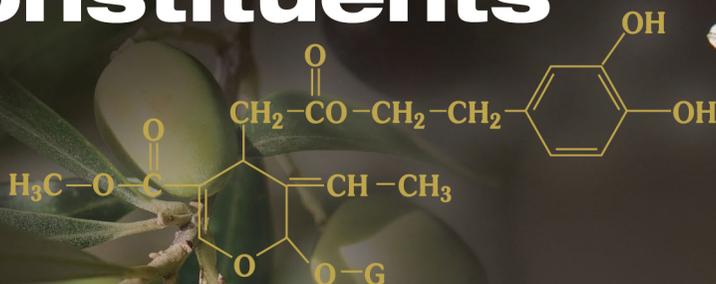


Olive and Olive Oil Bioactive Constituents



Editor

**Dimitrios
Boskou**



Olives and Olive Oil Bioactive Constituents

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Editor

Dimitrios Boskou



Urbana, Illinois

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Preface

Olive oil has a health nimbus as a basic ingredient of the Mediterranean diet. Studies on the favorable effects of biophenols and other olive and olive oil bioactive ingredients on markers of chronic inflammation, platelet aggregation in the blood, oxidized LDL cholesterol, joint health, skin conditions, and neurodegenerative disorders are continuously opening new paths for medical and pharmaceutical research. In addition, the olive oil market is becoming increasingly international because the positive role of virgin olive oil in the diet has become a topic of universal concern. New features of product optimization and development are emerging due to a better understanding of the chemistry of olives and olive oil minor constituents.

The bibliography for the biological activity of some minor compounds of olive and olive oil becomes more extensive every day, and a vast amount of published material has been accumulated. The growth of science aiming at unravelling exactly why olives and olive oil are so healthy co-occurs with experimental approaches for the identification and quantitation of bioactive ingredients in the various matrices (olive fruits, olive paste, virgin and other types of olive oil, intermediate and final products of processing, and biological fluids). Excellent studies do exist, but not all of the publications are equal; there are repetitions, discrepancies, and blanks due to difficulties deriving from the complex nature of compounds present in minute quantities in various matrices. An additional difficulty is the setting up of multidisciplinary studies with the involvement of food chemists, analytical chemists, and toxicologists who may provide guidance for the interpretation of results in relation to the actual chemistry of the compounds or isolates investigated, the expression of results, the presentation of levels and safety, or the efficacy of isolates and formulations. It is obvious that with the myriad of publications scattered in journals, books, and reference proceedings, a comprehensive understanding of olive and olive oil chemistry, biochemistry, and technology becomes difficult but also essential. This makes the systematic search for information necessary to better understand olive and olive bioactives, but this search is a challenge.

This book gathers together specialists who, with their deep reviews, cover the most important aspects of olive and olive oil biologically active constituents. Every effort has been made to provide information from authentic and highly regarded

sources and to bring the huge but disconnected bibliography in the area into a single volume resource, as analytically described here:

- The current state of the art in the study of bioactive molecules present in olive fruits, olive oil, olive paste, olive milling waste byproducts, and table olives is analytically presented.
- Olive oil phenol composition as affected by geographic origin, olive cultivar, cultivation systems and maturity, and the development of technology and innovative methods to retain optimum levels of bioactive ingredients in virgin olive oil and table olives are broadly discussed.
- Extended information is embodied for the biological importance of olive products, and individual bioactive compounds present in olive products are considered. The presentations focus on oxidative stress and inflammation, and evidence is provided from randomized, controlled human studies. Topics such as mechanisms of action, including molecular mechanisms emerging from genome-wide transcriptome analyses and findings in wound healing; cardiovascular effects; and anticancer properties of the major phenolics are considered, as well.
- The book contains also overviews of advanced techniques for the isolation, identification, and quantitation of phenolic compounds from various *Olea europaea* parts including mass spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The last part of the book describes the main byproducts of olive processing that are rich in bioactives and valorization methods and techniques for their recovery and their possible market utilization.

The subject matter is organized in eleven chapters. Chapter 1 is an introductory one. It provides an outline of the classes of olive and olive oil bioactive constituents, both phenolic and nonphenolic, and emphasizes the differences in the phenol composition between olive fruits and virgin olive oil. It stresses the importance of the level and nature of phenolics for the evaluation of quality characteristics, mainly stability, freshness, and specific sensations (bitterness, pungency). Because the myriad protective benefits of consuming olives and olive oil are supported by a wealth of scientific research and the literature is extremely extended, a synopsis of confirmed and putative health effects attributed to virgin olive oil biophenols is included with a short list of key publications. This chapter is a complement to Chapters 2 and 3 for those researchers who wish to better intergrate the results of past and ongoing experiments in the area of biosciences and relate them to the complexity and diversity of biophenols present in olive and olive oils. The last part of the chapter deals with olive oil substitutes and wellness products based on the addition of olive-derived phenols, derivatization of phenols, functionalization of food, and finally biophenols and culinary applications.

