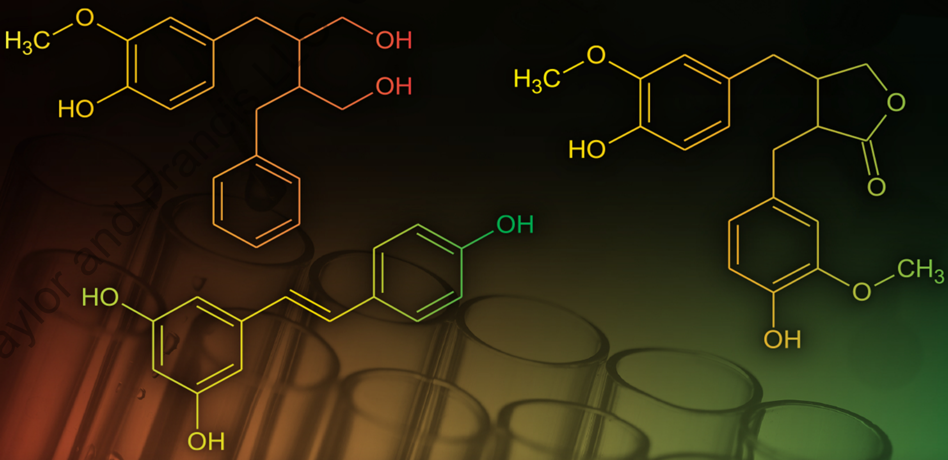
Food Analysis & Properties Series

Phenolic Compounds in Food

Characterization and Analysis



EDITED BY **LEO M.L. NOLLET**
JANET ALEJANDRA GUTIERREZ-URIBE

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Phenolic Compounds in Food

Characterization and Analysis

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Series Editor
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Flow Injection Analysis of Food Additives Edited by Claudia Ruiz-Capillas and Leo M. L. Nollet	**(2015)**

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Series Preface

There will always be a need for analyzing methods of food compounds and properties. Current trends in analyzing methods include automation, increasing the speed of analyses, and miniaturization. The unit of detection has evolved over the years from micrograms to picograms.

A classical pathway of analysis is sampling, sample preparation, cleanup, derivatization, separation, and detection. At every step, researchers are working and developing new methodologies. A large number of papers are published every year on all facets of analysis. So, there is a need for books that gather information on one kind of analysis technique or on analysis methods of a specific group of food components.

The scope of the CRC Series on Food Analysis & Properties aims to present a range of books edited by distinguished scientists and researchers who have significant experience in scientific pursuits and critical analysis. This series is designed to provide state-of-the-art coverage on topics such as

1. Recent analysis techniques on a range of food components
2. Developments and evolution in analysis techniques related to food
3. Recent trends in analysis techniques of specific food components and/or a group of related food components
4. The understanding of physical, chemical, and functional properties of foods

The book *Phenolic Coumpounds in Foods: Characterization and Analysis* is the fifth volume in this series.

I am happy to be a series editor of such books for the following reasons:

- I am able to pass on my experience in editing high-quality books related to food.
- I get to know colleagues from all over the world more personally.
- I continue to learn about interesting developments in food analysis.

A lot of work is involved in the preparation of a book. I have been assisted and supported by a number of people, all of whom I would like to thank. I would especially like to thank the team at CRC Press/Taylor & Francis, with a special word of thanks to Steve Zollo, Senior Editor.

Many, many thanks to all the editors and authors of this volume and future volumes. I very much appreciate all their effort, time, and willingness to do a great job.

I dedicate this series to

- My wife, for her patience with me (and all the time I spend on my computer)
- All patients suffering from prostate cancer; knowing what this means, I am hoping they will have some relief

Dr. Leo M. L. Nollet (Retired)
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Preface

Natural phenolic compounds have received a lot of attention in the last few years since a great amount of them can be found in plants and the consumption of vegetables and beverages with a high level of such compounds may reduce risks of the development of several diseases. This is partially due to their antioxidant power since other interactions with cell functions have been discovered.

Phenolic compounds are one of the biggest and most widely distributed groups of secondary metabolites in plants. They play a role of protection against insects and other plant stress elicitors. They are involved in many functions in plants, such as sensorial properties, structure, pollination, resistance to pests and predators, germination, processes of seed, development, and reproduction.

Phenolic compounds can be classified in different ways, ranging from simple molecules to highly polymerized compounds.

This book deals with all aspects of phenolic compounds in food. This book has five sections with 21 chapters:

Section I: Phenolic Compounds
Section II: Analysis Methods
Section III: Different Groups of Phenolic Compound Related to Foods
Section IV: Antioxidant Power
Section V: Phenolic Compounds in Different Foodstuffs

In the chapters of Section I, the classification and occurrence of phenolic compounds in nature and foodstuffs is addressed.

Section II discusses all major aspects of analysis of phenolic compounds in foods: extraction, clean-up, separation, and detection.

In Section III, the reader finds out more information about and facts on specific analysis methods of a number of classes of phenolic compounds, from simple molecules to complex compounds.

The antioxidant power of phenolic compounds is detailed in Section IV.

In Section V, specific analysis methods in different foodstuffs are discussed.

It is a great pleasure to thank all the contributors of each chapter. They did an excellent job, and spent a lot of time and effort to deliver outstanding manuscripts.

Leo M. L. Nollet
Janet Alejandra Gutiérrez-Uribe

> Nothing great was ever achieved without enthusiasm.
>
> Ralph Waldo Emerson

I congratulate my co-editor, Janet, for her superb and persistent work on this project.

