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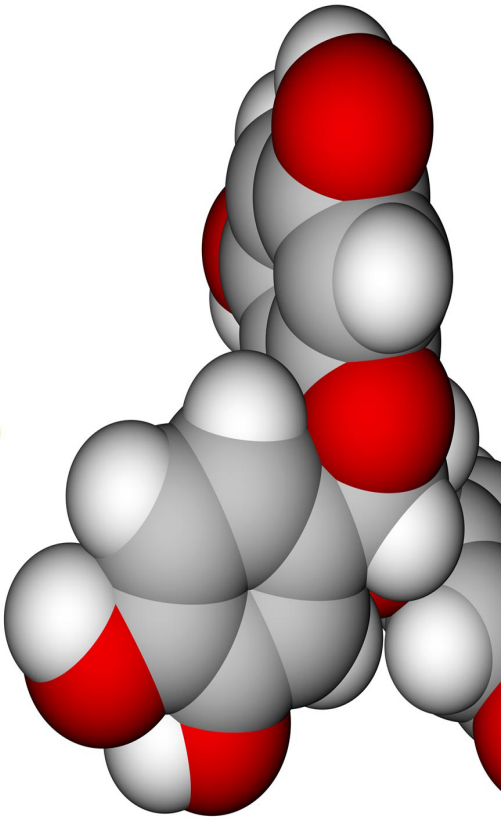
NATURAL BIOACTIVE COMPOUNDS FROM FRUITS AND VEGETABLES AS HEALTH PROMOTERS

PART 2



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Luís Rodrigues da Silva
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Natural Bioactive Compounds from Fruits and Vegetables as Health Promoters
Part II

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FOREWORD

For centuries, humans have considered food only as an "energy" source for survival. Clarification of nutritional relevant components, as protein, fat, carbohydrates, minerals and vitamins, was determinant to understand metabolic needs, and to adjust consumption patterns. However, this oversimplified definition of food resulted in processed foods composed by mixtures of ingredients rich in these components, while diet is increasingly claimed as being responsible for the most common diseases of modern society: cardiovascular diseases, obesity, and cancer.

When we look upon food from this simplified perspective, it is as if we are regarding food without its "soul". Indeed, although being difficult to demonstrate causality between food and health, there is now appreciable epidemiologic evidence for the protective role of diets rich in fruits and vegetables, being the Mediterranean diet an interesting example. These foods have thousands of components without nutritional essentiality that have been neglected. The interest on these components has increased tremendously in the last two decades, seeking to identify the dietary bioactive components (*i.e.*, those that have a measurable impact on human health), their amounts, and availability. Simultaneously, it is also becoming clear that each one of these components has different effects and potencies when ingested alone or when taking its part in the complex network of molecules present in whole foods. These are amazing days for food scientists because we are closer to understand these bioactive compounds, while the consumer is following closely scientific advances, being increasingly interested in the health properties of foods.

The editors took an enormous and successful effort to assemble a huge variety of knowledge on different natural bioactive components in foods, bringing together experts working of different fields of food composition and health. Following a first volume on fruits, this second volume was written to provide readers with a comprehensive review of bioactive constituents in several legumes, nuts, seeds and cereals, from the most traditional ones, as rice or tomatoes, to emerging potentials in modern nutrition, as quinoa or coffee residues. This assembled knowledge allows the reader to get acquainted with the most promising bioactive compounds in different foods, understand the care needed to preserve their bioactivity during storage or processing, while revealing also the hidden bioactive potential of commonly rejected parts, as shells or seeds.

Therefore, this book is designed for food scientists, nutritionists, pharmaceuticals, physicians, food industrials, as well as for health-conscious consumers.

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PREFACE

Plants have been widely used as food and medicines, since they provide, not only essential nutrients required for human life, but also other bioactive compounds which play important roles in health promotion and disease prevention, commonly known as phytochemicals. Moreover, in the recent years, the impact of lifestyle and dietary choices for human health has increased the interest in fruits and vegetables, as well as in foods enriched with bioactive compounds and nutraceuticals. In fact, epidemiological studies have consistently shown that the Mediterranean diet, characterized by the daily consumption of fruits and vegetables, is strongly associated with reduced risk of developing a wide range of chronic diseases, such as cancer, diabetes, neurodegenerative and cardiovascular diseases.

Phytochemicals are secondary metabolites present in fruits and vegetables in low concentrations that have been hypothesized to reduce the risk of several pathological conditions. There are thousands of dietary phytochemicals, namely flavonoids, phenolic acids, glucosinolates, terpenes, alkaloids, between many other classes of compounds, which present different bioactivities, such as antioxidant, antimutagenic, anticarcinogenic, antimicrobial, anti-inflammatory, hypocholesterolemic, hypoglicemic and other clinically relevant activities. The evidence suggests that the health benefits of fruits and vegetables consumption are attributed to the additive and synergistic interactions between these phytocomponents. Therefore, nutrients and bioactive compounds present in fruits and vegetables should be preferred instead of unnatural and expensive dietary supplements.

In this ebook, we provide an overview about the different classes of phytochemicals commonly found in fruits and vegetables, highlighting their chemical structures, occurrence in fruits and vegetables, biological importance and mechanisms of action. Part (II) is dedicated to the study of several legumes, nuts, seeds and cereals.

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CHAPTER 1

Bioactive Compounds of Legumes as Health Promoters

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Abstract: Legumes are a wide group of plants worldwide cultivated by the high nutritional quality of their seeds containing fibre, proteins, resistant starch, minerals and vitamins. The milk obtained from seeds of some legumes, mainly soybean, is used to obtain fermented products currently widely consumed as probiotics. Moreover, legumes are considered as nutraceuticals since they contain bioactive peptides (BAPs) and many phytochemicals endowed with useful biological activities. Legume BAPs have antioxidant, antihypertensive, hypocholesterolemic and antithrombotic activities. Flavonoids and particularly isoflavones have beneficial effects in different cancer types, have been related with lower cardiovascular risk and are protective against fatty liver disease, obesity, diabetes and other metabolic disorders.

