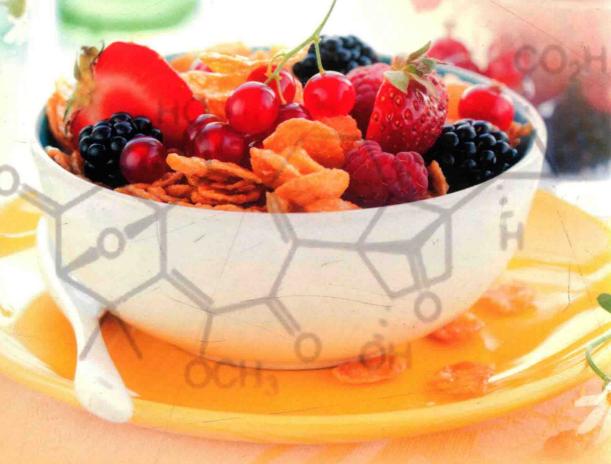
Fruit and Cereal Bioactives

Sources, Chemistry, and Applications



Edited by Özlem Tokuşoğlu Clifford Hall III



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Fruit and Cereal Bioactives

Sources, Chemistry, and Applications

To my mother, retired teacher Özden Tokuşoğlu & my father, retired senior colonel Armağan Tokuşoğlu, for their great emotional support and cordial encouragements.

Özlem Tokuşoğlu

Preface

Interest in bioactive compounds of fruit and cereals has reached a new high in recent years. The scientific and commercial attention devoted to fruit and cereal bioactives has been accentuated even further by efficiency reports regarding the beneficial and toxic health effects of such compounds. The beneficial bioactives of many fruit and cereals have been declared to possess anticarcinogenic, antimutagenic effects in test animals. Recently, the strong antioxidant capacities of many edible fruits and cereals have been revealed. These many bioactive compounds are responsible for several important characteristics of fruit and cereals: taste, flavor, color alteration, and antioxidant activity. Natural toxicant bioactives as mycotoxins have also been detected in specific fruits and cereals.

The specific focus for *Fruit and Cereal Bioactives* is on the chemistry of beneficial and nutritional bioactives (phytochemicals such as phenolics, flavonoids, tocols, carotenoids, phytosterols, avenanth-ramides, alkylresorcinols, some essential fatty acids) and toxicant bioactives (mycotoxins, aflatoxins, ocratoxin A, etc.) from sources such as pome, stone, and berry fruits, citrus fruits, tropical fruits and nuts, various cereals (and pseudocereals), pulses (e.g., legumes and edible beans), and so on. Overall, this book is a comprehensive and detailed reference guide to both major natural beneficial phytochemical bioactives and mycotoxic bioactives in edible fruits and cereals covering all the latest research from a wide range of experts.

This book is intended for senior undergraduate and graduate students, academicians, and those in government and the fruit and cereal industry. It provides a practical reference for a wide range of experts: fruit and cereal scientists, chemists, biochemists, nutritionists, fruit and cereal processors, government officials, commercial organizations, and other people who need to be aware of the main issues concerning bioactives.

Each chapter reviews dietary sources, occurrences, chemical properties, desirable and undesirable health effects, antioxidant activity, evidentiary findings, as well as toxicity of the above-mentioned bioactives and has been individually highlighted based on the fruit and cereal type. *Fruit and Cereal Bioactives* presents unique, up-to-date, and unified data of fruit and cereal chemistry from a biochemical standpoint.

Özlem Tokuşoğlu

Editors

Özlem Tokuşoğlu, who was born in İzmir, Turkey, completed her bachelor (1992) and master (1996) degrees at EGE University from the Department of Chemistry and completed her doctorate at EGE University from the Department of Food Engineering (2001). She worked as a research assistant and Dr. Assistant at EGE University from 1993 to 2001. She was the research assistant at the Food Science and Nutrition Department at the University of Florida–Gainesville during 1999–2000.

Dr. Tokuşoğlu has been an assistant professor at Celal Bayar University, Manisa, Turkey and is currently working there in the Department of Food Engineering. She is focusing on food quality control, food chemistry, food safety, and food processing technologies on traditional foods and beverages. Her specific study areas are phenolics, phytochemicals, bioactive antioxidative components, bioactive lipids, and their determinations by instrumental techniques, their effects on food and beverages quality, and the novel food processing effects on their levels.