Leo M. L. Nollet

About the Editors

Leo M. L. Nollet, PhD, earned an MS (1973) and PhD (1978) in biology from the Katholieke Universiteit Leuven, Belgium. He is an editor and associate editor of numerous books. He edited for M. Dekker, New York—now CRC Press of Taylor & Francis Publishing Group—the first, second, and third editions of *Food Analysis by HPLC* and *Handbook of Food Analysis*. The last edition is a two-volume book. Dr. Nollet also edited the *Handbook of Water Analysis* (first, second, and third editions) and *Chromatographic Analysis of the Environment*, third and fourth editions (CRC Press). With F. Toldrá, he coedited two books published in 2006, 2007, and 2017: *Advanced Technologies for Meat Processing* (CRC Press) and *Advances in Food Diagnostics* (Blackwell Publishing—now Wiley). With M. Poschl, he coedited the book *Radionuclide Concentrations in Foods and the Environment*, also published in 2006 (CRC Press). Dr. Nollet has also coedited with Y. H. Hui and other colleagues on several books: *Handbook of Food Product Manufacturing* (Wiley, 2007), *Handbook of Food Science, Technology, and Engineering* (CRC Press, 2005), *Food Biochemistry and Food Processing* (first and second editions; Blackwell Publishing—now Wiley—2006 and 2012), and the *Handbook of Fruits and Vegetable Flavors* (Wiley, 2010). In addition, he edited the *Handbook of Meat, Poultry, and Seafood Quality*, first and second editions (Blackwell Publishing—now Wiley—2007 and 2012). From 2008 to 2011, he published with F. Toldrá five volumes on animal product–related books: *Handbook of Muscle Foods Analysis*, *Handbook of Processed Meats and Poultry Analysis*, *Handbook of Seafood and Seafood Products Analysis*, *Handbook of Dairy Foods Analysis*, and *Handbook of Analysis of Edible Animal By-Products*. Also in 2011, with F. Toldrá, he coedited two volumes for CRC Press: *Safety Analysis of Foods of Animal Origin* and *Sensory Analysis of Foods of Animal Origin*. In 2012, they published the *Handbook of Analysis of Active Compounds in Functional Foods*. In a coedition with Hamir Rathore, *Handbook of Pesticides: Methods of Pesticides Residues Analysis* was marketed in 2009; *Pesticides: Evaluation of Environmental Pollution* in 2012; *Biopesticides Handbook* in 2015; and *Green Pesticides Handbook: Essential Oils for Pest Control* in 2017. Other finished book projects include *Food Allergens: Analysis, Instrumentation, and Methods* (with A. van Hengel; CRC Press, 2011) and *Analysis of Endocrine Compounds in Food* (Wiley-Blackwell, 2011). Dr. Nollet's recent projects include *Proteomics in Foods* with F. Toldrá (Springer, 2013) and *Transformation Products of Emerging Contaminants in the Environment: Analysis, Processes, Occurrence, Effects, and Risks* with D. Lambropoulou (Wiley, 2014). In the series Food Analysis &

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Janet Alejandra Gutiérrez-Uribe, PhD, is an associate professor in the NutriOmics research group at the School of Engineering and Science from Tecnológico de Monterrey. She is the director of the Bioengineering Department in the South Region of Tecnológico de Monterrey. Dr. Gutiérrez-Uribe is a food engineer with graduate studies in biotechnology. For more than 10 years, she has worked on phytochemistry and in the nutritional biochemistry of phenolic compounds and other nutraceuticals. Her research is focused on Mexican foods such as black beans, cacti, agave, and maize. She has published more than 60 papers in different prestigious journals and is the inventor of more than 10 patents and applications in Mexico and abroad. She has graduated more than 25 graduate students and her teaching skills go beyond lectures. Work with industry and social service are her main drivers in the development of challenges related to biochemistry, molecular biology, cell culture, and nutraceutical discovery.

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SECTION I

Phenolic Compounds

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CHAPTER 17

Phenolic Compounds in Herbs and Spices

Laura A. de la Rosa, Nina del Rocío Martínez-Ruíz,
J. Abraham Domínguez-Avila, and Emilio Alvarez-Parrilla

CONTENTS

17.1 INTRODUCTION

Spice (from Latin, *species*) is often used to refer to certain aromatic vegetable products used whole, sliced, or powdered for seasoning food to give them special flavor and scent. The concept of seasoning includes spices, but this term can also refer to products that do not have a direct vegetable origin such as salt, vinegar, beer, and others. The hard parts of certain aromatic plants, such as seeds or bark, are technically considered a spice. Aromatic herbs are sometimes confused with spices; their separation is not very clear, although flavors and scents in aromatic herbs are less concentrated and softer than in spices. Herbs and spices added to food can be fresh, dried, or industrially manufactured. Small quantities provide odors and flavors, generating a tasty and palatable food (Fálder-Rivero 2005).

The use of aromatic herbs and spices (H&S) is practically as old as humanity. Primitive humans collected all kinds of fruits and herbs. There were harmless and poisonous herbs, and with this, their recollection became selective. These people used many plants for medicinal purposes and to accelerate the death of hunted animals. The majority of spices can be considered native from tropical regions of Asia, and the Moluccan Islands in Indonesia, also known as the "Spice Islands." Some spices were grown in the Mediterranean (anise, mustard) and others were taken to Europe by the pathfinder of

America (e.g., vanilla, chili peppers, cocoa, and annatto). In China, Emperor Shen Nung (3000 BC), compiled the knowledge of aromatic and medicinal plants. The Sumerians used many aromatic plants in the preparation of food and medicines. This knowledge was taken to Mesopotamia and Egypt. Aromatic herbs such as laurel and thyme were cultivated in Babylon. Some exotic spices, such as saffron and cinnamon, migrated to Egypt and Greece from the East. Sesame, poppy seeds, coriander, and cumin entered Greece from Minor Asia. The Phoenicians spread spices and aromatic herbs such as onion, garlic, mint, peppermint, thyme, rosemary, oregano, coriander, dill, and others in the Mediterranean. They used some plants to prevent the spoilage of food. In the Middle Ages, many spices and herbs from the East (e.g., cinnamon, clove, pepper, ginger, saffron, and cardamom) were highly sought due to the difficult transport of those spices during the fall of the Roman Empire. The Arabs of North Africa carried spices and herbs from the Far East to Europe. Meanwhile, Marco Polo, through the East, and Columbus, through the West, tried to obtain spices from Asian producers. In the seventeenth century, the Netherlands, Portugal, Italy, and England monopolized the spice commerce, while the growing of different aromatic plants such as mustard began to spread in Central Europe (Civitello 2008; Fálder-Rivero 2005). Finally, in the eighteenth and nineteenth centuries, the active ingredients contained in many herbs and spices began to be synthesized in laboratories (Civitello 2008). Today, spices like oregano and rosemary are used as preservatives and antioxidants in industrially manufactured foods such as sausages and other meat products. Herbs and spices are an important group because they contain active principles like alkaloids, essences, flavonoid glycosides, tannins, minerals, polyphenolic compounds (PCs), and others that may bring benefits to human health (Cameroni 2012).