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Hydrophilic phytochemicals, such as ascorbic acid (vitamin C), phenolic acids and polyphenols, have been associated with a reduction of cancer risk and an enhancement of the immune system functionality. Lipophilic phytonutrients, such as carotenoids and tocopherols, may prevent the risk of cardiovascular diseases. In this chapter we revise the recent works focusing on legume bioactive compounds and human health prevention.

Keywords: Bioactive peptides, Carotenoids, Fatty acids, Isoflavones, Legumes, Phenolics, Tocopherols.

INTRODUCTION

The term 'legumes' refers to a wide group of angiospermal plants worldwide distributed that are able to grow in diverse aquatic and terrestrial environments, under different edapho-climatic conditions. Legumes seeds (or pulses) constitute the main source of vegetal protein consumed in the world [1] as green or processed beans and as "milk", such as soy milk [2]. The most consumed legume worldwide is *Glycine max* (soy, soybean) which contains the highest quality protein found to date in plants [3] followed by *Arachis hypogaea* (peanut) and *Phaseolus vulgaris* (common bean), whose seeds are highly appreciated for their quality proteins [4 - 6].

In addition to the high nutritive quality of their proteins the comsumption of peas, beans and chickpea [7 - 10] has been related with health benefits. Some pulses such as *Lens culinaris* (lentil), *Vicia faba* (faba bean), *Pisum sativum* (pea) and *Cicer arietinum* (chickpea) are included in the Mediterranean diet, whose benefits for human health are well documented [8, 11 - 14]. Several reports showed that pulses are functional foods that combat obesity [15], reduce metabolic syndrome risk factors in overweight and obese adults [16] and prevent hypercholesterolemia, hypertension, diabetes and cardiovascular and renal diseases [17 - 19].

Also, fermented derivatives of legumes, mainly those from soybean milk, are traditionally used worldwide as probiotics after fermentation with lactic bacteria, bifidobacteria and/or yeasts [20, 21]. Nevertheless in the last decade other pulses are explored as novel probiotics, such as peanut [22], lupin [23], pigeon pea [24], bambara groundnut [25], mung bean [26]. Even the fermentation of mixed legume

milks such as those of peanut and soybean are being investigated [27]. Legumes also contain polysaccharides considered as prebiotic, such as the raffinose family of oligosaccharides present in lupin and soybean seeds [23, 28]. In lentil the polysaccharides with prebiotic potential include those from raffinose-family oligosaccharides, sugar alcohols, fructooligosaccharides, and resistant starch, which varies with the variety and the location [29] and it has been reported that pectic oligosaccharides derived from chickpea (*Cicer arietinum*) have prebiotic and antioxidant activities [30].

Legumes are part of the named nutraceutical products due to their benefits for human health mainly based on their bioactive compounds, including BAPs, phenolic compounds, carotenoids, tocopherols and fatty acids, among other phytochemicals [11, 31 - 37]. Most of legumes have been rarely studied to date, but the interest in the research about their benefits for human health is increasing and in the last years many reports about the nutritional characteristics, chemical composition and antioxidant potential of several underutilized legumes have been published [38 - 46].

Bioactive Peptides (BAPs)

The food proteins release peptides of variable size in the intestinal lumen, some of them resistant to further digestion, which in some cases share structural motifs along with endogenous peptides, for example endorphins or exorphins, known to modulate physiological functions [47 - 49]. BAPs from animal origin (milk, eggs, *etc.*) have been widely studied, but also from different legumes (soybean, pea, lentil, beans and chickpea) are used to obtain BAPs [50], being lunasin, from soybean, exploited as commercial source of BAPs [36].

BAPs are peptides encrypted in intact molecules, which are released by different enzymes during gastrointestinal transit or by fermentation or ripening of foods [47, 51]. It has been reported that they have positive effects for the human health such as immunomodulating, antihypertensive, osteoprotective, antilipemic, opiate-like, anti-thrombotic, antioxidative, anticariogenic and antimicrobial [47, 48, 51]. Although these effects have been mainly studied in milk proteins, pulses are also a rich protein source in human diet being their consumption associated

CHAPTER 2

Bioactive Compounds from *Brassicaceae* as Health Promoters

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Abstract: This work provides an up to date review of the information available about bioactive compounds present in the *Brassicaceae*family (glucosinolates, phenolics and vitamins) in relation to human health. The *Brassicaceae*plant family includes a large variety of species and cultivars, some of the most known are *Brassica oleracea* (*e.g.* broccoli, cabbage, Brussels sprouts), *Brassica rapa* (*e.g.* turnips), *Brassica napus* (*e.g.* rapeseed), Raphanus sativus (radishes), and Sinapis alba (mustards). In the recent years, these crops are increasingly consumed for possible health benefits as a good source of bioactive compounds. The sulphur containing compounds glucosinolates are almost exclusively found in this family, being their beneficial health effect supposed to be induced by their hydrolysis products, the isothiocyanates. In *in vitro* (human cell lines) and *in vivo* studies (animal models and human intervention assays) isothiocyanates have demonstrated their protective effects in carcinogenesis, chronic inflammation and neurodegeneration. The phenolic compounds mainly studied are flavonols, anthocyanins and hydroxycinnamic acids, which principal bioactivity is their antioxidant capacity. The carotenoids β-carotene, lutein and zeaxanthin, as well as, vitamins C, E and K have also been considered as nutrients with biological activity. The phytochemical wealth of *Brassica* foods is gathering attention from the scientific community for being potentially protective for the cardiovascular system and against certain types of cancer, and neurological disorders, mainly because of their anti-inflammatory and antioxidant properties.

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Even it is not yet possible to recommend a particular "daily dose" for human consumption of cruciferous foods for disease prevention, there is growing evidence regarding the protective effects of *Brassica* bioactive compounds for health via regulation of signaling pathways and cellular metabolism

Keywords: Antiinflammatory, Antioxidant, *Brassicaceae*, Cardiovascular disease, Carotenoids, Chemoprevention, Cruciferous, Glucosinolates, Isothiocyanates, Minerals, Neurodegeneration, Phenolic compounds, Vitamins.

