain.

In biochemistry, the most common and perhaps most practical classification of proteinogenic amino acids is according to the side chain polarity and its ionic forms occurring in neutral solutions, which is related to non-bonding interactions in proteins (see Section 7.6.2.2). The following groups of amino acids are recognised:

- **hydrophobic amino acids** with non-polar side chains, which include valine, leucine, isoleucine, methionine, phenylalanine, tyrosine and proline; sometimes the hydrophobic amino acids also include glycine, alanine and tryptophan, even though these amino acids are rather amphiphilic amino acids, which forms a transition between the hydrophobic amino acids and the following group;
 - **hydrophilic amino acids** with polar side chains, which include serine, threonine, cysteine, selenocysteine, aspartic and glutamic acids and their amides asparagine and glutamine, as well as lysine, pyrrolysine, arginine and histidine.
- Hydrophilic amino acids are classified according to the ionic form in which they occur in living organisms into:
- **neutral** (polar side chain has no electric charge in neutral solutions), which includes most amino acids;
 - **acidic** (polar side chain has a negative charge in neutral solutions), which includes aspartic acid and glutamic acid;
 - **basic** (polar side chain has a positive charge in neutral solutions), such as lysine, pyrrolysine, arginine and histidine.
- According to the significance in human nutrition, proteinogenic amino acids are divided into:
- **essential** (or indispensable: valine, leucine, isoleucine, threonine, methionine, lysine, phenylalanine and tryptophan) that cannot be synthesised by the human body;
 - **semi-essential** (arginine and histidine);
 - **non-essential** (other amino acids; tyrosine forms by hydroxylation of the essential amino acid phenylalanine) that are synthesised by the human body *de novo*.

Amino acids that the body cannot synthesise must be obtained entirely from food. These amino acids are called **essential amino acids**. Essential amino acids are routine constituents of most protein-based foods or dietary proteins and are fairly readily available in a reasonably well-balanced diet. However, there are some amino acids that are present in lower concentrations than the same amino acid in a high quality protein (e.g. lysine in wheat and eggs). These amino acids are called **limiting amino acids**, because if a person's diet is deficient in one of them, this amino acid will limit the usefulness of the others (and will limit the extent of protein synthesis in the body), even if the others are present in what would otherwise be large enough quantities. Limiting amino acids are distinct from non-essential amino acids that the body can synthesise and are therefore sometimes used for food and animal feed enrichment.

In rapidly growing organisms (such as infants, for instance), some non-essential amino acids (arginine and histidine), which the young organism cannot synthesise in sufficient quantities, become essential amino acids. These amino acids are sometimes called **semi-essential amino acids**. Arginine is synthesised at a rate that is insufficient to meet the growth needs of the body, and the majority of it that is synthesised is cleaved to form urea. Histidine was initially thought to only be essential for infants, but longer-term studies established that it is also essential for adult humans. The amino acids methionine and phenylalanine are also sometimes considered semi-essential for reasons not directly related to lack

of synthesis. Methionine is required in large amounts to produce cysteine if the latter amino acid is not adequately supplied in the diet. Similarly, phenylalanine is needed in large amounts to form tyrosine if the latter is not adequately supplied in the diet.

