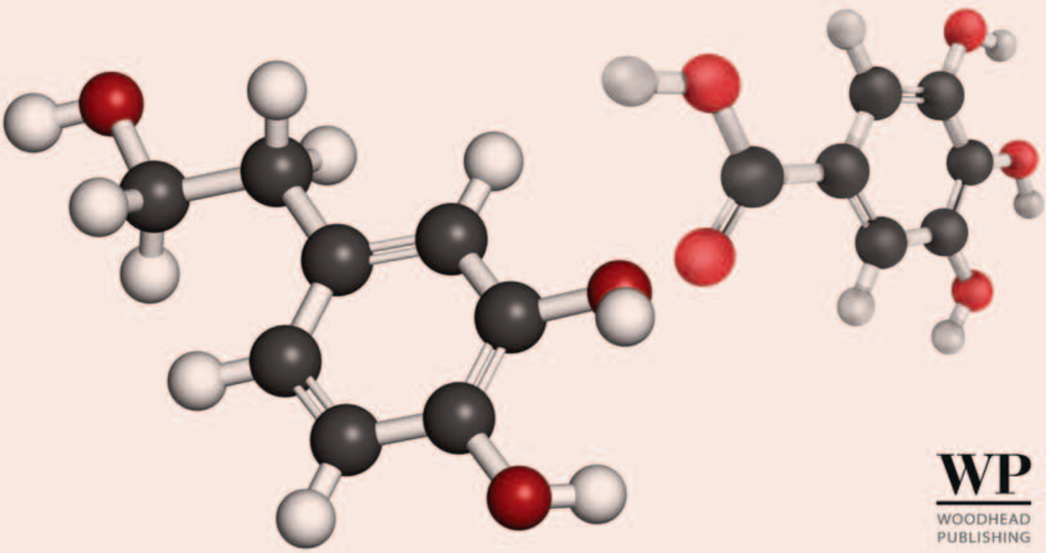
Polyphenols: Properties, Recovery, and Applications

Edited by Charis M. Galanakis



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WOODHEAD
PUBLISHING
An imprint of Elsevier

Woodhead Publishing is an imprint of Elsevier
The Officers' Mess Business Centre, Royston Road, Duxford, CB22 4QH, United Kingdom
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States
The Boulevard, Langford Lane, Kidlington, OX5 1GB, United Kingdom

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-12-813572-3 (print)
ISBN: 978-0-12-813573-0 (online)

Publisher: Andre Gerhard Wolff
Acquisition Editor: Megan R. Ball
Editorial Project Manager: Katerina Zaliva
Production Project Manager: Joy Christel Neumarin Honest Thangiah
Designer: Mark Rogers

Typeset by TNQ Books and Journals

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Preface

Polyphenols are reactive metabolites abundant in plant-derived foods (particularly fruits, seeds, and plants) that have well-noted antioxidant properties and exert preventive activity against chronic diseases. The effectiveness of polyphenols depends on preserving their stability, bioactivity, and bioavailability during handling, extraction, and processing. To this line, researchers investigated the above issues over the last years, whereas the development of polyphenols' applications in functional foods, nutraceutical, pharmaceutical, and cosmetic industries is increasingly gaining more and more attention. Besides, with the recent advantages in food processing (e.g., non-thermal technologies, modern encapsulation techniques, etc.), new developments, data, and state of the art come up in the field. All these accelerated advances confuse modern food chemists, scientists, and technologists who seek for more integral information on polyphenol's applications. Subsequently, there is a need for a new reference connecting properties and health effect of polyphenols with recovery, processing, and encapsulation issues prior exploring industrial applications. The current book aspires to fill in this gap by providing a guide covering the most important assets (properties, processing, and applications) of polyphenols in 3 parts and 12 chapters.