INTRODUCTION

Brassicaceae family, commonly termed the mustard family or Cruciferae, represents a monophyletic group including approximately 350 genera and 3,700 species, which has been the subject of much scientific interest, with many crops of socioeconomical relevance (food and spices, condiments, oils), forage or ornamental. This family includes common species of food staples such as: broccoli, cauliflower, Brussels sprouts, cabbages, belonging to *Brassica* oleracea; turnips and Chinese cabbages of *Brassica* rapa; oilseeds of *Brassica* napus (rapeseed, leaf rape); mustards (*Sinapis alba*); and radishes (*Raphanus sativus*), among others. *Brassicaceae* crops are dated in Europe and northern Asia for at least 600 years and in the earlier part of the 20th century they have grown in North America, with productions in Europe around the 70 million tons/annum [1].

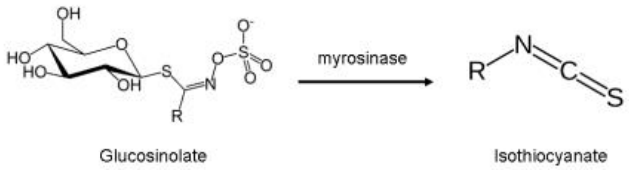
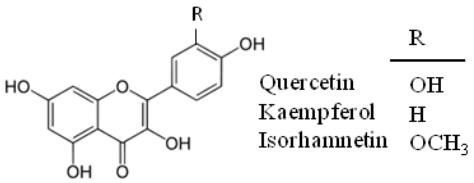
Brassicaceae crops are widely distributed in the World: Southwestern and Central Asia, Mediterranean Europe, and North and South America. *Brassica* production and consumption has increased worldwide in the last years, but only from a few cultivated genera [2]. There are numerous further species with great potential for exploitation in 21st century agricultural and food commodities, particularly as sources of bioactive phytonutrients.

PHYTONUTRIENTS IN CRUCIFEROUS PLANTS AND FOODS

The *Brassicaceae* vegetables have been widely studied for their beneficial effects on human health through epidemiological studies [3], being nutritive foods rich in essential nutrients and phytochemicals that may act synergistically in the food matrix to modulate the cell metabolism and help in the prevention and treatment

of certain types of cancer, cardiovascular health problems, and neurodegenerative conditions of the aging human being (Table **1**) [4]. Although vegetable cruciferous plants are sources of fiber, folate, vitamins (A, E, C, and K) and minerals (Ca, Fe, K, Cu, Zn, P, Mn, and Mg, among others), the major body of evidence in the scientific literature is concentrated in the contents of secondary metabolites, such as flavonoids and carotenoids, and specially glucosinolates (GLSs). These compounds are mainly present in this family and are hydrolyzed to isothiocyanates (ITCs), which may be responsible of the chemoprotective activity and the reduction in the risk of suffering a number of cancers associated with the intake of cruciferous foods. Also the health-promoting effects of crucifers have been attributed at least in part to their bioactive composition rich in natural antioxidants, such as vitamins (C, A, E, K, *etc.*), carotenoids and phenolic compounds [5].

Table 1. Nutrients and phytochemicals presents in cruciferous plants and their physiological functions.

Compounds and chemical structures	Physiological functions	References
GLSs and ITCs  Glucosinolate Isothiocyanate	Induction of detoxification enzymes Apoptosis and arrest of tumor cell growth Decrease adipogenesis and inflammation Reduce oxidative stresses	[4, 6 - 8]
Flavonols 	Prevent the oxidation of LDL Capillary protective effect Reduce serum levels of glucose Tumor inhibitory effect Anti-inflammatory, antimicrobial and anti-allergic	[5, 9, 10]

R	
Quercetin	OH
Kaempferol	H
Isorhamnetin	OCH_3

CHAPTER 3

Bioactive Compounds of Tomatoes as Health Promoters

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Abstract: Tomato (*Lycopersicon esculentum* Mill.) is one of the most consumed vegetables in the world and probably the most preferred garden crop. It is a key component of the Mediterranean diet, commonly associated with a reduced risk of chronic degenerative diseases. Currently there are a large number of tomato cultivars with different morphological and sensorial characteristics and tomato-based products, being major sources of nourishment for the world's population. Its consumption brings health benefits, linked with its high levels of bioactive ingredients. The main compounds are carotenoids such as β-carotene, a precursor of vitamin A, and mostly lycopene, which is responsible for the red colour, vitamins in particular ascorbic acid and tocopherols, phenolic compounds including hydroxycinnamic acid derivatives and flavonoids, and lectins. The content of these compounds is variety dependent. Besides, unlike unripe tomatoes, which contain a high content of tomatine (glycoalkaloid) but no lycopene, ripe red tomatoes contain high amounts of lycopene and a lower quantity of glycoalkaloids. Current studies demonstrate the several benefits of these bioactive compounds, either isolated or in combined extracts, namely anticarcinogenic, cardioprotective and hepatoprotective effects among other health benefits, mainly due to its antioxidant and anti-inflammatory properties. The chemistry, bioavailability and bioactivity of these bioactive compounds will be discussed, as well as the main mechanisms of action against cancer and other bioactivities including antioxidant, anti-inflammatory, cardiovascular and hepatoprotective effects in humans. Possible applications of tomato bioactive compounds in the industry will also be proposed.

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Keywords: Anticarcinogenic, Anti-inflammatory, Antioxidant, Ascorbic Acid, Bioactivity, Bioavailability, Cardioprotection, Clinical trials, Flavonoids, Functional food, Glycoalkaloids, Human health, Hydroxycinnamic acids, Lycopene, *Lycopersicon esculentum*, Nutraceuticals, Phenolic compounds, Tocopherols, Tomatine, Tomato.

INTRODUCTION

The tomato plant (*Lycopersicon esculentum* Mill.) was imported from the Andean region to Europe in the 16th century. It belongs to the Solanaceae family that includes many other plants of economic importance, including potatoes, eggplants, peppers and tobacco [1]. Today, this species is widespread throughout the world, representing the most economically important vegetable crop worldwide. In fact, tomato is the most consumed vegetable after potatoes and probably the most preferred garden crop. In 2013, about 164 million tonnes of tomatoes were produced in the world, having been registered an increase above 2.6 million tonnes over 2012. The three main producing countries are China, India and United States of America, but it is in the Mediterranean and Arabian countries that their consumption is higher [2].