Dr. Tokuşoğlu performed academic research studies and presentations at Geneva, Switzerland in 1997; Gainesville, Florida in 1999; Anaheim–Los Angeles, California in 2002; Sarawak, Malaysia in 2002; Chicago, Illinois in 2003; Katowice-Szczyrk, Poland in 2005; Ghent, Belgium in 2005; Madrid, Spain in 2006; New Orleans, Louisiana in 2008; Athens, Greece in 2008; Anaheim–Los Angeles, California in 2009; and Skopje, the Republic of Macedonia in 2009; Chicago, Illinois in 2010; Munich, Germany in 2010. She was also a visiting professor at the School of Food Science, Washington State University, Pullman, in the state of Washington for one month during 2010.

Dr. Tokuşoğlu has professional affiliations at the Institute of Food Technologists (IFT) and the American Oil Chemists' Society (AOCS) in the United States and has a professional responsibility with the Turkey National Olive and Olive Oil Council (UZZK) as a research and consultative board member and as a Turkish Lipid Group (YABITED) founder administrative board member and consultative board member in the European Federation for Science and Technology (Euro Fed Lipid). Dr. Tokuşoğlu has 78 international studies containing 25 papers published in peer-reviewed international journals covered by the *Science Citation Index* (SIC) and 11 papers published in peer-reviewed international index covered journals, 42 presentations (as orals and posters) presented at the international congress and other organizations. She has advised two masters' students to completion. Dr. Tokuşoğlu has several editorial assignments in international index covered journals.

Clifford Hall III completed his bachelor degree in 1988 at the University of Wisconsin–River Falls; his masters (1991) and doctoral (1996) degrees at the University of Nebraska–Lincoln in the area of food science and technology. He completed a postdoctoral experience at the University of Arkansas in Fayetteville. Dr. Hall is currently an associate professor in the Department of Cereal and Food Sciences in the School of Food Systems at North Dakota State University (NDSU). He is the associate director of the Great Plains Institute of Food Safety and food science coordinator for the Food Science program at NDSU.

Much of his research deals with lipid oxidation and antioxidant chemistry, stability of phytochemicals in food processing, and utilization of nontraditional ingredients in food systems. The stability of flaxseed bioactives and antioxidant activity of raisins has been his major focus recently, including the evaluation of flaxseed lignan stability in extruded bean snacks. He has published his research in 28 peer-reviewed international journals, and 12 proceedings, and has published 10 book chapters. His research has created 60 oral and poster presentations at the American Oil Chemists' Society, Institute of Food Technologists, International Society of Nutraceutical and Functional Foods, and AACC International annual meetings. He has advised five PhD and two masters' students to completion and currently advises two PhD and three masters' students. He has also mentored 28 undergraduate researchers and has served on 26 graduate student committees. Professionally, Clifford has been most active in the AOCS and AACC International.

xii Editors

He served as the secretary/treasurer, 2003; vice chairperson, 2004; and chairperson, 2005–2007 for the Lipid Oxidation and Quality Division of the American Oil Chemists' Society. He served as the chair of the Best Paper Competition Committee for the Lipid Oxidation and Quality Division, 2003–2006. He has also served as the chairperson of the Education Division for AACC International, 2007–2009 and on the AACC International Foundation as a board member, 2008 to the present; and chair, 2009. He has also served as an associate editor from 1998 to 2006 and senior associate editor from 2006 to the present for the *Journal of the American Oil Chemists' Society*. In addition, he is an ad hoc reviewer for *Food Chemistry*, *Journal of Food Science*, and *Journal of Agricultural and Food Chemistry*.

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Contents

		ix
		xi
Cont	tributor	rsxiii
Par	t I	Introduction
1.		luction to Bioactives in Fruits and Cereals
2.		h Promoting Effects of Cereal and Cereal Products
Par	t II	Chemistry and Mechanisms of Beneficial Bioactives in Fruits and Cereals
3.		chemicals in Cereals, Pseudocereals, and Pulses
4.		olic and Beneficial Bioactives in Drupe Fruits
5.		tive Phytochemicals in Pome Fruits
6.		chemicals in Citrus and Tropical Fruit
7.		chemical Bioactives in Berries
8.		olic Bioactives in Grapes and Grape-Based Products
9.	of Aln	ioactives: Phytochemicals and Lipid-Based Components nonds, Hazelnuts, Peanuts, Pistachios, and Walnuts
10.	of Bra	ioactives: Phytochemicals and Lipid-Based Components azil Nuts, Cashews, Macadamias, Pecans, and Pine Nuts
11.	Bioact	tive Lipids in Cereals and Cereal Products