Part A (Metabolism and Health Effects of Polyphenols) includes four chapters. Chapter 1 presents basic and introductory information on polyphenols, covering historical background, evolution of chemical definitions, and classifications. The structural diversity of polyphenols is also elaborated and related to common food sources. In addition, recent advances for probing the antioxidant activity of polyphenols in the gastrointestinal tract and the effects of controlled polyphenol-rich foods on selected parameters of oxidative stress after consumption are denoted. In Chapter 2, the absorption, bioavailability, and metabolomics of polyphenols are critically discussed. Chapter 3 revises the association between polyphenols from different sources with cardiometabolic, hormone-dependent (including menopausal symptoms and osteoporosis), and neurodegenerative diseases (including Parkinson's and Alzheimer's disease) as well as with certain cancers (including breast, lung, and colorectal) and affective disorders (including depression). An in-depth discussion on the safety issues of polyphenols' consumption is provided, too. Chapter 4 discusses the correlation between genes and polyphenols, as well as the major progresses in polyphenols–gene interaction of specific food groups. The recent international initiatives related with nutrigenomics and the developing personalized nutrition are also presented.

Part B (Recovery and Processing of Polyphenols From Target Sources) includes five Chapters. Chapter 5 provides a description of the different natural sources of polyphenols, e.g., fruit and vegetables, cereals, legumes, coffee, tea, olive oil, cocoa, herbs, and species. The industrial processing of these natural substrates leads to the production of huge amount of by-products that comprise rich sources of polyphenols. Within the sustainability frame of the modern food industry, the recovery of these high added-value compounds from underutilized sources is an important issue and thus specific attention is given to this direction. Subsequently, Chapter 6 provides a broad view on the developed methods for polyphenols' extraction and analysis. The different workflows and steps involved in polyphenols analysis are presented. Furthermore, the spectrophotometric methods used to determine polyphenols as well as to measure the antioxidant capacity of their extracts are critically discussed, whereas the state of the art regarding advanced analytical techniques for the characterization of polyphenols is addressed. Chapter 7 revises the application of conventional techniques for the recovery of polyphenols from different sources as adapted to the integral "5-stages universal recovery process." Similarly, Chapter 8 deals with the recovery of polyphenols using emerging technologies, namely supercritical and subcritical fluid extraction, pulsed electric fields, high-voltage electrical discharges, ultrasounds, microwaves, infrared-assisted extraction, high-pressure processing, "instant controlled pressure drop," and "intensification of vaporization by decompression to the vacuum." Chapter 9 discusses the stability of polyphenols under different processing and storage factors, such as pH, temperature, light, oxygen, enzymes, proteins, metal ions, and association with other food constituents.

Part C of the book (Applications of Polyphenols in the Industry) is divided into three chapters. Chapter 10 focuses on the application of polyphenols as food additives. The technological features of polyphenols could contribute to replace the currently used synthetic molecules, guarantee the proper preservation of manufactured food products (e.g., when used as inhibitors), and enhance the physical properties of foodstuffs. In a more target approach, Chapter 11 highlights the high potential of some polyphenolic compounds as food colorants providing red, yellow-orange, and blue hues. Besides coloring properties, the presented novel pigment sources are characterized by assumed health-promoting properties, suggesting their additional use as functional food ingredients. Finally, Chapter 12 deals with the skin effects of polyphenols and the most recent patents regarding the incorporation of the latest in cosmetics.

Conclusively, the book supports the current industrial applications of polyphenols and reveals those that are under development. It is intended to support nutritionists, food scientists, technologists, and chemists working in the whole food science area, new product developers, as well as relevant researchers, academics, and professionals. It could be used by university libraries and institutes all around the world as a textbook and/or ancillary reading in undergraduates and postgraduate-level multidiscipline courses dealing with nutritional and food chemistry, as well as food science, technology, and processing.

I would like to take this opportunity to thank all the authors for their fruitful collaboration and high-quality work in bringing together all key and interconnected issues of polyphenols in an integral and comprehensive text. I consider myself fortunate to have had the opportunity to collaborate with so many knowledgeable colleagues from China, Croatia, Ecuador, Italy, Lebanon, Macau, Poland, Portugal, Serbia, Spain, Turkey, and the UK. Their acceptance of book's approach and editorial guidelines is highly appreciated. I would also like to acknowledge the support of Food Waste

Recovery Group of ISEKI Food Association, as well as to thank the acquisition editor Megan Ball for her honorary invitation to lead this project, Katerina Zaliva (the book manager) and all the Elsevier team of Elsevier for their assistance during production.