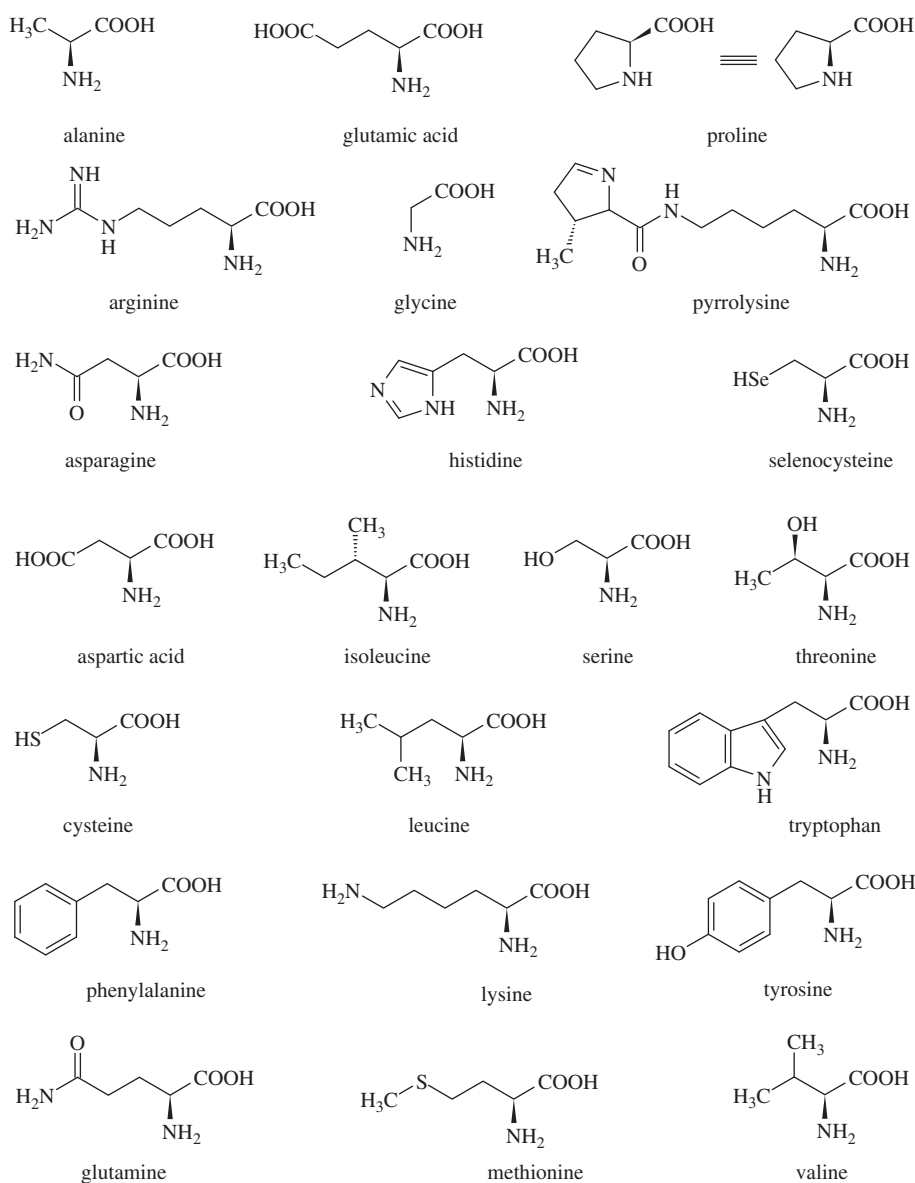
The amino acids that the body can synthesise are called **non-essential amino acids**. They are biosynthesised from intermediates of the citric acid cycle used by all aerobic organisms to generate energy and through other metabolic pathways (glycolysis and the pentose cycle). All living organisms, including humans, synthesise glutamic acid from 2-oxoglutaric acid (derived from the citric acid cycle) and ammonium ions. This reaction is known as reductive amination. Glutamic acid then becomes the precursor of glutamine, proline, ornithine and arginine. Transamination of oxaloacetic acid (from the citric acid cycle) yields aspartic acid that is a precursor of asparagine. Transamination of pyruvic acid (a product of glycolysis) yields alanine. Another intermediate of glycolysis, 3-phospho-D-glyceric acid (and D-ribulose 1,5-bisphosphate in plants), yields serine, which is a precursor of glycine, cysteine and selenocysteine. D-Ribose 5-phosphate from the pentose cycle (the product of photosynthesis in plants) is a precursor of histidine.