Pa	rt III	Mycotoxic Bioactives of Fruits and Cereals			
12.	Mycotox Anuradh	cic Bioactives in Cereals and Cereal-Based Foods			
13.	on Myco	Assessments and Possible Inactivation Mechanisms otoxin Bioactives of Fruits and Cereals			
14.		of Mycotoxin Bioactives in Nuts: Farm to Fork			
Par	rt IV	Functionality, Processing, Characterization, and Applications of Fruit and Cereal Bioactives			
15.		n Characterization of Bioactive Compounds in Fruits and Cereals			
16.	Effect of Bioactive Components on Dough Rheology, Baking, and Extrusion				
17.	Impacts of Food and Microbial Processing on the Bioactive Phenolics of Olive Fruit Products				
18.		dant Activity/Capacity Assay Methods Applied to Fruit and Cereals			
19.		itical Fluid Extraction of Bioactive Compounds from Cereals			
20.		cal Methodology for Characterization of Grape and Wine Phenolic Bioactives 409 Stefova and Violeta Ivanova			
21.		ressure Processing Technology on Bioactives in Fruits and Cereals			
Ind	ex	443			

Part I Introduction

Introduction to Bioactives in Fruits and Cereals

Özlem Tokuşoğlu and Clifford Hall III

CONTENTS

Phytochemicals in Fruit and Cereals	3				
Phenolics in Fruit and Cereals	3				
Carotenoids in Fruit and Cereals	5				
Functional Lipids and Lipid Soluble Constituents	5				
Mycotoxic Bioactives in Fruits and Cereals					
Concluding Remarks	7				
References	7				

Fruit and cereal bioactives are classified as phytochemicals and toxicant secondary metabolites. Phytochemicals containing polyphenols, carotenoids, and functional lipids are naturally derived substances that have health-promoting, and/or nutraceutical and medicinal proper while mycotoxigenic bioactives are toxic substances that are secondary metabolites synthesized by toxigenic fungal species. A wide variety of mycotoxins are produced by various fungi, often a single fungal species can synthesize more than one type of mycotoxic bioactive under optimal conditions.

Interest in the bioactive compounds of fruit and cereals has reached a new high in recent years. Especially, the scientific and commercial attention in fruit and cereal bioactives have been accentuated by efficiency reports regarding both beneficial and toxical health effects of such compounds.

According to the National Institutes of Health (NIH), bioactive food phytochemicals including polyphenols, carotenoids, and functional lipids are "constituents in foods or dietary supplements, other than those needed to meet basic human nutritional needs, that are responsible for changes in health status." Major sources of these bioactive food components are plants, especially fruits, vegetables, and cereals. But major sources of both phytochemicals and mycotoxins are fruits, nuts, and more major in cereals.

In this book context, a brief description of the chemistry, sources, and applications of the abovementioned major bioactives in fruits and cereals.

Phytochemicals in Fruit and Cereals

Phenolics in Fruit and Cereals

As the name suggests, phytochemicals working together with chemical nutrients found in fruits, cereals, and nuts may help slow the aging process and reduce the risk of many diseases, including cancer, heart disease, stroke, high blood pressure, cataracts, osteoporosis, and urinary tract infections (Meskin et al. 2003; Omaye et al. 2000).

Polyphenols occur as plant secondary metabolites. Their ubiquitous presence in plants and plant foods, favors animal consumption and accumulation in tissues. Polyphenols are widely distributed in the plant kingdom and represent an abundant antioxidant component of the human diet (Ho, Rafi and Ghai, 2007). Interest in the possible health benefits of polyphenols has increased due to the

corresponding antioxidant capacities (Gharras, 2009). Recent evidences show that there is a great interest to anticarcinogenic effects of polyphenolic compounds, as well as the potential to prevent cardiovascular and cerebrovascular diseases (Cheynier 2005).

Polyphenols divide into several subgroups including flavonoids, hydroxybenzoic and hydroxycinnamic acids, lignans, stilbens, tannins, and coumarins that have specific physiological and biogical effects (Andersen and Markham 2006; Meskin et al. 2003; Tokuşoğlu 2001; Figure 1.1).

Flavonoids are a chemically defined family of polyphenols that includes several thousand compounds. The flavonoids have a basic structure (Figure 1.2), and several subclasses of flavonoids are characterized by a substitution pattern in the B- and C-rings. The main subclasses of flavonoids include flavan-3-ols, flavonols, flavonoes, flavanones, isoflavones, anthocyanidins, anthocyanins, flavononols, and chalcons (Figure 1.3) that are distributed in plants and food of plant origin (Crozier, Jaganath, and Clifford 2006).

Flavonoids in the circulation may protect against cardiovascular disease through their interaction with low-density lipoprotein (LDL). Biochemical and clinical studies in both humans and experimental animals have suggested that oxidized low-density lipoprotein (oLDL) has its atherogenic action through the formation of lipid hydroperoxides and the products derived therefrom. The in vivo antioxidant status of the LDL particles and the plasma are thus important determinants of the susceptibility of LDL to lipid peroxidation (Hertog et al. 1993).