Culinary use of herbal extracts and essential oils have increased in popularity as natural sources of preservative agents, mainly due to the extensive growth of these plants and their effective and safe consumption. Spices such as garlic, onion, cinnamon, clove, and mustard have been effective in inhibiting the microbial spoilage of food (Stankevičius et al. 2011). Parsley, fresh or dried, inhibits the growth of *Listeria monocytogenes* L. and *Escherichia coli* (Manderfeld et al. 1997). However, the functional activity of PCs contained in herbs and spices is influenced by factors like food culture and sensory preference of individuals (Mercado-Mercado et al. 2013). An average PC consumption of 1 g/day was suggested 25 years ago (Scalbert and Williamson 2000). However, there is limited data that reveals with certainty the amount and type of PC consumed today. The profiles and identification of PCs in herbs and spices are still limited due mainly to the wide variety of structures of the natural compounds, the lack of availability of commercial standards (Vallverdú-Queralt et al. 2014), and the different methods used to identify and quantify these compounds (Stankevičius et al. 2011). The aim of this chapter is to present relevant information about the main PCs, their biological activity, and the proximate analysis and vitamin content found in the herbs and spices of greatest use in the world. In order to systematize this analysis, the USDA National Nutrient Database for Standard Reference was used.

17.2 NUTRITIONAL CHARACTERISTICS

One of the most complete available compositional sets of information on the nutritional properties of H&S is that published by the USDA (2014). Table 17.1 summarizes the compositional and nutritional characteristics of the main H&S consumed in the United States and other Western countries (USDA 2014). As previously stated, H&S are a wide

TABLE 17.1 Macronutrient Contents (g/100 g) in Herbs and Spices

Herbs and Spices	**Water**	**Protein**	**Lipids**	**Carbohydrates**	**Fiber**
Annatto paste[a]	60.60	3.10	2.80	22.60	
Anise seed	9.54	17.60	15.90	50.02	14.60
Basil (fresh)	92.06	3.15	0.64	2.65	1.60
Basil dried	10.35	22.98	4.07	47.75	37.70
Bay leaf	5.44	7.61	8.36	74.97	26.30
Cardamom	8.28	10.76	6.7	68.47	28.00
Celery seed	6.04	18.07	25.27	41.35	11.80
Cinnamon (ground)	10.58	3.99	1.24	80.59	53.10
Clove (ground)	9.87	5.97	13.00	65.53	33.90
Coriander leaf (dried)	7.30	21.93	4.78	52.1	10.40
Coriander seed	8.86	12.37	17.77	54.99	41.90
Cumin seed	8.06	17.81	22.27	44.24	10.50
Dill seed	7.70	15.98	14.54	55.17	21.10
Dill weed (dried)	7.30	19.96	4.36	55.82	13.60
Dill weed (fresh)	85.95	3.46	1.12	7.02	2.10
Epazote (raw)	89.21	0.33	0.52	7.44	3.80
Fennel seed	8.81	15.8	14.87	52.29	39.8
Garlic powder	6.45	16.55	0.73	72.73	9.00
Ginger (ground)	9.94	8.98	4.24	71.62	14.10
Mustard seed (ground)	5.27	26.08	36.24	28.09	12.20
Nutmeg (ground)	6.23	5.84	36.31	49.29	20.80
Onion powder	5.39	10.41	1.04	79.12	15.20
Oregano (dried)	9.93	9.00	4.28	68.92	42.50
Paprika	11.24	14.14	12.89	53.99	34.90
Parsley (dried)	5.89	26.63	5.48	50.64	26.70
Parsley (fresh)	87.71	2.97	0.79	6.33	3.30
Dry pepper (Pasilla)	14.84	12.35	15.85	51.13	26.80
Pepper	12.46	10.39	3.26	63.95	25.30
Pepper (red)	8.05	12.01	17.27	56.63	27.20
Peppermint (fresh)	78.65	3.75	0.94	14.89	8.00
Rosemary (dried)	9.31	4.88	15.22	64.06	42.60
Rosemary (fresh)	67.77	3.31	5.86	20.7	14.10
Saffron	11.90	11.43	5.85	65.37	3.90
Sage (ground)	7.96	10.63	12.75	60.73	40.30
Star anise[b]		0.12			
Tarragon (dried)	7.74	22.77	7.24	50.22	7.40
Thyme (dried)	7.79	9.11	7.43	63.94	37.00
Thyme (fresh)	65.11	5.56	1.68	24.45	14.00
Turmeric (ground)	12.85	9.68	3.25	67.14	22.70
Vanilla extract	52.58	0.06	0.06	12.65	

Source: All data from the U.S. Department of Agriculture, USDA National Nutrient Database for Standard Reference, Release 27, 2014, except where indicated:

[a] Alvarez-Parrilla, E. et al., *Food Science and Technology Campinas*, 34, 371–378, 2014.