Essential and semi-essential amino acids

- **Valine** Valine occurs in animal and plant proteins (meat, cereals) in amounts of 5–7% (average content is 6.9%). Egg and milk proteins contain 7–8% valine. The structural protein elastin has the highest amount of valine (16%).
- **Leucine** Leucine occurs in all common proteins, usually in amounts of 7–10% (average content is 7.5%). Cereals contain a variable amount of leucine, wheat proteins contain about 7% and maize proteins about 13%. Free leucine forms in larger amounts during cheese ripening due to bacterial activity.
- **Isoleucine** The largest amounts of isoleucine are found in milk and egg proteins (6–7%), while meat and grains contain 4–5% of leucine (average content is 4.6%).
- **Threonine** A rich source of threonine is meat and brewer's yeast. Its content in animal proteins (meat, eggs and milk) is around 5%. There is a relatively high amount of threonine in wheat, but its content in other cereals is lower (often around 3%), meaning that threonine sometimes becomes the limiting amino acid.
- **Methionine** Animal proteins contain 2–4% of methionine, whereas plant proteins contain only 1–2% (average content is 1.7%). Methionine is the limiting amino acid in legumes. Methionine (and cysteine) is present only in small amounts in histones and is completely lacking in protamines.
- **Lysine** The average content of lysine in proteins is 7%. High amounts of lysine are found in most animal proteins; meat, eggs and milk proteins commonly contain 7–9% of lysine, fish and shellfish proteins contain 10–11% of lysine. In contrast, vegetable proteins, such as proteins of cereals (especially gliadins, but not glutelins) and cereal products contain only 2–4% of lysine, which is the limiting amino acid.
- **Phenylalanine** Good sources of phenylalanine are meat, fish and most protein containing foods, where this amino acid occurs in sufficient amounts (4–5%, average content is 3.5%). In some individuals, its presence in the diet causes phenylketonuria, an inherited defect in which phenylalanine is incompletely and abnormally metabolised (see Section 10.3.1.2).
- **Tryptophan** The average tryptophan content in proteins is 1.1%. Animal proteins contain 1–2% of tryptophan, except for histones and collagen, which do not contain tryptophan at all. Tryptophan is also not present in gelatine or in acid protein hydrolysates used as soup seasonings. Therefore, the tryptophan content in meat products can serve as an indicator of the quality of the meat used. (The contents of 3-methylhistidine or creatinine have been measured for the same purpose.) Cereals contain <1% of tryptophan; the glutenine fraction of gluten has a somewhat higher content of tryptophan. In fruits and fruit juices N^1 -(β -D-glucopyranosyl)-L-tryptophan is also found. Its amount in juices ranges from 0.1 to >10 mg/l. The highest amount of this glycoconjugate was found in pear juices (13.5 mg/l). Humans can partly use tryptophan for biosynthesis of nicotinic acid (see Section 5.8.3). In ruminants, if present in excessive amounts in the diet, tryptophan causes pulmonary oedema (fluid accumulation in the lungs) that may cause respiratory failure. The cause is the heterocyclic compound 3-methylindole (skatole), which is a fermentation product of tryptophan in the rumen.
- **Arginine** Arginine occurs in all proteins in amounts of 3–6% (average content is 4.7%). Basic proteins protamines from fish roes have particularly high levels of arginine. Peanuts and other oilseeds are also rich sources (arginine content of up to 11%).
- **Histidine** Common proteins contain 2–3% histidine (average content is 2.1%), and blood plasma proteins contain up to 6% histidine. The flesh of some fish (especially mackerel and tuna) contains from 0.6 to 1.3% (and sometimes more than 2%) of free histidine. The free histidine content in the flesh of other fish is only 0.005–0.05%.

Non-essential amino acids

- **Glycine** Glycine is contained in a significant amount (25–30%) mainly in the structural protein collagen and in gelatine; in the majority of albumins it is not present at all (average content is 7.5%).
- **Alanine** Alanine occurs in almost all proteins in amounts of 2–12% (average content is 9.0%). Maize prolamine protein zein and animal protein gelatine contain about 9% of alanine.
- **Serine** Serine is found in many proteins; generally in an amount of 4–8% (average content is 7.1%).



2-4, basic amino acids

- **Cysteine** The highest amount of this amino acid and its oxidation product cystine (2-5) is present in keratin (up to 17%); it occurs in many other proteins in smaller amounts (1–2%). The average content is 2.8%. In the organism, cysteine can partially replace the essential amino acid methionine.
- **Aspartic acid and asparagine** The average content of aspartic acid in proteins is 5.5%; the average content of asparagine is 4.4%. Aspartic acid is the major amino acid of animal proteins known as globulins and albumins (6–10%). Vegetable proteins contain 3–13% aspartic acid, mainly in the form of asparagine (e.g. wheat proteins contain about 4% and maize proteins about 12%).
- **Glutamic acid and glutamine** The average content of glutamic acid and glutamine in proteins is 6.2 and 3.9%, respectively.