Tomato is a very versatile fruit, being consumed fresh but also processed as paste, soup, juice, sauce, powder, or concentrate. In addition, there are several tomato cultivars and varieties with a wide range of morphological and sensorial characteristics which affect the way how they are prepared and consumed [1, 3, 4]. Tomatoes and tomato-based food products are an important source of nourishment for the world's population. Regarding its nutritional value, if one takes into consideration only the proteins, fat, carbohydrates, or sugars content, it appears clearly that it does not have a high nutritional value. However, it represents an important source of other nutrients and non-nutrients endowed with important health promoting properties, namely carotenoids such as β-carotene (provitamin A) and mostly lycopene, which provides the deep red colour, vitamins such as ascorbic acid (vitamin C) and tocopherols (vitamin E), phenolic compounds including hydroxycinnamic acid derivatives and flavonoids, lectins, and minerals (K, Mn, Ca, Cu and Zn) [3 - 5].

Tomatoes are the most important component of the Mediterranean diet, known to be beneficial for human health [6]. A relationship between the consumption of tomatoes and tomato-based foods and the prevention of chronic degenerative disease induced by oxidative stress and inflammation has been indicated in several studies [7 - 10]. However, the bioaccessibility and bioavailability of tomato compounds is affected by the way how tomatoes are consumed (*i.e.*, raw or processed), which affects its subsequent bioactivity. Clinical trials performed in the last years elucidate the positive effects and mechanisms involved in the activity of tomato compounds against cardiovascular disease and various types of cancer [9 - 12]. Indeed, tomato extracts, as well as lycopene, α-tomatine and some phenolic compounds have been highlighted as having increased potential for the development of new drugs, nutraceuticals and functional foods.

This chapter highlights the tomato fruit as a functional food and as a source of nutraceutical ingredients of industrial value. In this sense, the major health promoting compounds of tomatoes are described chemically and their bio-availability, bioactivity and impact on human health are discussed. Recent *in vitro* and *in vivo* clinical trials are presented, with particular attention paid to the mechanisms behind the protective effects of tomato bioactive compounds against the most common degenerative diseases associated to oxidative stress and inflammation, including cardiovascular and hepatocellular diseases, diabetes and various types of cancer, among other health problems.

TOMATO BIOACTIVE COMPOUNDS

Nowadays, consumers are increasingly made aware and better informed about the health benefits provided by food beyond its basic nutritional role. Actually, they are looking for foods with health promoting properties called “functional foods”. The tomato fruit is a good example, whose functionality or health claim properties are conferred by biologically active ingredients responsible for decreasing the risk of susceptibility to certain diseases. The major compounds of this fruit (Fig. **1**) are carotenoids (β-carotene and mainly lycopene), vitamins (ascorbic acid and tocopherols), and phenolic compounds including hydrocinnamic acids (mainly caffeic acid and its ester chlorogenic acid) and flavonoids such as narigenin and rutin [4, 5, 13]. Other bioactive compounds, such as glycoalkaloids and lectins

CHAPTER 4

Bioactive Compounds from *Capsicum annuum* as Health Promoters

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Abstract: *Capsicum annuum* (Pepper) is an agricultural crop of the Solanaceae family which is important as a vegetable food (bell pepper), as a spice (chili pepper), and as a colorant (paprika). It is native to Mexico and Central America but it is consumed worldwide and used in a great variety of dishes depending on its texture, flavor and color. *C. annuum* is a good source of bioactive compounds, such as polyphenols (flavonoids and phenolic acids), capsaicinoids, capsinoids, carotenoids and vitamins, with well-known anti-oxidant and anti-inflammatory effects. Since the human body cannot produce many of these compounds, this crop assumes an important role in health protection, and might present new pharmacological solutions to several conditions. In this chapter, we aim to summarize the phytochemical composition of

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C. annuum and emphasize the major and most recent findings concerning health promoting benefits of its bioactive compounds (polyphenols, capsaicinoids, capsinoids, carotenoids, vitamins, and phytosterols), particularly those related with anti-oxidant, anti-nociceptive, anti-neoplastic, and anti-obesity properties.

Keywords: Antioxidant, Bioactive compounds, *Capsicum annuum*, Health.

INTRODUCTION

Capsicum annuum (Pepper) is an agricultural crop of the Solanaceae family and it is important as a vegetable food (bell pepper), as a spice (chili pepper) and colorant (paprika) [1].

Fig. (1). *Capsicum annuum* plant.

The Sonanaceae family includes 90 genera and 2000 species. The five most cultivated are *Capsicumannuum* (the dominant species) (Fig. **1**), *C. baccatum*, *C. chinense*, *C. frutescens*, and *C. pubescens* [2]. *C. annuum* is native to Mexico and Central America, but it is consumed worldwide and used in a great variety of dishes depending on its texture, flavor and color [1].

Pepper fruits are collected in distinct stages of maturation (visually distinguished by their color), from the most immature (green peppers – (Fig. **2**)) to the most mature (red peppers) [1]. This variation on color is related to the pepper's capacity

to synthesize carotenoids and retain chlorophyll [3], and therefore different maturity stages present different composition. Additionally, during ripening, the fruits not only undergo a transformation in color but also in aroma and texture [3].

Fig. (2). *Capsicum annuum* fruit.

Apart from its culinary uses, *C. annuum* is also a good source of bioactive compounds, such as polyphenols (flavonoids and phenolic acids), capsaicinoids, capsinoids, carotenoids and vitamins, with well-known anti-oxidant and anti-inflammatory effects [3]. Since the human body cannot produce many of these compounds, this crop assumes an important role in health protection, and might present new pharmacological solutions to several conditions. Moreover, some of these bioactive compounds have antimicrobial activity against bacteria and yeasts [4 - 8] and antitumoral activity [8]. On the other hand, inoculation with some bacteria can modify the bioactive compounds content of *C. annuum* [9, 10].

In this chapter, we aim to summarize the phytochemical composition of *C. annuum* and emphasize the major and most recent findings concerning health promoting benefits of its bioactive compounds (polyphenols, capsaicinoids, capsinoids, carotenoids, vitamins, and phytosterols), especially those related to its anti-oxidant, anti-nociceptive, anti-neoplasic and anti-obesity properties.

CHAPTER 5

Phytochemical, Nutritional, Antioxidant and Anticancer Properties of *Juglans regia* (L.)