[b] Dinesha, R. et al., *Journal of Pharmacology and Phytochemistry*, 2, 98–103, 2014.

range of fresh and dry seeds, leafs, flowers, and other plant parts. According to water content, H&S can be classified as fresh (water content higher than 65%), dry (water content lower than 23%), and seeds (water content lower than 10%). Annatto paste (60.6% water content) is an exception to this behavior, and can be explained considering that annatto paste is a complex mixture that includes annatto seeds mixed with corn starch, ground pepper, salt, and other condiments. Protein content varies from 0.06 g/100 g in vanilla extract to 26.63 g/100 g in dried parsley. In general terms, seeds and dry H&S show higher protein content compared with fresh samples. Lipid content varies from 0.06 g/100 g in vanilla extract to 36.31 g/100 g in nutmeg. Interestingly, vanilla extract showed the lowest protein and lipid content, mainly because this sample is an ethanolic extract. As in the case of proteins, seed showed the higher lipid content, followed by dry H&S and finally fresh samples. Carbohydrate content ranged from 2.65 g/100 g in fresh basil to 80.59 g/100 g in cinnamon, and showed the same pattern in lipids and proteins. Of particular interest is the fact that most herbs and spices contain at least a modest fiber amount and a low sugar content, which makes them an adequate option to include as part of a healthy diet.

17.3 MAIN PHENOLIC COMPOUNDS FOUND IN H&S

H&S are, in general terms, good sources of phenolic compounds and other bioactive phytochemicals. For this reason, many of them have been traditionally used not only as food ingredients but also as natural remedies. Table 17.2 summarizes the information reported by several authors on the content of total phenolic compounds, total flavonoids, and the major phenolic compounds found in some of the most popular herbs and spices around the world. All data are reported in dry weight basis and, when possible, in the same units, in order to make comparison possible.

Phenolic compounds are a diverse group of phytochemicals containing at least one hydroxyl group in an aromatic ring. Classes of phenolic compounds include the phenolic acids (hydroxyphenolic and hydroxycinnamic acids) and their derivatives, flavonoids (flavones, isoflavones, flavonols, flavanones, flavan-3-ols, anthocyanidins, and others) and their derivatives, and other compounds with diverse structures including coumarins, stilbenes, volatile compounds, and others (Naczk and Shahidi 2004; Andrés-Lacueva et al. 2010). This structural complexity makes their identification and quantification a difficult task; moreover, since they are secondary metabolites, their contents in the plant tissues are dependent on many factors including genetics, developmental stage, environment, and growing conditions (Beato et al. 2011; Lv et al. 2012; Bae et al. 2014). Many authors studying phenolic compounds in H&S and other foods have used the Folin–Ciocalteu assay (Singleton and Rossi 1965) to quantify total phenolic compounds. This is a simple, sensitive, and reproducible spectroscopic method based on the generic reducing property of all polyphenols, which makes it quite unspecific (Pérez-Jiménez et al. 2010). This low specificity has the advantage that the method may account for almost all classes of phenolic compounds, but the disadvantage that other nonphenolic reducing compounds (ascorbic acid or sugars, for example) can interfere and cause overestimation of the content of total phenolic compounds (Naczk and Shahidi 2004). Nevertheless, the Folin–Ciocalteu assay is very useful as a first approach to compare the content of phenolic compounds in different plant samples. When assayed with the Folin–Ciocalteu method, total phenolic compounds are expressed as equivalent to a simple phenolic standard (mainly gallic acid) or to the main phenolic compound found in the sample. Table 17.2 shows that the

TABLE 17.2 Content and Profile of Phenolic Compounds Present in Herbs and Spices

Common Name	Scientific Name	Family	Total Phenolic Compounds (% of Dry Material)	Total Flavonoids (mg/g of Dry Material)	Main Polyphenolic Compounds	References
Annatto (achiote)	*Orellana americana* Kuntze	Bixaceae	0.09–0.18 (1)		*Phenolic acids*: caffeoyl derivatives. *Flavonoids*: hypolaetin.	Cardarelli et al. 2008
Anise seed	*Pimpinella anisum* L.	Apiaceae	0.05–5.39 (1)	52.6 (6)	*Phenolic acids*: protocatechuic, caffeic, gallic, ferulic and rosmarinic acids, caffeoyl derivatives. *Flavonoids*: catechin. *Other*: anethole, eugenol, epirosmanol, carvacrol.	Liu et al. 2008; Shan et al. 2005; Christova-Bagdassarian et al. 2014; Rothwell et al. 2013
Basil	*Ocimum basilicum* L.	Lamiaceae	3.64–4.32 (1)		*Phenolic acids*: rosmarinic, vanillic, gentisic, caffeic, ferulic and chlorogenic acids, caffeoyl derivatives. *Flavonoids*: catechin, kaempferol. *Other*: eugenol, epirosmanol, carvacrol, linalool, estragole, lignans.	Shan et al. 2005; Rothwell et al. 2013
Bay leaf	*Laurus nobilis* L.	Lauraceae	4.17 (1)		Phenolic acids and derivatives, flavonoids, and volatile phenols.	Shan et al. 2005; Rothwell et al. 2013
Cardamom	*Elettaria cardamomum* (L.) *Maton*	Zingiberaceae	0.46 (1)		*Phenolic acids*: caffeic, protocatechuic, and *p*-coumaric acids.	Shan et al. 2005; Rothwell et al. 2013
Celery seed	*Apium graveolens* var. *dulce* Pers.	Apiaceae		4.2(?)	*Flavonoids*: luteolin, apigenin, chrysoeriol, and their glycosides.	Lin et al. 2007; Bhagwat et al. 2014; Rothwell et al. 2013

(Continued)

TABLE 17.2 (CONTINUED) Content and Profile of Phenolic Compounds Present in Herbs and Spices