Glutamic acid is the most abundant amino acid in the nervous tissue. In conventional proteins, both amino acids are usually found in larger quantities (especially in globulins) in cereal and legume proteins (18–40%). Wheat gluten (in its component gliadin) contains about 40%, soy protein contains about 18% and milk proteins contain about 22% of glutamic acid.

- **Selenocysteine** In most foods of both vegetable and animal origin, selenocysteine is the main form of selenium bound in proteins. The content of this amino acid, as well as the contents of other amino acids and peptides containing selenium (L-selenocystine, Se-methyl-L-selenocysteine, L,L-selenocystathionine, L-selenomethionine and γ -glutamyl-Se-methyl-L-selenocysteine), is unknown. Selenocysteine is typically located in a small number of active centres of proteins of Archaea, bacteria and eukaryotes (in glutathione

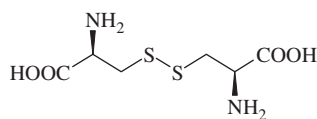
peroxidase, thioredoxin reductase, formate dehydrogenase, glycine reductase and in some hydrogenases). Usually only one molecule of selenocysteine is bound in the peptide chain; however proteins containing multiple molecules of this amino acid are also known. For example, the isoenzyme of mammalian glutathione peroxidase, known under the abbreviation GPx6, is a selenoprotein in humans with cysteine-containing homologues in rodents.

- **Tyrosine** Tyrosine accompanies phenylalanine in most proteins in an amount of 2–6% (average content is 3.5%). Gelatine contains only traces of tyrosine.
- **Proline** Proline is present in most proteins in amounts of 4–7%; the average content is 4.6%. Its content in the component of wheat gluten, gliadin, is about 10%, and about 12% of proline contains casein. Proline content in gelatine can be up to 13%. In bacteria, plants and animals it also plays a role as an osmoprotectant that helps stabilise proteins and cell membranes from the damaging effect of high osmotic pressure.

2.2.1.1.2 Modified proteinogenic amino acids

Post-translational modification, which extends the range of functions of the protein, is one of the later steps in the biosynthesis of many proteins. Post-translational modification of proteins occurs by methylation, hydroxylation, acetylation and phosphorylation of the protein functional groups, by attaching various lipids and carbohydrates to the protein molecule and by making structural changes such as the formation of disulfide bonds from cysteine residues by oxidation.

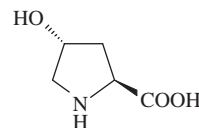
Post-translational oxidation of the thiol groups of cysteine residues in proteins yields **L-cystine** (Cys-Cys, **2-5**). The disulfide bond (or bridge) plays an important role in the structure of many proteins, as it combines two different polypeptide chains or two molecules of cysteine in the same peptide chain. For example, the major globular protein of milk β -lactoglobulin contains two disulfide bridges, and the glycoprotein of egg white ovomucoid has three domains connected by disulfide bridges. The protein keratin has a high cystine content: for example, human hairs contain about 5% cystine.



2-5, cystine

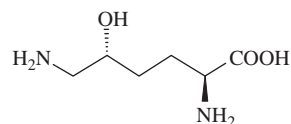
Another common post-translationally modified amino acid is the proline derivative **L-4-hydroxyproline**, (*2S,4R*)-4-hydroxyproline, also known as **L-4-hydroxypyrrrolidine-2-carboxylic acid** (abbreviated Hyp, **2-6**), which is an important structural component of collagen, gelatine (about 12% of content) and the polypeptide (glycopeptide) of plant cell walls known by the trivial name extensin (see Section 4.5.1.3.1). Its content is low in most other proteins. The amount of 4-hydroxyproline in meat products

therefore correlates with the lower quality of raw material used, for instance where the products contain skin, wherein collagen is the major protein. 4-Hydroxyproline also occurs in smaller amounts in plants. For example, concentrations ranging from 1.0 to 4.2 mg/kg have been found in the edible part of bergamot fruits (*Citrus bergamia*, Rutaceae).