Many of the phytochemicals and some vitamins (vitamin E, tocopherol) have antioxidant activity in vitro, which has led to the use of the general term "antioxidants."

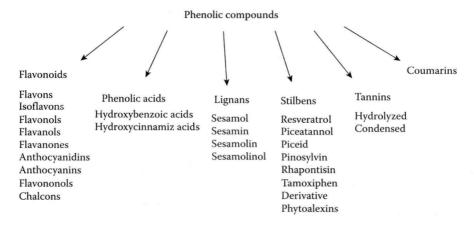


FIGURE 1.1 Family of phenolic compounds. (From Andersen, Q. M., and Markham, K. R., Flavonoids. Chemistry, Biochemistry, and Applications, CRC Press, Taylor & Francis, Boca Raton, FL, 2006; Meskin, M. S., Bidlack W. R., Davies, A. J., Lewis, D. S., and R. K. Randolph, Phytochemicals: Mechanisms of Action. CRC Press, Boca Raton, FL, 2003; Tokuşoğlu, Ö., The Determination of the Major Phenolic Compounds (Flavanols, Flavonols, Tannins and Aroma Properties of Black Teas, PhD Thesis, Department of Food Engineering, Bornova, Izmir, Turkey: Ege University, 2001).)

FIGURE 1.2 Chemical structure of flavonoids.

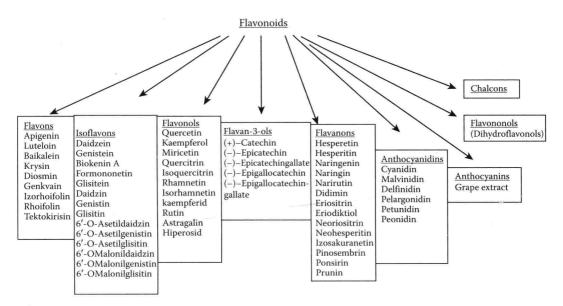


FIGURE 1.3 Flavonoid family in food plants. (Adopted from Tokuşoğlu, Ö., The Determination of the Major Phenolic Compounds (Flavanols, Flavonols, Tannins and Aroma Properties of Black Teas, PhD Thesis, Department of Food Engineering, Bornova, Izmir, Turkey: Ege University, 2001; Merken, H. M., and Beecher, G. R., *J. Agric. Food Chem.*, 48(3), 579–95, 2000; Beecher, G. R., *Antioxidant Food Supplements in Human Health*, Academic Press, New York, 1999; Fennema, O. R., *Food Chemistry*, Marcel Dekker, New York, 681–96, 1996; Vinson, J. A., Dabbagh, Y. A., Serry, M. M., and Jang, J., *J. Agric. Food Chem.*, 43, 2800–2802, 1995.)

Carotenoids in Fruit and Cereals

Carotenoids (Figure 1.4), a group of lipid-soluble compounds responsible for yellow, orange, red, and violet colors of various fruits and cereals products, are one of the most important groups of natural pigments, owing to their wide distribution, structural diversity, and numerous biological functions (Astorg 1997; Fraser and Bramley 2004).

The provitamin A activity of some carotenoid bioactives, recently, have demonstrated to be effective in preventing chronic diseases such as cardiovascular disease and skin cancer. Carotenoid bioactives are classified into four groups: carotenoid hydrocarbons, carotenoid alcohols (xanthophylls), carotenoid ketons, carotenoid acids.

Hydrocarbon carotenoids are known as *carotenes*, and the oxygenated derivatives are termed *xan-thophylls* (Astorg 1997; Fraser and Bramley 2004; Lee and Schwartz 2005)

Functional Lipids and Lipid Soluble Constituents

There has been a great interest concerning functional lipids in cereals due to their promotion for health and preventing diseases. Fatty acids play a central role in growth and development through their roles in membrane lipids, as ligands for receptors and transcription factors that regulate gene expression, as a precursor for eicosanoids, in cellular communication, and through direct interactions with proteins.

The main fatty acids in cereals are the saturated fatty acids, palmitic (16:0) and stearic (18:0), the monounsaturated fatty acid oleic acid (18:1), and the diunsaturated fatty acid inoleic acid (18:2) existing with smaller amounts of other fatty acids. These fatty acids are mainly assembled in glycerolipids; that is, triacylglycerols (TAG) and variable amounts of phospholipids (PL), glycolipids (GL), in sterol esters (SE), and waxes (or policosanols) in the different cereal grains.

Lipid soluble vitamins tocopherols and amphiphilic lipids alkylresorcinols, and terpen alcohol compounds are also important bioactive constituents in cereal grains (Figure 1.5). Cereal lipids have high levels of tocotrienols that coexist with tocopherols, which are the biologically most active antioxidants