Common Name	Scientific Name	Family	Total Phenolic Compounds (% of Dry Material)	Total Flavonoids (mg/g of Dry Material)	Main Polyphenolic Compounds	References
Chili pepper (dry spice)	*Capsicum annuum* var. *Annuum* L.	Solanaceae	0.86–1.03 (1)	5.5 (4)	*Phenolic acids*: *p*-coumaric and ferulic acids. *Flavonoids*.	Lu et al. 2011; Alvarez-Parrilla et al. 2014; Shan et al. 2005
Cinnamon	*Cinnamomum versum* J. Presl	Lauraceae	6.34–11.90 (1)		*Phenolic acids*: 2-hydroxybenzoic, protocatechuic, syringic, caffeic, and *p*-coumaric acids. *Flavonoids*: catechin. *Other*: cinnamyl aldehydes.	Shan et al. 2005; Rothwell et al. 2013
Clove	*Syzygium aromaticum* (L.) Merr. & L.M. Perry	Myrtaceae	14.38–19.44 (1)	46.3 (6)	*Phenolic acids*: gallic, protocatechuic, syringic, and *p*-coumaric acids. *Flavonoids*: quercetin, kaempferol. *Other*: eugenol, hydrolizable tannins.	Liu et al. 2008; Shan et al. 2005; Pérez-Jiménez et al. 2010; Rothwell et al. 2013
Coriander (leaf)	*Coriandrum sativum* L.	Apiaceae	0.36–2.22 (1)		*Phenolic acids*: vanillic, *p*-coumaric, ferulic acids. *Flavonoids*: kaempferol, quercetin.	Vanisha et al. 2010; Pérez-Jiménez et al. 2010; Wangensteen et al. 2004; Rothwell et al. 2013
Coriander seed	*Coriandrum sativum* L.	Apiaceae	0.02–1.89 (1)	0.11 (?)		Wangensteen et al. 2004; Christova-Bagdassarian et al. 2014

(*Continued*)

TABLE 17.2 (CONTINUED) Content and Profile of Phenolic Compounds Present in Herbs and Spices

Common Name	Scientific Name	Family	Total Phenolic Compounds (% of Dry Material)	Total Flavonoids (mg/g of Dry Material)	Main Polyphenolic Compounds	References
Cumin seed	*Cuminum cyminum* L.	Apiaceae	0.11–2.04 (1)	0.5–5.9 (4)	*Phenolic acids*: gallic, caffeic, chlorogenic, syrigic, vanillic, *p*-coumaric, ferulic, rosmarinic, cinnamic, and other acids. *Flavonoids*: luteolin, eriodictyol, catechin, quercetin, apigenin, kaempferol.	Ani et al. 2006; Mariod et al. 2009; Rebey et al. 2012; Pérez-Jiménez et al. 2010; Rothwell et al. 2013
Dill (leaf)	*Anethum graveolens* L.	Apiaceae	1.40–13.65 (1)	37.2 (4)	*Phenolic acids*: vanillic and protocatechuic acids. *Flavonoids*: isorhamnetin, kaempferol, myricetin, quercetin, catechin.	Shyu et al. 2009; Shan et al. 2005; Stankevičius et al. 2011; Bhagwat et al. 2014; Rothwell et al. 2013
Dill seed	*Anethum graveolens* L.	Apiaceae	13.05 (1)	33.6 (4)		Shyu et al. 2009
Epazote (wormseed)	*Chenopodium ambrosioides* L.	Chenopodiaceae	0.8 (1)	2.9 (4)	*Phenolic acids*: *p*-coumaric acid. *Flavonoids*: quercetin and kaempferol glycosides.	Barros et al. 2013; Mercado-Mercado et al. 2013
Fennel seed	*Foeniculum vulgare Mill.*	Apiaceae	0.63–9.00 (1)	1.1–6.8 (4)	*Phenolic acids*: gallic, caffeic and ferulic acids. *Flavonoids*: quercetin.	Anwar et al. 2009; Przygodzka et al. 2014; Oktay et al. 2003; Rothwell et al. 2013
Garlic powder	*Allium sativum* L.	Amaryllidaceae	0.01–10.80 (1)	0.15–0.60 (6)	*Phenolic acids*: gallic, caffeic, ferulic, vanillic, *p*-coumaric, *m*-coumaric. *Flavonoids*: quercetin, apigenin, catechin, epicatechin.	Kim et al. 2013; Chen et al. 2013; Beato et al. 2011; Alarcón-Flores et al. 2014; Wongsa et al. 2012

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TABLE 17.2 (CONTINUED) Content and Profile of Phenolic Compounds Present in Herbs and Spices

Common Name	Scientific Name	Family	Total Phenolic Compounds (% of Dry Material)	Total Flavonoids (mg/g of Dry Material)	Main Polyphenolic Compounds	References
Ginger	*Zingiber officinale* Roscoe	Zingiberaceae	0.06–1.08 (1); 0.70–1.58 (2)	0.34–3.8 (7); 8.0 (4)	*Phenolic acids*: caffeic acid. *Other*: Gingerols and shogaols (0.13–8.33 g/100g of dry material).	Oboh et al. 2012; Przygodzka et al. 2014; Pawar et al. 2011; Ranilla et al. 2010; Cheng et al. 2011; Schwertner and Rios 2007; Rothwell et al. 2013
Mustard seed	*Brassica juncea* (L.) Czern.	Brassicaceae	0.78–1.37 (3)		*Phenolic acids*: sinapic acid. *Other*: sinapine.	Dubie et al. 2013; Engels et al. 2012
Nutmeg	*Myristica fragrans* Houtt.	Myristicaceae	0.26–1.08 (1)	10.0 (4)	*Phenolic acids*: protocatechuic, syringic, caffeic, and *p*-coumaric acids. *Flavonoids*: catechin. *Other*: volatile phenolics.	Su et al. 2007; Shan et al. 2005; Przygodzka et al. 2014; Rothwell et al. 2013
Onion powder	*Allium cepa* L.	Amaryllidaceae	0.46–7.41 (1)	2.2–17.7 (6)	*Phenolic acids*: gallic and ferulic acids. *Flavonoids*: quercetin and kaempferol (and their glycosides).	Prakash et al. 2007; Cheng et al. 2013; Stankevičius et al. 2011
Oregano	*Origanum vulgare* L.	Lamiaceae	0.22–23.50 (1)	57.1–132.0 (6)	*Phenolic acids*: rosmarinic, caffeic, chlorogenic, ferulic, protocatechuic, *p*-coumaric, *p*-hydroxybenzoic, syringic, gallic, vanillic. *Flavonoids*: luteolin, apigenin, quercetin, kaempferol, myricetin. *Other*: lignans.	Vallverdú-Queralt et al. 2014; Teixeira et al. 2013; Aranha and Jorge 2012; Licina et al. 2013; Martins et al. 2014; Danila et al. 2011; Rababah et al. 2010; Bhagwat et al. 2014; Rothwell et al. 2013