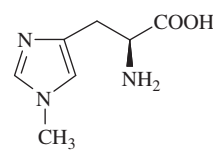
2-6, 4-hydroxyproline

4-Hydroxyproline in collagen is accompanied by a small amount of its isomer, **L-3-hydroxyproline** (**L-3-hydroxypyrrrolidine-2-carboxylic acid**) and by a hydroxy derivative of lysine, also known as **L-5-hydroxylysine**, (*2S,5R*)-5-hydroxylysine, **L-5-hydroxy-2,6-diaminohexanoic acid** (abbreviated Hyl, **2-7**). In glycoproteins, hydroxylysine is bound as *O*-glycoside. Small amounts of hydroxylysine occur in plant materials (as a free amino acid in alfalfa forage, *Medicago sativa*, Fabaceae).



2-7, 5-hydroxylysine

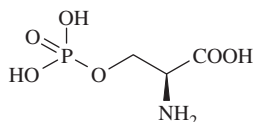
The minor amino acid typically present in the meat myofibrillar protein actin (also in some myosin isoforms and in dipeptide anserine, see Section 2.3.3.1.3) is **L-3-methylhistidine** (**2-8**), which is formed by methylation of histidine bound at the 73rd position of the protein chain. The functional significance of this modification of actin is not known; it is probably related to the metabolism of phosphates, with which the side chain of methylhistidine interacts. Methylhistidine does not occur in other protein-rich foods such as milk, eggs and soybeans. Its contents might therefore serve as a criterion for determining the quality ingredients in meat products.



2-8, 3-methylhistidine

The other amino acid that is usually modified is **L-serine**. It can be esterified with phosphoric acid. This ester, **O-phosphoserine** (**2-9**), occurs in many proteins, such as glycoposphoprotein phosphovitin (also known as phosphovitin) from egg yolk (see Section 2.4.5.3.2). Phosvitins are one of the most phosphorylated (10%) proteins in nature, and are important for sequestering cations of calcium, iron and other metals for the developing embryo. Serine in phosphovitin represents nearly 50% of the amino acids and there

are about 90% of the molecules of serine phosphorylated. Phosphoserine also occurs in the glycoprotein α_{S1} -casein (eight phosphoserine residues) and β -casein (five phosphoserine residues). Phosphoserine (as phosphatidyl-L-serine) is also a component of phospholipids distributed widely among animals, plants and microorganisms. Phosphoserine usually constitutes less than 10% of the total phospholipids, the greatest concentration being in myelin from brain tissue and in wheat germ. Threonine residues in proteins are also esterified fairly frequently with phosphoric acid yielding **O-phosphothreonine**. Phosphatidyl-L-threonine was first detected in animal brains and tuna muscle, before it was characterised definitively as a minor component of neurons, macrophages, viruses and some bacterial species.



2-9, O-phosphoserine

2.2.1.2 Other amino acids

Plants and microorganisms are able to generate all 21 amino acids necessary for protein synthesis, and they can additionally synthesise many more. Foods contain numerous other less common amino acids in addition to those that are constituents of proteins (proteinogenic) and modified proteinogenic amino acids. It is estimated that there are around 700 amino acids known in nature, of which at least 300 are found in plants. They are often bound in peptides (see Section 2.3) or are present as free amino acids. In biochemistry, these **non-protein amino acids** are often classified as the so-called secondary metabolites, as they are the products of three major routes: modification of an existing (often proteinogenic) amino acid, modification of an existing pathway and by novel pathways. These amino acids become the biosynthetic precursors of many biologically active nitrogenous compounds, such as signalling molecules, vitamins, alkaloids (such as valine, leucine, isoleucine, threonine, arginine, lysine, phenylalanine and tryptophan), bile acids and pigments. Some of these amino acids also have specific functions in organisms; they act as neurotransmitters, stimulants and hormones. For example, phenylalanine (or 3,4-dihydroxyphenylalanine) is a precursor of adrenal hormones catecholamines (such as epinephrine, which is also known as adrenaline; see Section 10.3.2.10.1) and of the thyroid hormone thyroxine (see Section 2.2.1.2.5). Other amino acids increase plant tolerance to abiotic stress factors, act as toxic substances which protect plants against invading viruses, microorganisms, other plants and predators (e.g. the arginine analogue canavanine found in some legumes) and also serve as a storage and transport form of nitrogen and sulfur. Some of the unusual amino acids form secondarily during storage of raw materials and food processing via the activities of microorganisms and by chemical transformation of proteins (e.g. lysinoalanine, see 2-121), peptides or free amino acids.