Last but not least, a message for you, the reader. This kind of collaborative projects might contain errors or generate debates on specific scientific matters. Instructive comments and even criticism are and always will be welcome. Therefore, if you find any mistake or if you have objection for the content of the book, please do not hesitate to contact me.

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Part A

Metabolism and Health Effects of Polyphenols

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Overview of polyphenols and their properties

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1. Introduction

In the past 10 years, the growing interest of consumers has risen to a number of "superfoods," which has been motivated by their high content of polyphenols (Panza et al., 2008; Dreosti, 2000). These compounds constitute a heterogeneous group of molecules that differentiate according to their chemical structure (Manach et al., 2004), and due to the considerable diversity of their structures, polyphenols are considered even more efficient than other antioxidants. The main reason for the interest of scientists and consumers for polyphenols is the recognition of their antioxidant properties, their great abundance in our diet, and their probable role in the prevention of various diseases associated with oxidative stress, such as cancer and cardiovascular and neurodegenerative diseases (Scalbert et al., 2005). Driven by beneficial biological activities, researchers all over the world have provided a vast body of scientific evidences by publicizing up to 40,000 research papers from 1990 about the contents, mechanisms of action, and in vitro and in vivo biological activities of polyphenols (Science Citation Index—WoS). Despite the promising evidence regarding the possible role of polyphenols in disease prevention, data regarding their consumption at the population level are still insufficient to suggest optimal intake levels and dietary recommendations (Williamson and Holst, 2008). However, in the recent years, a few European investigations were conducted aiming to provide an insight in the consumed amounts of dietary polyphenols and to establish corresponding databases with the same compounds (Perez-Jimenez et al., 2011; Tresserra-Rimbau et al., 2013; Neveu et al., 2010; Zujko et al., 2012; Peasey et al., 2006). To establish conclusive evidence for the effectiveness of polyphenols in disease prevention and human health improvement, it is essential to determine the nature and distribution of these compounds in our diet and to better identify which of the hundreds of existing polyphenols are likely to provide the greatest effects (Stahl et al., 2002). This chapter serves as a starting point for all interested in polyphenols and provides a complete background, chemical definitions, main food contributors, and properties of dietary polyphenols.

2. Historical background and definition of polyphenols

Chemically, polyphenols are a group of natural compounds with phenolic structural features. It is a collective term for several subgroups of compounds; however, the use of the term "polyphenols" has been somewhat confusing and its implied chemical

Polyphenols: Properties, Recovery, and Applications. https://doi.org/10.1016/B978-0-12-813572-3.00001-4

structures are often vague even to researchers (Tsao, 2010). Even today the scientific community is not consistent with a universal use of the term denoting plant polyphenols, since some call them "plant phenols" while some use the term "polyphenols." According to Quideau et al. (2011), the use of the term "polyphenols" is still preferred mainly for commercial communications. Strictly chemically speaking, the term "phenols" includes the arene ring and its hydroxy substituent(s), and according to that concept, the term "polyphenol" should be restricted to structures bearing at least two phenolic moieties, irrespective of the number of hydroxy groups they each bear (Quideau et al., 2011).

The definition of plant polyphenols was traditionally based on structural characteristics and protein precipitation (Haslam and Cai, 1994), but in the recent years it has been markedly revised, taking into account structural features and biosynthetic routes (Quideau et al., 2011).

The history of polyphenols and their definition reveals that before being called polyphenols, these plant-derived natural products were globally referred to as "vegetable tannins" as a consequence of their use from various plant extracts in the conversion of animal skins into leather. The first definition of "plant polyphenols" in the scientific literature pertains to this initial utilization of polyphenolic plant extracts. As these compounds were highly required in the leather industry, considerable efforts were devoted from the beginning of the 20th century onward to the study of the chemistry of tanning plant extracts in an attempt to tackle the structural characterization of their polyphenolic constituents (Quideau et al., 2011). Research on plant polyphenols shifted gears after 1945, as the discovery of paper chromatography and more and more other advanced analytical techniques made it possible to separate innumerous individual constituents (Cheynier et al., 2015). In 1957, an industrial chemist, Theodore White, pointed out that the term "tannin" should strictly refer to plant polyphenolic materials having molecular masses between 500 and 3000 Da and a sufficiently large number of phenolic groups to be capable of forming hydrogen-bonded cross-linked structures with collagen molecules (the act of tanning).