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TABLE 17.2 (CONTINUED) Content and Profile of Phenolic Compounds Present in Herbs and Spices

Common Name	Scientific Name	Family	Total Phenolic Compounds (% of Dry Material)	Total Flavonoids (mg/g of Dry Material)	Main Polyphenolic Compounds	References
Paprika	*Capsicum annuum* L.	Solanaceae	1.36 (1); 0.24 (4)		*Flavonoids*: quercetin, luteolin, kaempferol, apigenin, and myricetin.	Vega-Gálvez et al. 2009; Park et al. 2011; Bae et al. 2014
Parsley	*Petroselinum crispum* (Mill.) Fuss	Apiaceae	0.97–2.92 (1)		*Phenolic acids*: 4-hydroxybenzoic, gallic, gentisic, vanillic, *p*-coumaric, and caffeic acid. *Flavonoids*: apigenin, luteolin, isorhamnetin. *Other*: furanocoumarins.	Pérez-Jiménez et al. 2010; Shan et al. 2005; Bhagwat et al. 2014; Rothwell et al. 2013
Pepper, black, green, or white	*Piper nigrum* L.	Piperaceae	0.30–2.80 (1)	3.0–23.6 (7)	Phenolic amides	Pérez-Jiménez et al. 2010; Shan et al. 2005
Pepper, red or cayenne	*Capsicum annuum* L. var Cayenne	Solanaceae	0.88–1.70 (4)		*Flavonoids*: quercetin, luteolin, kaempferol, apigenin, and myricetin.	Bae et al. 2012, 2014
Peppermint	*Mentha x piperita* L.	Lamiaceae	2.58–19.12 (1)	8.6–43.3 (4)	*Phenolic acids*: rosmarinic, caffeic, syringic, *p*-coumaric, *o*-coumaric, ferulic, chlorogenic. *Flavonoids*: hesperidin, hesperetin, quercetin, luteolin, apigenin, other flavones, catechin, gallocatechin-gallate, epigallocatechin-gallate, eriocitrin, eriodictyol.	Pérez et al. 2014; Capecka et al. 2005; Lv et al. 2012; Riachi et al. 2015; Bhagwat et al. 2014; Rothwell et al. 2013

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TABLE 17.2 (CONTINUED) Content and Profile of Phenolic Compounds Present in Herbs and Spices

Common Name	Scientific Name	Family	Total Phenolic Compounds (% of Dry Material)	Total Flavonoids (mg/g of Dry Material)	Main Polyphenolic Compounds	References
Rosemary	*Rosmarinus officinalis* L.	Lamiaceae	2.52–9.4 (1)	15.0 (7)	*Phenolic acids*: syringnic, vanillic, chlorogenic, caffeic, ferulic, *p*-coumaric, and rosmarinic acids. *Flavonoids*: naringenin, luteolin and catechin. *Other*: carnosic acid, carnosol, carvacrol.	Pérez-Jiménez et al. 2010; Shan et al. 2005; Bhagwat et al. 2014; Rothwell et al. 2013
Saffron	*Crocus sativus* L.	Iridaceae	0.65–0.83 (1)	3.5–3.6 (6)	*Flavonoids*: naringenin, kaempferol, and taxifolin	Baba et al. 2015; Rothwell et al. 2013
Sage	*Salvia officinalis* L.	Labitae or Lamiaceae	2.92–5.32 (1)		*Phenolic acids*: gallic, syringic, vanillic, 5-caffeoylquinic, caffeic, ferulic, *p*-coumaric, and rosmarinic acids. *Flavonoids*: apigenin, luteolin. *Other*: carnosic acid, phenolic volatiles.	Pérez-Jiménez et al. 2010; Shan et al. 2005; Bhagwat et al. 2014; Rothwell et al. 2013
Star anise	*Illicium verum* Hook.f.	Illiciaceae	1.49–17.00 (1); 23.77 (4)	14.00–115.84 (4)	*Phenolic acids*: protocatechuic, caffeic and *p*-coumaric acids. *Flavonoids*: rutin, kaempferol, quercetin. *Other*: anethole.	Lu et al. 2011; Kannatt et al. 2014; Hoque et al. 2011; Chung 2009; Padmashree et al. 2007; Przygodzka et al. 2014; Ohira et al. 2009; Rothwell et al. 2013

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TABLE 17.2 (CONTINUED) Content and Profile of Phenolic Compounds Present in Herbs and Spices

Common Name	Scientific Name	Family	Total Phenolic Compounds (% of Dry Material)	Total Flavonoids (mg/g of Dry Material)	Main Polyphenolic Compounds	References
Tarragon	*Artemisia dracunculus* L.	Asteraceae	0.57–10.2 (1)	22.0 (7)	*Flavonoids*: luteolin, isorhamnetin, kaempferol, quercetin. *Other*: coumarins, estragole.	Pérez-Jiménez et al. 2010; Eisenman et al. 2011; Bhagwat et al. 2014
Thyme	*Thymus vulgaris* L.	Lamiaceae	1.82–15.7 (1)	34.0 (7)	*Phenolic acids:* gallic, syringic, vanillic, caffeic, ferulic, *p*-coumaric, and rosmarinic acids. *Flavonoids*: apigenin, luteolin. *Other*: thymol, phenolic diterpenes.	Pérez-Jiménez et al. 2010; Shan et al. 2005; Bhagwat et al. 2014; Rothwell et al. 2013
Turmeric	*Curcuma longa* L.	Zingiberaceae	2.00–9.18 (5)		*Phenolic acids*: caffeic, *p*-coumaric, and protocatechuic acids. *Other*: curcuminoids (curcumin, demethoxycurcumin and bisdemethoxycurcumin).	Jayaprakasha et al. 2002; Suhaj 2006
Vanilla extract	*Vanilla planifolia* Andrews	Orchidaceae	0.50 (1)	16.5 (4)	*Phenolic acids*: vanillic acid. Other: vanillin, 4-hydroxybenzyl alcohol, 4-hydroxybenzaldehyde.	Maruenda et al. 2013; Salazar-Rojas et al. 2012; Przygodzka et al. 2014; Sinha et al. 2007; Pérez-Silva et al. 2011