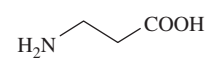
The following sections of this chapter present some of the most important non-protein amino acids in foods and feeds. For clarity, they are sorted according to the structure in which they are present

in living organisms and not by function (these functions often are not well known).

2.2.1.2.1 Neutral aliphatic and alicyclic amino acids

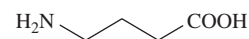
3-Amino acids and 4-amino acids

In addition to α -amino acids, β - and γ -amino acids can also be found in food. Naturally occurring β -alanine (3-aminopropionic acid, 2-10) acts in the biosynthesis of pantothenic acid, acetyl coenzyme A, other acyl coenzymes A (see Section 5.9.1) and some histidine dipeptides. β -Alanine is synthesised in several different ways, by aspartic acid decarboxylation (in bacteria), but also by the transformation of propionic acid (in bacteria and some plants), by degradation of the polyamines spermine and spermidine (in yeasts and many plants, such as tomato, soybean and maize), or arising from the pyrimidine derivative uracil that occurs in all animals and in some plants, such as wheat.



2-10, β -alanine

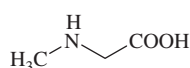
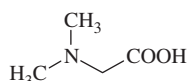
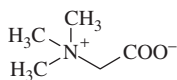
The higher homologue of β -alanine is γ -aminobutyric acid (4-aminobutanoic acid), known under the acronym of GABA (2-11), which is formed almost exclusively by enzymatic decarboxylation of glutamic acid. It is mainly present in the brain tissue of animals, where it acts as an inhibitor of nerve impulse transmissions. It is also found in plants and microbial cells, where it has a role as a signal molecule, and is also a constituent of some peptides such as nisine (see Section 11.2.1.2.1).



2-11, γ -aminobutyric acid

N-Substituted amino acids

N-Alkylsubstituted amino acids are commonly found in foods. The simplest of these amino acids is N-methylglycine (sarcosine, 2-12), which is a product of the catabolism of choline (see Section 3.5.1.1.1), creatine (see Section 2.2.1.2.4) or forms by N-methylation of glycine. Sarcosine probably has a regulatory function in methylation reactions. The subsequent N-methylation of sarcosine gives N,N-dimethylglycine (2-13), which is a component of pangamic acid ranked first among the vitamins (see Section 5.15). N,N,N-Trimethylglycine (N,N,N-trimethylammonioacetate, 2-14) was named glycinebetaine or just betaine after its discovery in sugar beet (*Beta vulgaris*, Amaranthaceae), where it occurs in the amount of about 2.5 g/kg in the root. Glycinebetaine is a very effective osmolyte of microorganisms and higher plants, which results from choline or by N-methylation of glycine and sarcosine, respectively, and acts in various transmethylation reactions. It is present in higher amounts in sugar beets and molasses. Glycinebetaine was found to accumulate at high levels in some higher fungi. For example, its content in horse mushroom (*Agaricus arvensis*) is 7.8% dry matter.

2-12, *N*-methylglycine (sarcosine)2-13, *N,N*-dimethylglycine2-14, *N,N,N*-trimethylglycine