Chapter 2 discusses data related to the health benefits provided by olive oil phenolic compounds, such as the improvement of HDL lipoprotein functionality, reduction of the oxidation of lipids, decrease of inflammation, improvement of endothelial function, and decrease of systolic blood pressure. Postulated mechanisms by which olive oil phenolics can exert their beneficial effects are illustrated. The key work, randomized, controlled human studies that are capable of providing evidence for the benefits of the consumption of olive oils rich in phenolic compounds is summarized. Why this type of evidence is the prerequisite for approving nutritional recommendations at a population level is analyzed.

Chapter 3 explores the traditional medicinal properties and early uses of olives and olive oil. It further discusses the evolution and health benefits of the Mediterranean diet and focuses on cellular and molecular effects of bioactive phenolic compounds in olives and olive oil, mainly hydroxytyrosol and oleuropein. Emphasis is placed on molecular mechanisms of action emerging from genome-wide transcriptome analyses.

Chapter 4 analytically examines the factors affecting the occurrence and abundance of phenolics in olive fruits and the oil produced. These factors—variety, geographical origin, farming, irrigation, fertilization, edaphoclimatic conditions, and processing of olives, isolated or in conjunction, greatly influence olives, table olives, and olive oil phenolic composition. Without proper control of these factors, the availability of phenolic compounds in olive products will be reduced drastically with serious adverse effects on the quality, stability, sensory characteristics, and favorable health properties of the oil.

Chapter 5 focuses mainly on the effect of fruit ripening on the phenolic content and antioxidant potential of the extracted olive oil. It demonstrates the significance of the correct ripeness stage and points out that determining the optimal harvesting period is important to obtain various types of olive oils (fruity, bitter, sweet) to fulfill the required market characteristics and necessary typicality in composition.

Chapter 6 analyzes the benefits of high-resolution mass spectroscopy and the latest generations of analyzers for quantitative and simultaneously qualitative monitoring of small molecules in the complex olive matrices. Experimental work disclosing the transformations and levels of olive key secondary metabolites in the different production steps (from olive drups to olive oil) is extensively and critically discussed in this chapter. The general trends for the formation of bioactives from molecules initially present in the drups during crushing, malaxation, and centrifugation are presented. The generation of important phenols and triterpene acids, such as hydroxytyrosol, tyrosol, oleacein, oleocanthal, and maslinic acid, and reduction of oleuropein and ligstroside oleuropein and ligstroside aglycons is monitored by measuring concentrations in the paste and the final product (olive oil).

Chapter 7 analyzes virgin olive oil production steps in relation to minor bioactive constituents. A lot of information is provided for the preprocessing of olives, crushing, particle size, innovative crushing and malaxation systems, control of oxygen, enzyme activities, separation of phases, filtration, and storage. Theoretical considerations are included for the dissolution of phenols in virgin olive oil during crushing and malaxation, and for the drop diameters and viscosity. Finally, employment of ultrasounds and microwaves and proposed strategies to develop continuous plants are described.

Chapter 8 deals with table olive processing methods in relation to the levels of phenols and other bioactive constituents. Table olives have more or less the same health properties as olive oil, but this aspect was overlooked because, with the exception of Mediterranean countries, this product was seen as a piece of decoration for pizzas and breads. Debittering techniques that are internationally applied are described, as are local practices and popularity of certain preparations that give an image of the rich Mediterranean culture and tradition. Innovative proposals for debittering, targeting of oleuropein hydrolysis, packing under modified atmosphere, improvement of cultivars to obtain larger phenolic levels in fruits, fermentation with the use of probiotic bacteria from olive's natural flora, and generally the combination of tradition and innovation indicate that this product can now become an important "functional" food.

Chapter 9 explores advances in analytical science and related methodologies. The determination of minor compounds in olive oil, such as biophenols, is a challenge for today's analyst, who may combine hyphenation of chromatography and electrophoresis techniques with UV, fluorescence, and mass spectrometry (MS), as well as fluorescence, infrared (IR) and NMR spectroscopies, and ambient MS. High-resolution spectroscopy can be further coupled to the facilities of computerized mathematical and statistical processing. The discussion in this chapter concentrates on the application of these methodologies to determine phenolic compounds in olive fruit and olive oil and their metabolites in biological samples, based mainly on literature published in the last five years.