Note: (1) GAE (gallic acid equivalents); (2) TAE (tannic acid equivalents); (3) SAE (sinapic acid equivalents); (4) CE (catechin equivalents); (5) Total curcuminoids; (6) RE (rutin equivalents); (7) QE (quercetin equivalents).

content of total phenolic compounds varies widely among commonly consumed H&S. Clove (*Syzygium aromaticum* L.), oregano (*Origanum vulgare* L.), peppermint (*Mentha x piperita* L.), and star anise (*Illicium verum* Hook f.) are among the spices with the highest contents of total phenolic compounds (close to 20% gallic acid equivalents [GAE] in dry weight); however, many other spices are also good sources of these compounds, containing around 5–15% in dry weight (anise, cinnamon, dill, fennel, garlic powder, onion powder, rosemary, sage, tarragon, thyme, and turmeric). Actually, clove, peppermint, and star anise are the three foods richest in polyphenolic compounds according to the Phenol-Explorer database (Rothwell et al. 2013), and many other spices are among the 100 richest dietary sources of polyphenols (Pérez-Jiménez et al. 2010). Important variation can be observed also in the values of total phenolic compounds found for the same herb or spice by different authors or even in a single study. For example, fennel seeds have been reported to contain between 0.63 and 9.00 g GAE/g of dry weight, depending on the sample (whole seeds or commercial spices) and solvent used for extraction (water, methanol, ethanol, or water/alcohol combinations). The same is true for almost all H&S listed in Table 17.2. The most common sources of natural variation are plant variety or type of sample, and the most common experimental factor of variation is the type of solvent used for extraction. In general, all studies show that the best solvents for the extraction of phenolic compounds from H&S samples are water or alcohol/water (50/50 or 80/20) combinations.

Among the different classes of phenolic compounds, flavonoids are remarkable for their bioactivity and are widely distributed among the plant kingdom. They comprise several structural classes and in nature are found mostly glycosylated in different positions and with different types and numbers of sugar moieties. Identification and quantification of individual flavonoids is usually carried out by HPLC, and many times only the aglycone component of the molecule can be identified, since commercial standards for the glycosides are difficult to obtain. However, a simple spectroscopic method has been developed, and is sometimes used to quantify total flavonoids by their reaction with sodium nitrate followed by the formation of a flavonoid–aluminum complex, which is detected at 510 nm (Zhishen et al. 1999). Total flavonoids determined by the aluminum complexation method in spices are reported as equivalents of catechin (a flavan-3-ol), quercetin (a flavonol), and rutin (a quercetin glycoside), which are among the most widely distributed flavonoid compounds. Their contents range from under 1 milligram/gram of dry sample (in coriander and cumin seed, and garlic powder) to over 100 milligrams/gram in oregano and star anise, which are also high in total phenolic compounds.

Individual phenolic compounds (flavonoids and other classes) have been identified in herbs and spices by means of HPLC and, more recently, HPLC/MS. As mentioned before, HPLC analysis is hampered by a lack of standards due to the great diversity of individual phenolic compounds in the plant kingdom. Some phenolic compounds are fairly common in almost all herbs and spices, and actually in almost all plant foods, like the flavonoid quercetin and the hydroxycinammic acid caffeic acid; however, they are almost always present in the form of derivatives. Caffeic acid is usually sterified with quinic acid forming chlorogenic acid or other caffeoyl-quinic derivatives; quercetin is always glycosylated (Andrés-Lacueva et al. 2010). In H&S, the flavones luteolin and apigenin are some of the most common flavonoids (see Table 17.2) and the presence of volatile phenols, such as eugenol, anethole, and carvacrol, is also frequent. In addition to to these ubiquitous phenolic compounds, some families of H&S contain some unique phenolic components, many of them with strong biological activity.

Rosmarinic acid is a hydroxycinnamic acid abundant in spices from the Lamiaceae family (basil, oregano, peppermint, rosemary, sage, thyme) and some of the Apiaceae family (anise and cumin). Other characteristic compounds of some species of the family Lamiaceae are the phenolic terpenoids carnosol, carnosic acid (rosemary and sage), and thymol (thyme). Peppermint also contains the uncommon flavonoid eriodictyol.

Sinapic acid and its derivative sinapine are the major phenolic compounds in mustard, from the Brassicaceae family, but cannot be found in other spices although they are also present in other foods, but are not common (Rothwell et al. 2013). Vanilla extract (*Vanilla planifolia* Andrews, family Orchidaceae) is recognized for its unique component vanillin, derived from vanillic acid (which is, in contrast, a quite common hydroxybenzoic acid) and phenolic alcohols and aldehydes.

Finally, spices from the Zingiberaceae family possess some of the most remarkable phenolic compounds. Ginger (*Zingiber officinale* Roscoe) contains gingerols and shogaols, while turmeric, the dried rhizome of *Curcuma longa L.*, contains high amounts (up to 9.18%) of curcuminoids, unique polyphenolic compounds, with strong biological activity.

17.4 HEALTH EFFECTS OF H&S

Recently, H&S have been considered an important source of bioactive compounds like polyphenols with benefits to human health (i.e., stimulants digestive, anti-inflammatory, antimicrobial, and anticarcinogenic activity, among others). As formerly reported, H&S present a high content of PCs such as flavonoids and hydroxycinnamic acids, which have shown biological effects in the chelation for heavy metals, scavenging radicals, inhibition of cell proliferation, enzyme modulation, and signal transduction (Vallverdú-Queralt et al. 2014). The radicals scavenging activity of PCs (antioxidant capacity) has been associated with vasodilator, vascular protective, antithrombotic, antilipemic, antiatherosclerotic, and antiapoptotic effects (Mercado-Mercado et al. 2013). An indirect protective effect of PCs has been proposed, in which PCs reduce food lipid oxidation (conjugated dienes, hydroperoxides, hexanal) during cooking and storage, preventing the formation of free radicals and cytotoxic and genotoxic compounds in the gastrointestinal tract (Mercado-Mercado et al. 2013). In this context, annatto and dry hot peppers showed protection against chopped cooked pork meat stored at 4 °C for 16 days, indicating that the use of spices or spice extracts may protect meat against lipid oxidation (Alvarez-Parrilla et al. 2014). Even though several H&S have been used in traditional medicine, the number of clinical studies to prove their activity is scarce. Among H&S, garlic and turmeric may be two of the most studied spices. In the following section the effect of H&S on several diseases will be described.