ammonium ion



phosphonium ion



arsonium ion



sulfonium ion

2-15, general structures of some onium ions

The terms **betaines** include glycinebetaine and similar zwitterionic ammonium compounds derived from other amino acids. By extension, betaines are also neutral molecules having charge-separated forms with an onium atom which bears no hydrogen atoms (such as phosphonium, sulfonium and arsonium ions) that is not adjacent to the anionic atom. Examples of the most common onium ions (ammonium, phosphonium, sulfonium and arsonium ions) are given by the general formulae 2-15. The attached atoms are typically organic substituents, for example methyl groups. The most common betaines are quaternary ammonium compounds that occur in foods of animal and plant origin. In animals, betaines participate (along with *S*-adenosyl-*L*-methionine, pyridoxine, folic acid and vitamin B₁₂) in the protection of the cardiovascular system by lowering the potentially toxic concentrations of *L*-homocysteine. *L*-Carnitine plays an important role in the metabolism of fatty acids in biological systems plays (see Section 5.15). An arsenic analogue of betaine, arsenobetaine, accumulates in the body of some fish (see Section 6.2.3.1). Betaines are particularly ubiquitous in plants. They are generally referred to as osmolytes as they, like their amino acid precursors, tend to accumulate in the cytoplasm and intercellular fluids, where they exert protective functions for proteins, nucleic acids and cell membranes in response to abiotic stresses, such as cold, freezing, high temperature, the presence of toxic metals, reduced availability of water and high salinity. Some of the major betaines are listed in Table 2.2. Their structures are given by formulae 2-16.

An important group of *N*-substituted amino acids are *N*-acylamino acids (2-17). An important metabolite is hippuric acid, also known as *N*-benzoylglycine (2-17). Hippuric acid arises from glycine as a result of detoxification of benzoic acid and other aromatic acids in humans and animals. In higher concentrations it occurs in the urine of herbivores and reportedly inhibits some pathogenic bacteria in the urinary tract. Benzoic acid is found (usually in small amounts) in many plant materials, including fruit, vegetables and forage crops (see Section 8.2.6.1.6), and is also used as a food preservative (see Section 11.2.1.1.1). Cows partially excrete hippuric acid into their milk, up to a concentration of 60 mg/kg. Microorganisms used in the production of fermented dairy products hydrolyse hippuric acid to glycine and benzoic acid. For example, the content of benzoic acid in yoghurts can reach, on average, 15 mg/kg.

N-phenylpropenoyl amino acids (2-17) have been identified as the key contributors to the astringent taste of non-fermented cocoa beans and cocoa products. Besides the already known (*E*)-*N*-[3',4'-dihydroxycinnamoyl-3-hydroxy-*L*-tyrosine (known as clovamide), (*E*)-*N*-(4'-hydroxycinnamoyl)-*L*-tyrosine (deoxyclovamide) and (*E*)-*N*-(3',4'-dihydroxycinnamoyl)-*L*-tyrosine, seven additional amides derived from cinnamic, 4-coumaric, caffeic and ferulic acids, namely, (+)-(*E*)-*N*-(cinnamoyl)-*L*-aspartic acid, (+)-(*E*)-*N*-(4'-hydroxycinnamoyl)-*L*-aspartic acid, (+)-(*E*)-*N*-(3',4'-dihydroxycinnamoyl)-*L*-aspartic acid, (+)-(*E*)-*N*-(4'-hydroxy-3'-methoxycinnamoyl)-*L*-aspartic acid, (-)-(*E*)-*N*-(4'-hydroxycinnamoyl)-*L*-glutamic acid, (-)-(*E*)-*N*-(3',4'-dihydroxycinnamoyl)-*L*-glutamic acid and (-)-(*E*)-*N*-(4'-hydroxycinnamoyl)-3-hydroxy-*L*-tyrosine, were recently identified.

Table 2.2 Some important betaines.

Betaine	Initial amino acid	Occurrence
β-Alaninebetaine (homobetaine)	β-Alanine	Plants of the Plumbaginaceae family, citrus species, meat
Gababetaine	γ-Aminobutyric acid	Molluscs, citrus species
L-Carnitine	Lysine and methionine	Meat, dairy products, legumes, vegetables, higher fungi
Laminine (lysinebetaine)	Lysine	Some higher plants
Stachydrine (cadabine, prolinebetaine)	Proline	Higher plants (e.g. citrus species), fungi
Betonicine (4-hydroxystachydrine, 4-hydroxyprolinebetaine)	4-Hydroxyproline	Plants of the Lamiaceae family
Hercynine (histidinebetaine)	Histidine	Higher fungi, citrus species
L-Ergothioneine (2-thioimidazolebetaine)	2-Mercaptohistidine	Higher fungi, plants
Homarine	Pyridine-2-carboxylic acid	Some higher plants
(Dimethylsulfonium)propanoate	Methionine	Marine phytoplankton, seaweeds

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