Chapter 10 covers studies carried out during the last decade focusing mainly on the new developments in multinuclear and multidimensional liquid high-resolution NMR spectroscopy, as well as solid state NMR spectroscopy that made possible the detection and identification of new microconstituents. A number of figures are included with useful spectroscopic parameters and structures or transformations of biophenols and other minor constituents. A lot of references are cited, providing more detailed information about chemical shifts, assignment of signal, and other spectroscopic characteristics of molecules. Examples are given mainly from sources such as olive oil, olive fruit, table olives, and olive leaves.

Chapter 11 features a valuable section on olive bioactive compounds found in olive leaves, pomace, milling waste water, and table olive processing waste water, the main byproducts of the olive processing industry. Among the compounds present in these materials, the phenolic compounds constitute the most interesting group, endowed with a wide array of biological activities. Extraction is described from conventional methods to advanced techniques of fractionation and isolation. Possible use of olive byproducts for the development of pharmaceuticals, nutraceuticals, and cosmeceuticals is discussed.

It is hoped that the book will be of special value to food and health scientists, nutritionists, dieticians, cardiovascular disease epidemiologists, pharmacologists, food technologists, agronomists, analytical chemists, and researchers and professionals in the area of bioscience involved in studies related to natural antioxidants, oxidative stress, inflammation, and chemoprevention.

I thankfully acknowledge the work of the specialists who contributed to this book, and I consider myself fortunate for having the opportunity to work with so many experienced colleagues from universities and research institutes in Spain, Italy, Greece, Portugal, Tunisia, the United States, and Australia. Their reviews may suggest future research not only to understand better the role of phenols in the light of recent chemical knowledge, but also to assess the magnitude of the contribution of each bioactive compound to the overall positive health impact, an issue that has not yet been properly addressed.

—Dimitrios Boskou

About the Editor



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Dimitrios Boskou received his diploma and doctor's degree in chemistry from the School of Chemistry, Aristotle University of Thessaloniki, Hellas; his Ph.D. in Food Science from the University of London; and a Doctor of Science degree from the School of Chemistry, Aristotle University. He served as an assistant lecturer, assistant professor, associate professor, professor, and head of the Laboratory of Food

Chemistry and Technology, School of Chemistry, Aristotle University (1970–2006). In the period from 1986 to 1998 he was a member of the IUPAC Oils, Fats, and Derivatives Commission. He served as a member of the Supreme Chemical Council, Athens (1995–2005), and a member of the Scientific Committee for Food of the European Commission and an expert of the Food Additives Panel of the European Food Safety Authority (1995–2012).

Dr. Boskou has published over 90 papers and reviews. He is the editor of 7 books and the author of 20 chapters in books related to the major and minor constituents of fats, natural antioxidants, olive oil, and heated fats, published in the United States, the United Kingdom, France, India, and Croatia. He is also a contributor to international scientific encyclopedias and the Lexicon of Lipid Nutrition, a joint IUPAC/IUNS work.

Research and Innovative Approaches to Obtain Virgin Olive Oils with a Higher Level of Bioactive Constituents

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Introduction

Virgin olive oil is the main component of the Mediterranean diet due to its sensory and nutritional qualities. The benefits of consuming olive oil have been known since antiquity. The ancient Greeks believed that the goddess Athena had created the olive tree. King David hired guards to protect Israel's olive groves and warehouses. Ancient peoples used olive oil not only for consumption and cooking, but also as perfume, ointment for the dead, soap, and in oil lamps. In ancient Greece, the athletes ritually rubbed it all over their bodies. It has been considered symbol of great wealth and power, therefore, it has anointed the noblest heads throughout history. Olive oil was used to produce both medicine and cosmetics; Hippocrates called it “great healer” and Homer “liquid gold,” and Galen praised it for its positive effects on health (Clodoveo et al., 2014a). It is now well established that most of these effects can be attributed to the phenolic fraction of olive oil (Boskou, 2006, 2011).