17.4.1 Cardiovascular Diseases (CD)

The beneficial effects of H&S on CD have been related to the decrease on plasma triglycerides, cholesterol, and LDL-cholesterol, as well as platelet aggregation and LDL-oxidation inhibition (Viuda-Martos et al. 2011). Lee et al. (2006) reported that carnasol, a phenolic diterpene present in H&S from the Laminaceae family (basil, oregano, peppermint, rosemary, sage, thyme) inhibited platelet aggregation by inhibition of the thromboxane A2 receptor. Other studies have associated the presence of flavonoids (quercetin, luteolin, and kaempherol) and chlorogenic acid–impeded platelet aggregation (Viuda-Martos et al. 2011). Srinivasan (2005) reported that the consumption of large amounts of garlic and onion reduced total cholesterol in humans. Meta-analysis and clinical trials showed that supplementation with curcumin, the main component of turmeric, significantly reduced the risk factor of cardiovascular disease and has been effective against atherosclerosis, myocardial infarction, platelet aggregation, and LDL-oxidation (Prasad et al. 2014).

17.4.2 Cancer

Even though clinical studies have not conclusively correlated the consumption of H&S with protection against cancer, several in vitro and animal studies have demonstrated the protective effect of H&S extracts against several cancers (Wargovich et al. 2001; Viuda-Martos et al. 2011). This protective effect of H&S phenolic compounds against cancer has been related to different mechanisms which include: (1) scavenging of ROS species, (2) scavenging of carcinogenic species, (3) inhibition of phase I enzymes, (4) induction of phase II enzymes, and (5) induction of apoptosis, among others (Viuda-Martos et al. 2011; Mercado-Mercado et al. 2013). Several authors have suggested that capsaicin, the main phytochemical of peppers, promotes apoptosis of carcinogenic cells, probably through a stress-related mechanism (Sánchez et al. 2008). Carnosol, a phenolic diterpene found in rosemary, showed anticarcinogenic activity in leukemia cells due to cell apoptosis caused by mitochondrial membrane depolarization (Dörrie et al. 2001). Probably one of the most studied H&S phenolic compounds as anticarcinogenic is curcumin. It has been demonstrated its action against leukemia, lymphoma, melanoma, sarcoma, as well as gastrointestinal, breast, ovarian, lung, and neurological cancers, among others, by modulating multiple cell signaling pathways (Prasad et al. 2014).

17.4.3 Inflammation

Probably one of the most-studied effects of H&S PCs is their anti-inflammatory activity. There are several in vitro, in vivo, and clinical trials that demonstrate the anti-inflammatory effect of extracts or pure PCs (curcumin, eugenol, capsaicin) (Srinivasan 2005). Currently, there are several topical creams and tablets used to treat inflammatory processes associated with rheumatism, backache, skin rashes, and as odontological analgesics, in which extracts or pure PC such as capsaicin are used. The administration of a single dose of curcumin, eugenol, or capsaicin reduced by about 50 percent the carrageenan-induced inflammation in rats. Several H&S extracts (bay leaf, anise, lemon myrtle, pepper) and pure PCs (curcumin, galangin, quercetin) have shown anti-inflammatory activity in cell and rat models through the inhibition of COX-2, COX-1, and iNOS enzymes (Viuda-Martos et al. 2011; Guo et al. 2014; Prasad et al. 2014). Srinvansan et al. (2005) proposed that the anti-inflammatory activity of H&S is due to the phenolic compounds that reduce the synthesis of prostaglandin E_2 and other proinflammatory compounds.

17.4.4 Obesity

In the last few years there has been an increasing interest in studying the effect of H&S in obesity and metabolic syndrome control, because these two diseases are becoming prime health issues in both developed and developing countries. According to the World Health Organization, every year 2.8 million people died from overweight- and obesity-related diseases (WHO 2013). Several mechanisms of action have been proposed to explain the antiobesity effect of H&S. They are known to activate the gastric system, increasing salivation and release of gastric and bile juices, which favor the digestion process and exert a thermogenic effect (Viuda-Martos et al. 2011). Another mechanism of action of polyphenolic compounds present in H&S in weight control, is that these compounds are able to inhibit pancreatic lipase through a noncompetitive pattern, decreasing lipid absorption (Wu et al. 2013). In vitro and in vivo studies have shown that flavonoids, stilbenes, phenolic acids, capsaicin, and procyanidins control obesity through downregulating adipogenesis as well as some obesity-related inflammatory markers (Mukherjee et al. 2015). Capsaicin inhibited adipogenesis and promoted adipocyte apoptosis through the activation of AMKP in pre-adipocyte 3T3-L1 cells (Alcalá Hernández et al. 2015). The antiobesity and anti-inflammatory activity of this compound has been also attributed to the reduction of adipose TNFα, MCP-1, and IL-6, and the increase of adiponectine levels when measured in obese mice fed with a capsaicin rich diet (Kang et al. 2007).

17.5 CONCLUSION

H&S are, in general terms, good sources of phenolic compounds and other bioactive phytochemicals. The major PCs present in H&S are flavones such as luteolin and apigenin, and volatile phenolics such as eugenol, carbacrol, and anetole. They also contain common phenolic acids and unique compounds such as rosmarinic acid, gingeriols, and curcuminoids. Their large diversity makes it necessary to carry out systematic characterization of compounds in some spices that have not been well-studied. In vitro and in vivo studies, and some clinical trials, suggest that the polyphenolics compounds present in H&S may be associated with beneficial effects against several diseases, including cardiovascular diseases, cancer, inflammation, and obesity.

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