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Abstract: *Juglans regia* (L.) is a deciduous tree, spread throughout the world due to its nutritional and sensory value. Although walnuts, the *J. regia* seeds, have been part of the human diet for a long time, only in the recent years several studies have surfaced on this botanical species as a rich and inexpensive source of bioactive compounds. In fact, much research is available depicting the human health benefits of *J. regia* seeds, leaves and green husks for a wide variety of diseases mediated by oxidative stress, namelly cancer, and neurodegenerative disorders. Among bioactive compounds, polyphenols play an important role. They are well known for their strong antioxidant, antihemolytic, antidiabetic, antimicrobial, antimutagenic and anticarcinogenic activities and are considered by many researchers responsible for the beneficial health effects of *J. regia* and its derivatives. In this chapter, we aim to emphasize the phytochemical composition, nutritional value and health promoting properties of *J. regia*, especially those related to its antioxidant and anticancer activities. Among several nut types, walnut stands up as a functional food, rich in antioxidants, especially in phenolic compounds and tocopherols. The potential for *J. regia* to be used as both preventive and therapeutic measure in several human diseases is high. For that reason, a lot of

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attention has been given to *J. regia* in the last decade.

Our chapter, summarizes the main studies about *J. regia* and its beneficial effects on human health, focusing on its antioxidant and anticancer activities.

Keywords: Antioxidants, Cancer, *Juglans regia*, Juglone, Polyphenols, Walnut.

INTRODUCTION

Walnut tree (*Juglans regia* L.) is the best known member of the *Juglans* genus, being regarded as a valuable crop all over the world [1]. This deciduous tree species, native to central Asia, the western Himalayan chain and Kyrgyzstan [2], is now cultivated around the World, namely in North and South America, North Africa, East Asia and Europe [3]. Part of the high worth attributed to *J. regia* is due to its nutritional and pharmaceutical properties, and commercial value of several of its components, particularly its leaves [1, 4], dry seeds [5], green husks [6] and alcoholic beverages produced from the green fruits [7]. The most widely used morphological part of *J. regia* is the seed, the walnut, and valued for its nutritional and sensorial attributes and, health benefits. Walnuts have been consumed since pre-agriculture times [8] mainly because they are a nutrient-dense food, rich in polyunsaturated fats and proteins [8, 9]. It can be consumed fresh or toasted [10]. The walnut also has a very interesting micronutrient profile, containing several vitamins and minerals [5]. If left in its shell, the walnut can be stored for a long time without losing its nutritional properties [9]. It has a slight astringent flavor, associated to the presence of phenolic compounds, which possess potent antioxidant properties [11, 12]. Moreover, walnuts present the highest antioxidant activity when compared with several other types of nuts [9], namely peanuts, pistachios, hazelnuts and almonds. Besides, walnut antiproliferative activity against human colon and kidney cancers has already been reported by Carvalho *et al*. [3].

J. regia leaves are not as popular as the seeds, however they are used in the preparation of infusions in several European countries, especially in rural areas [1]. Noteworthy, several beneficial effects have been attributed to these leaves such as antidiarrheic, antihelmintic, depurative, keratolytic, antifungal, hypoglycaemic, hypotensive, anti-scrofulous as well as sedative and astringent

properties [13 - 17]. More recently, the antioxidant and antiproliferative effects of *J. regia* leaves have started to be studied with promising results [1, 3]. Walnut green husk (WGH), a waste from the walnut production, is produced in large quantity. Its use is scarce and the possible beneficial effects are not very explored. However, it has been recently reported that the methanolic extracts of WGH present high antioxidant and antiproliferative effects, comparable to the seeds and leaves [1, 3]. Thus, it is expected that these extracts may present great health benefits.

In this chapter we intend to discuss the recent findings concerning the phytochemical, nutritional, antioxidant and anticancer properties of *J. regia,* focusing in the seeds, leaves and green husks. Overall, we intend to present an up-to-date overview of the potential health beneficial effects of *J. regia*.

CHEMICAL COMPOSITION AND NUTRITIONAL PROPERTIES

Walnut is one of the most popular nuts probably due to its attractive sensorial attributes and also to its health promoting properties. This is a nutrient dense food with high total caloric value and a significant content of important nutrients and bioactive phytocomponents with great relevance in human health. In fact, this nut possesses a complex composition containing hundreds of compounds, which belong to several different classes. Of note is that walnuts constitute a significant dietary source of polyunsaturated fats, proteins, fibers, melatonin, vitamin E, and polyphenols [1, 3, 9, 12, 18 - 20]. When compared with other types of nuts, walnuts are very rich in antioxidants, mainly phenolic compounds and tocopherols. A great part of polyphenols can be found in the pellicles [3, 9].

Major Components

Due to walnut high lipid content and low moisture, it presents a high total caloric content of approximately 700 Kcal / 100 g of edible portion [12]. Indeed, its major food components are lipids, followed by proteins (Fig. **1**) [12]. Other major components include fibers, water and carbohydrates, although present in much lower amounts (Fig. **1**) [12].

CHAPTER 6

Bioactive Compounds of Chestnuts as Health Promoters

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Abstract: Different chestnut species can be cultivated for fruit production, the most valorised part for nutritional purposes. However *Castanea sativa* Mill., the "European chestnut", is one of the most valorised worldwide. Its fruits are consumed either raw or after processing, being boiling and roasting the most usual ones. The nutritional composition of fresh chestnut is variable, with interesting amounts of carbohydrates and fibre, together with low fat content, with differences between cultivars and producing regions. In respect to the presence of bioactive compounds, such as phenolic compounds, vitamins, fatty acids, among others, some studies had focused on the fruit benefits to human health but few reported the effect of processing in those compounds. In this context, this chapter intended to review the current knowledge on chestnut composition, together with the influence of diverse post-harvest technologies, such as refrigeration, flame peeling, freezing with CO_2, irradiation, boiling and roasting on the bioactive compounds of chestnut.

Keywords: Antioxidant activity, Bioactive compounds, Boiling, Carbohydrates, *Castanea sativa* Miller, Cold storage, Drying, Fatty acids, Fibre, Irradiation, Minerals, Nutritional composition, Organic acids, Osmotic dehydration, Phenolic compounds, Processing, Proteins, Roasting, Vitamin C, Vitamin E.