The explosion of activity on polyphenols research led to the foundation, in 1957, of the Plant Phenolic Group by two pioneers in the area, E. C. Bate-Smith and Tony Swain (Cheynier et al., 2015). In 1962, Bate-Smith and Swain came up with their own proposal for a definition of plant polyphenols as "water-soluble phenolic compounds having molecular weights between 500 and 3000 (Da) and, besides giving the usual phenolic reactions, they have special properties such as the ability to precipitate alkaloids, gelatin and other proteins from solution" (Swain and Bate-Smith, 1962). This definition was later refined at the molecular level by Edwin Haslam who expanded the definitions of those of Bate-Smith, Swain, and White such that the term "polyphenols" should be used as a descriptor for water-soluble plant phenolic compounds having molecular masses ranging from 500 to 3000–4000 Da and possessing 12 to 16 phenolic hydroxy groups on 5 to 7 aromatic rings per 1000 Da of relative molecular mass (Haslam and Cai, 1994). The focal criterion from which White, Bate-Smith, Swain, and Haslam (WBSSH) originally based their classification of plant phenolics as "polyphenols" or not was first and foremost the capacity to engage in complexation with other biomolecules. However, that definition was still not exact enough, since according to it, the polyphenolic substances would be divided into only three classes of polyhydroxyphenyl-containing natural products that conform to the restrictions implied by the initial definition. Bearing all chemical considerations in mind, Quideau et al. (2011) proposed a new definition of polyphenols as follows: "The term "polyphenol" should be used to define plant secondary metabolites derived exclusively from the shikimate derived phenylpropanoid and/or the polyketide pathway(s), featuring more than one phenolic ring and being devoid of any nitrogen-based functional group in their most basic structural expression."

3. Structural diversity and classification of polyphenols

Phenolic compounds are constituted in one of the biggest and widely distributed groups of secondary metabolites in plants (Scalbert and Williamson, 2000). As previously mentioned, polyphenols not only comprise a wide variety of molecules that have a polyphenol structure (i.e., several hydroxyl groups on aromatic rings) but also molecules with one phenol ring, such as phenolic acids and phenolic alcohols. Although polyphenols are chemically characterized as compounds with phenolic structural features, this group of natural products is highly diverse and contains several subgroups of phenolic compounds.

Biogenetically, phenolic compounds proceed of two metabolic pathways: the shikimic acid pathway where, mainly, phenylpropanoids are formed and the acetic acid pathway in which the main products are the simple phenols (Sánchez-Moreno, 2002). It is estimated that 100,000 to 200,000 secondary metabolites exist and some 20% of the carbon fixed by photosynthesis is channeled into the phenylpropanoid pathway (Pereira et al., 2009). Most plants' phenolic compounds are synthesized through the phenylpropanoid pathway (Hollman, 2001). The combination of both pathways leads to the formation of flavonoids, the most plentiful group of phenolic compounds in nature (Sánchez-Moreno, 2002). Through the biosynthetic pathways to the flavonoids synthesis, among the not well-elucidated condensation and polymerization phases, the condensed tannins or nonhydrolysable tannins are formed. Hydrolysable tannins are derivatives of gallic acid or hexahydroxydiphenic acid (Stafford, 1983). In addition to the chemical diversity, polyphenols may be associated with various carbohydrates (existing as glycosides with different sugar units and acylated sugars at different positions of the polyphenol skeletons) and organic acids or with one another (Manach et al., 2004).

Several thousand different polyphenolic compounds (among them over 8150 flavonoids) have been identified with a large range of structures (Lattanzio et al., 2008). The diversity and wide distribution of polyphenols in plants have led to different ways of categorizing these naturally occurring compounds, as can be seen in Fig. 1.1. Polyphenols have been classified by their *source of origin, natural distribution, biological function,* and *chemical structure*.