Olive fruit contains appreciable concentration, 1–3% of fresh pulp weight, of hydrophilic (phenolic acids, phenolic alcohols, flavonoids, and secoiridoids) and lipophilic phenolic compounds that are known to possess multiple biological properties such as antioxidant, anticarcinogenic, anti-inflammatory, antimicrobial, antihypertensive, antidyslipidemic, cardioprotective, laxative, and antiplatelet benefits (Ghanbari et al., 2012). For some activities of olive oil phenolic compounds the evidence is already strong enough to enable the legal use of health claims on foods (Martín-Peláez et al., 2013). A health claim is defined as any claim that states, suggests, or implies that a relationship exists between a food category, a food, or one of its constituents and health. A health claim on “olive oil polyphenols,” even if not accurate in the choice of terminology and the subject of some controversies (Mastralexi et al., 2014a and 2014b; Romero and Brenes, 2014), was made only very recently

Table Olives as Sources of Bioactive Compounds

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Salvatore Camposeo and Maria Lisa Clodoveo ■ *Department of Agricultural and Environmental Science, University of Bari, Bari, Italy*

Introduction

Table olives are prepared from the fruit of the olive tree (*Olea europaea* L.). Fresh olives are picked when green-ripe, turning color, or black-ripe, depending on the mode of processing to be used. Fresh olives are not edible because of the presence of oleuropein, a bitter glucoside. Processing of fresh olives reduces bitterness and makes them edible. Processing involves soaking in water, brine, or diluted alkali or drying by heating or salting. In general, larger-scale table olive processors may use lye treatments, which speeds up processing. Small- and very-small-scale producers favor more “natural methods.” The residual bitter taste of processed table olives depends on the type and quantity of phenolic compounds present after the processing, and it is an important characteristic favored by consumers.

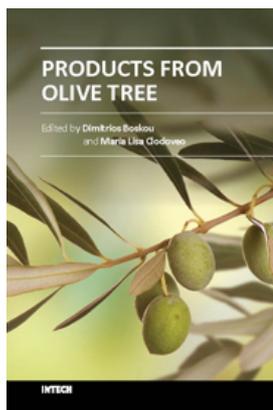
Table olives are a highly functional food with a balanced content of fats made up mainly of monounsaturated oleic acid. Eating olives also provides energy, fiber, vitamins, and minerals and contributes to the daily intake of nutritional antioxidants. The protein content is low (1.0–2.2%), but olives’ proteins are rich in essential amino acids. Olives constitute an essential element of the Mediterranean diet and are a featured ingredient in hundreds of dishes. They are important from a nutritional point of view for the general population in many Mediterranean countries, especially during long periods of fasting. They are of vital importance for the Christian orthodox monks and nuns, who consume large quantities of olives. In Portugal, stoned, halved table olives, known as *alcaparra*, are largely consumed, and their production is an important agroeconomic factor for the local producers.

There are three main types of commercial table olives: Spanish-style green olives, Greek-style natural black olives, and California-style black olives. In the Spanish and Californian procedures, olives are treated with a diluted aqueous NaOH solution that brings about several changes in biophenols, tocopherols, and triterpenic acids, but the composition of the triacylglycerols remains unaffected. After the treatment, the olives are rinsed to remove the alkali, and the fruit is then left to ferment in brine for several months. The production of naturally black olives in brine, according to the Greek traditional method and its variations, is a simple, natural process that does not use chemicals.

Products from Olive Tree by InTech Publishing

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A brand new academic publication about the products of the Olive Tree, entitled “Products from Olive Tree” is available since October 26th by InTech publishing, bearing the signatures of professors **Dimitrios Boskou** and **Maria Lisa Clodoveo** as editors of the volume.

A synopsis of the publication:

Olive tree products provide a number of documented presentations of the production and quality of the two most important olive tree products: virgin olive oil and table olives. It is a source that familiarizes readers with recent approaches and innovations that can be introduced in the virgin olive oil extraction and stabilization

technology and the preparation of table olives with emphasis on the presence of bioactive constituents. It also describes advances in the methods of checking authenticity and in the evaluation of attributes that may influence consumers' perceptions and preferences. Other topics discussed are squalene, a trove of metabolic actions, pigments, geographical indication, biotechnology in table olive preparation, and recovery of hydroxytyrosol from olive-milling wastes.

Editors' bios

Dimitrios Boskou received his diploma and doctor's degree in chemistry from the School of Chemistry, Aristotle University of Thessaloniki, Hellas; his Ph.D. in Food Science from the University of London; and a Doctor of Science degree from the School of Chemistry, Aristotle University.

He served as an assistant lecturer, assistant professor, associate professor, professor, and head of the Laboratory of Food Chemistry and Technology, School of Chemistry, Aristotle University (1970–2006).

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