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INTRODUCTION

The genus *Castanea* belongs to the angiosperm family *Fagaceae*. Throughout the world, several different species of chestnut can be found, such as *Castanea creanata* Sieb. in Asia, *C. creanata* Zucc. in Japan, *C. mollissima* Bl. in China and Korea, *C. dentada* Borkh in North America, and *C. sativa* Mill. in Europe being, also called "European chestnut" [1, 2].

The specie *C. sativa* Mill. is one of the most valorised worldwide. However, to improve chestnut production and the resistance to certain common diseases of the tree, some hybrids have emerged over the years [3].

Chestnut production has a high importance in the world's primary economy. China is the main producer, with about 1650000 tonnes (t) in 2012, followed by Republic of Korea (70000 t), Turkey (59789 t), Boli*via* (57000 t), Italy (52000 t), Greece (28700 t), Japan (20900 t) and Portugal, the eighth largest world's producer (19100 t) [4]. Despite these figures, due to the small country size, chestnut production in Portugal still represents a high contribution for the trade balance. The greatest production area for this fruit is located in Trás-os-Montes region (northeast of Portugal). Being a natural product, chestnut production can be affected by several factors including climatic conditions such as temperature, sunlight and precipitation, and also cultivation inputs, for exemple nutrients, minerals, and diseases and pests [3].

From a botanical point of view, chestnut fruit is a starchy nut composed by a seed protected by a membrane called the pellicle (episperm) and followed by a brown peel called "shell". This last involves the nut that is shielded by a spiny bur. When the fruit begins to mature, the bur modifies its colour, from green to yellow-brown, and breaks in 2-4 lengthways lines liberating three nuts. Sometimes the bur releases the chestnut fruits from the tree; however, more often the bur falls and opens completely on the ground as a result of the high humidity, liberating the fruits [5] (Fig. **1**). Even though the shell and pellicle are difficult to remove, this nut presents interesting properties which will be presented throughout this chapter.

Fig. (1). *Castanea sativa*: **(a)** Tree, **(b)** Chestnut fruit in the bur, **(c)** Fruit.

There are some review studies that discuss the nutritional properties of chestnuts *in natura* [3, 6]; however, despite not being usual to consume it raw, there are few works reporting the effects of different types of processing on its physicochemical properties and bioactivity. Thus, in this chapter we intend to evidence the beneficial effects of chestnut on human health and in which way processing may affect the physicochemical properties of this fruit.

PHYSICOCHEMICAL PROPERTIES OF CHESTNUT

Numerous studies on the physicochemical characterization of different varieties of chestnuts from different countries have been published. From the nutritional point of view, chestnut has interesting properties. Chestnuts are a good source of fibres, starch, protein, aminoacids, minerals, lipids, vitamin E and phenolic compounds, being a naturally gluten-free product.

The proximate nutritional composition of raw chestnuts(*Castanea sativa* Mill.) is detailed in Table **1**. The major compound is water, with moisture ranging between 40 and 64 g/100 g fresh weight (FW). This high moisture content represents a strong disadvantage for long-term preservation purposes, due to the high probability of mould formation, together with a significant weight loss during storage. On dry basis (DM), carbohydrates are the main components of chestnuts (75-91%), particularly starch (39 and 82%). Several studies have been reported about the specific content of amylose and amylopectin [15, 19, 20], accounting approximately for 33% and 67% of the starch content, respectively. The starch can improve health by giving energy from the catabolism process of amylose and amylopectin into glucose, as well as it can have a positive role on gut functions

CHAPTER 7

Bioactive Compounds of Hazelnuts as Health Promoters

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Abstract: Hazelnut (*Corylus avellana* L.) belongs to the Betulaceae family and is one of the most popular and commonly consumed tree nuts worldwide. Hazelnuts are highly nutritious, providing macronutrients (fat, protein and carbohydrates), micronutrients (vitamins and minerals) and several bioactive phytochemicals. So far, different phytochemicals have been described in hazelnuts, such as phenolic acids, flavonoids, condensed tannins and phytosterols. Among the array of phytochemicals present in hazelnuts, several have been associated with interesting properties such as antioxidant, anti-inflammatory, anti-proliferative and hipocholesterolemic activities thus potentially contributing for beneficial health effects related to hazelnut consumption. Even though hazelnuts have a high fat content, its inclusion has been recommended as part of a healthy-diet. The health benefits of hazelnut consumption have been mainly associated with its favourable lipidic composition and fat-soluble bioactives but also to its content in other compounds such as L-arginine and antioxidant phytochemicals. This chapter aims at providing detailed and up-to-date information on hazelnut bioactive compounds composition and related health aspects, including data from epidemiological and clinical studies.

Keywords: Chemical composition, Hazelnut, Health benefits.

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INTRODUCTION

Hazelnut (*Corylus avellana* L.) is a highly appreciated nut, being mainly cultivated in the Black Sea region of Turkey, in southern European countries, such as Italy, Spain, France, Greece and Portugal, and in the United States of America (USA). Other countries with relevant production of hazelnut include Azerbaijan, Georgia, Iran and China [1]. As happens with most crops, the world annual production of hazelnuts shows some fluctuation depending on the climatic conditions variations from year to year.

In the last decade, overall production of in-shell hazelnut varied among 742,125 tonnes in 2011 and 1069,175 tonnes in 2008 [1]. Turkey is the largest producer of hazelnut, comprising 64% of the world's total production in 2013, followed by Italy with a production corresponding to 11% [1]. Turkish hazelnut is generally divided into two main groups according to the quality of the nut, namely "Giresun" (or prime quality hazelnut) and "Levant" (or secondary quality) [2]. Among the prime quality hazelnuts, which are mainly grown in the Giresun province and neighbouring cities, Tombul cultivar is the most known and requested worldwide due to its high oil content and distinctive organoleptic properties [2, 3]. In Italy, the second world largest producer, hazelnut is mainly grown in the provinces of Campania, Lazio, Piemonte and Sicilia. Currently, "Nocciola Romana", corresponding to the Italian cultivars Tonda Gentile Romana and Nocchione in at least 90% and Tonda di Giffoni and Barretona in less than 10%, is commercialized under PDO (Protected Designation of Origin) designation. Among the Italian hazelnuts, two cultivars have also been attributed with PGI (Protected Geographical Indication) designation, namely "Nocciola di Giffoni", corresponding to cultivar Tonda di Giffoni, and "Nocciola del Piemonte", corresponding to cultivar Tonda Gentile delle Langhe [4]. Additionally, the Spanish "Avellana de Reus", comprising the cultivars Negreta, Pauetet, Gironella, Morella and Culplana, and the Frech "Noisette de Cervione" corresponding to the cultivar Fertille de Coutard, have also been designated with PDO and PGI designations, respectively [4].