With respect to their *distribution in nature*, phenolic compounds can be divided into three classes: shortly distributed (as simple phenols, pyrocatechol, hydroquinone, resorcinol, aldehydes derived from benzoic acids that are components of essential oils,

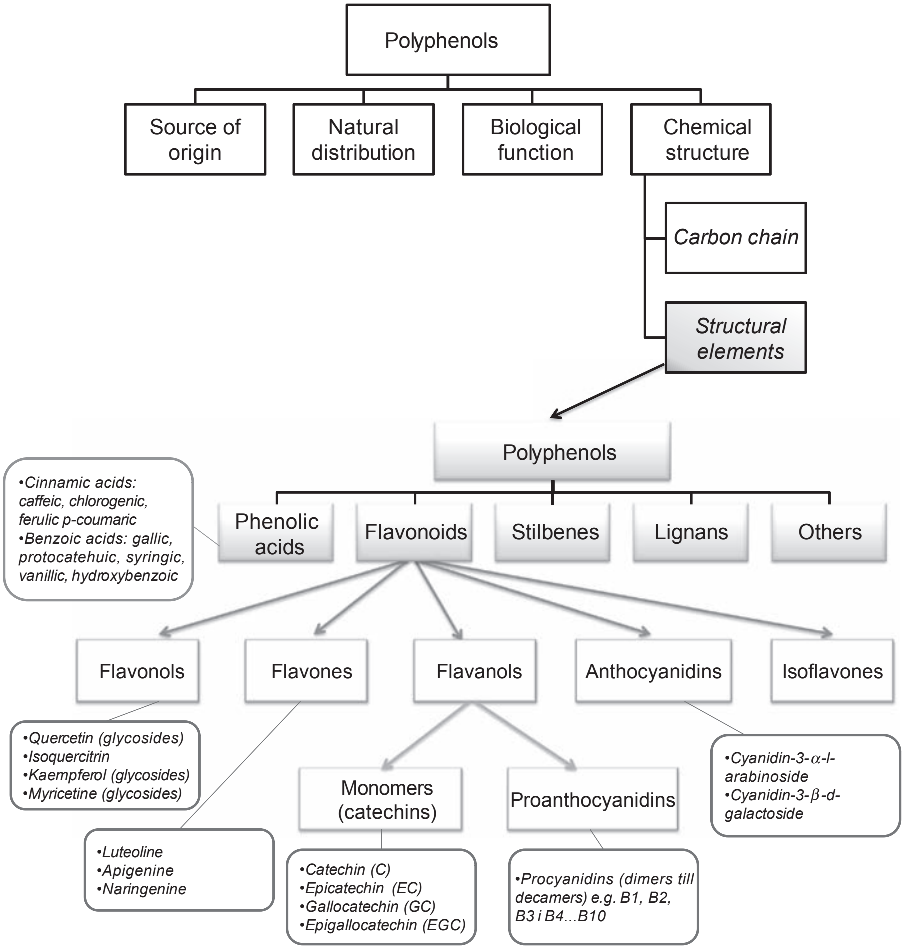

Figure 1.1 Different classifications of plant polyphenols and polyphenolic classes based on the number of phenol rings and their structural elements.

such as vanillin), widely distributed (divided in flavonoids and their derivatives, coumarins, and phenolic acids, such as benzoic and cinnamic acid and their derivatives), and polymers (tannins and lignins) (Bravo, 1998).

As to the *location in the plant* (free in the soluble fraction of cell or bound to compounds of cell wall), together with the chemical structure of these substances, phenolic compounds may also be classified as: simple phenols (flavonoids and tannins of low and medium molecular weight not bound to membranes' compounds) and essentially constituted phenols (condensed tannins, phenolic acids, and other phenolic compounds of low-molecular weight bound to cell wall polysaccharides or proteins forming insoluble stable complexes). This classification is useful from the nutritional viewpoint to the extent that the metabolic fate in the gastrointestinal tract and the physiological effects of each group will depend largely on their solubility characteristics.