The great majority of hazelnuts (~90%) is used in the food industry, as ingredient in chocolates, pastry and bakery, desserts and to add flavour and texture in other

formulations, with approximately 10% of world's production being sold as fresh unshelled nuts, to be consumed raw or roasted [5, 6]. Besides the high quality and absence of defects, frequently other requisites mainly related to kernel's physical features are required by the food industry, such as uniformity, size and shape [4]. Due to its characteristics, the cultivars more frequently used in the food industry include the Italian Tonda Gentile delle Langhe, Tonda Gentile Romana, Tonda di Giffoni, San Giovanni and Mortarella, the Turkish Tombul, Sivri, Palaz and Fosa and the Spanish Negret and Pauetet [4]. By the contrary, hazelnuts with large kernels such as cultivars Butler, Ennis and Lansing, which are frequently produced in the USA, are generally considered as being "table hazelnuts" since they are mainly intended to be consumed raw [7].

Hazelnut is considered to be a highly nutritious nut since it is rich in monounsaturated fatty acids (MUFA) and also contains a wide variety of vitamins, minerals and phytochemicals. Besides being regarded as a good source of nutrients, the consumption of hazelnuts has been recently associated with different health benefits. For these reasons, this chapter intends to provide a comprehensive overview on the existing knowledge on hazelnut composition, focusing in what concerns health promoting substances. Where possible, the composition of hazelnut by-products will be also mentioned since they potentially can be used as a source of phytochemicals.

CHEMICAL COMPOSITION

Proximate Composition

Up to now, several researchers have examined the proximate composition of several hazelnut cultivars grown in different countries, including Iran, Italy, New Zealand, Portugal, Spain, Turkey and USA [2, 8 - 14]. Although several factors can influence the final composition of hazelnut, including genetics, edaphoclimatic factors, geographical origin and harvesting time, among others, fat is the predominant component of hazelnut, followed by carbohydrate and protein, which sometimes present very close values among each other. Considering the reported values for several cultivars grown in different countries, fat is reported to vary among 43.2-69.0 g/100 g, carbohydrates among 5.8-26.0 g/100 g, protein

CHAPTER 8

Bioactive Compounds in Coffee as Health Promotors

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Abstract: Coffee is the most consumed beverage in the world after water. In 2014 approximately 141 million tons of coffee bags were produced. In terms of international trade only crude oil has a bigger share. The world coffee trade is increasing every year showing the importance of coffee to the world economy. The composition of the two main coffee species (Arabica and Robusta) varies according to the origin, storage and terroir conditions. During the roasting process there are a number of reactions that give rise to the organoleptic properties of coffee. The main bioactive compounds in coffee are chlorogenic acids, caffeine, trigonelline, melanoidins and diterpenes. These compounds are known to have a number of beneficial health effects. Many epidemiological studies suggest that coffee consumption can lead to health benefits in several diseases such as type 2 diabetes, several types of cancers, Parkinson's and Alzheimer's disease. These benefits are related with coffee antioxidant, anti-inflammatory, anti-mutagenic and anti-carcinogenic properties. Chlorogenic acids are known to have chemopreventive and anticarcinogenic activities and also to act as antithrombotic agents. Caffeine is the most recognized bioactive constituent of coffee and can have a number of positive effects in health, most of them associated with the antagonism of the A1 and A2 subtypes of the adenosine receptor. Its stimulatory effect is due to the synergetic interaction with adrenalin and noradrenaline. Trigonelline is connected to neuroprotective, estrogenic, hypoglycemic, anti-invasive, and antibacterial responses.

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The biological activities commonly associated with melanoidins are antioxidant and metal chelating, antimicrobial, and anticarcinogenic. These compounds also have the ability to modulate colonic microflora. Research has showed that the diterpenes, cafestol and kahweol have a chemopreventive potential by enhancing defense systems against oxidative stress. It is clear from the epidemiological studies that coffee has indeed health benefits. Nevertheless some caution has to be taken into account since there are a number of issues regarding these studies, as many of them were not designed specifically for coffee. Furthermore, health problems history and individual lifestyle can introduce misleading factors.

Keywords: Alzheimer's disease, Antioxidant, Bioactive compounds, Caffeine, Cancer, Chlorogenic acids, Coffee, Diterpenes, Health benefits, Melanoidins, Parkinson's diseasee, Trigonelline, Type 2 diabetes.

INTRODUCTION

The coffee plant belongs to the genus *Coffea* [1] and the most important species are *Coffea canephora* (Robusta coffee) and *Coffea Arabica* (Arabica coffee) [2]. Approximately 75% of world coffee production derives from the Arabica coffee species that are considered to have better organoleptic characteristics, while the Robusta coffee species provide the remaining world production and are more resistant to plagues [3]. Coffee is cultivated in tropical areas, Brazil, Vietnam, and Colombia being the main producers and responsible for more than 50% of the worldwide production [4].

There are references in ancient manuscripts dating as far back as 575 AD showing that the Arabs were the first promoters of coffee culture [3] and according to some legends, coffee trees originated in the Ethiopian province of Kaffa [4]. The first known occurrence of coffee beans roasting and conversion into a beverage dates from the XVI century in Persia. Since then coffee dissemination started, and coffee plant arrived in Europe around 1615 AD, brought by travellers. The first cultivation of coffee in Europe was in the botanical garden of Amsterdam, followed by French cultivations in the islands of Sandwich and Bourbon. It took several years before the first coffee house was opened. This happened in the middle of the XVII century in England. Due to a higher demand of the beverage,

coffee plantation expanded to European colonies in Africa and South/Central America [3]. It is curious that, until the 20th century, coffee divided the scientific community whether it should be considered as food or medicine due to its long list of human health benefits.

Nowadays, coffee is very much appreciated around the world (mainly in the developed countries) and is the most consumed beverage in the world after water (only crude oil has bigger share in the international trade market) [3]. In 2015, around 141 million tons of coffee bags (60 kg each bag) were reported as the annual worldwide production for 2014 by the International Coffee Organization [4]. The production of coffee is mainly located in developing countries where it plays a crucial role in obtaining foreign exchange earnings as well as tax income and gross domestic product. The annual exports of coffee in 2010 were estimated in US$15.4 billion with about 26 million persons in 52 countries involved [4, 5]. These numbers show the substantial impact of this industry over world's economy and it is expected to continue to grow year after year. The product trade is carried out mainly as green coffee beans. Its price depends on coffee species and variety, geographic location, the methodology used in the processing of green coffee beans and also the care taken during production. The top three importing countries/regions, European Union, USA and Japan, are responsible for more than 70% of total coffee imports in 2015 [4].

The composition of green coffee beans varies according to the species, origin, storage and terroir conditions (the composition of the soil and its fertilisation, altitude, weather). The degree of maturation of the green coffee beans is also critical to obtain high quality coffee. Due to this fact, the harvesting process is only performed when the majority of fruits are ripe through a mechanical or manual process.

The major components of green coffee beans for both Arabica and Robusta species are: carbohydrates, lipids, proteins, chlorogenic acids (CGAs), minerals, trigonelline and caffeine [3]. The most abundant carbohydrate is sucrose which acts as an aroma precursor during roasting [6]. Trigonelline is a pyridine derivative present at high levels that contributes indirectly to the formation of desirable flavour products during coffee roasting [7]. Proteins are also responsible

CHAPTER 9

Bioactive Compounds of Rice as Health Promoters

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Abstract: Rice (*Oryza sativa* L.) is one of the major cereal food crops in the world. It serves as a principal source of carbohydrate. Rice is also traditionally used for therapeutic purposes. The health promoting properties of brown rice has generated research interest. The health promoting properties are attributed to the bioactive compounds in the rice bran. These include vitamins, minerals, phenolic compounds, γ - oryzanol, tocopherols, tocotrienols, anthocyanins, phytosterols and dietary fibre. The concentration of bioactive properties is more in pigmented rice varieties. The bioactives in rice impart cholesterol reduction, anti-inflammatory, anti-tumor, anti-diabetic and anti-oxidative effects. Ferulic acid is the major phenolic acid in rice whose esters predominantly form γ-oryzanol and remains in the human blood stream for longer time than other phenolics thereby offering greater radical scavenging efficiency. The rice bran anthocyanin pigments contribute to the total phenolic and antioxidant properties of rice to a notable extent. The tocols also are potent antioxidants. Both in vivo and in vitro experiments have ascertained the effect of these compounds in animals and human beings. The bioactive potential of rice has been found to widely vary with variety, extent of polishing and processing. Cooking steaming, parboiling, fermentation and germination of rice result in marked changes in proportion and activities of different bioactive components. This chapter focuses on the bioactive compounds in rice, the potential health benefits of rice consumption, and processing effects on bioactivity.

Keywords: Anti-cancer, Anthocyanin, Anti-inflammatory, Antioxidant, Bioactive compounds, Bran, Cooking, Fermentation, Ferulic acid, Non-pigmented rice, γ oryzanol, Parboiling, Phenolics, Pigmented rice, Plasma cholesterol, Rice, Therapeutic, Tocopherols, Tocotrienols, Tricin.

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INTRODUCTION

Rice *(Oryza sativa)* is a leading cereal crop and staple food to more than half of the world's population. The harvested paddy undergoes milling and polishing to yield white rice. The first step of milling consists of hulling *i.e.* removal of the outer layer or hull to yield brown rice. The brown rice is further milled to remove the bran layer and germ. The resulting white rice is then polished and graded. The appearance and flavour of rice improves on polishing. However, compared to the brown rice, it has lower nutritional and therapeutic value as the bran layer that is removed on polishing is rich in vitamins, phenolic compounds, minerals, dietary fibre and other bioactive compounds such as γ-oryzanol, tocopherols, tocotrienols, and phytosterols [1, 2]. Bioactive compounds are the non-nutrient secondary metabolites having health promoting functional properties.

Rice varieties are classified into two broad categories as non-pigmented and pigmented rice depending on their bran colour. Non-pigmented rices have brown coloured bran and are commonly grown worldwide. Varieties with black, red and purple coloured bran are classified as pigmented rice varieties. Until recently, the pigmented rice varieties were being cultivated in a very limited quantity in isolated places of the world either for making specific traditional foods or beverage products. Nowadays, the pigmented rices are gaining popularity owing to their many therapeutic uses [3] and growing consumer awareness about the goodness of the rice. The content of bioactive compounds is more in pigmented rices [4, 5] and therapeutic properties are attributed to these compounds.

Traditional Therapeutic Uses of Rice

The traditional medicinal system in many Asian countries recognises the therapeutic properties of rice [6]. From ancient times, rice is used in the treatment of number of gastrointestinal disorders, diabetes, high cholesterol conditions, skin disorders, jaundice, *etc.* [6 - 8]. In traditional Chinese medicine, pigmented rice has been used for strengthening kidney function, treating anaemia, promoting blood circulation, removing blood stasis, improving blood flow, treating diabetes, and strengthening sight [9]. Red yeast rice, a fermented rice product, is used in traditional Chinese medicine for its cholesterol lowering properties [10]. In China,

dried and sprouted rice is used as an aid for digestion. Boiled rice is used to treat acute inflammation of the inner body tissues in many Asian countries. Similarly, rice bran extract is used to prevent and cure beriberi, a disease caused due to Vitamin B-1 (thiamine) deficiency. A variety of black rice, Njavara, cultivated in Kerala, India is referred to in Ayurveda for the treatment of rheumatoid arthritis, paralysis, neurodegenerative diseases and in rejuvenation therapy [11]. Rakthashali, a red rice variety of India, besides its nutritional significance is used in various medications like in allergies, skin ailments, uterus related problems, nerve disorders, gastro-intestinal problems, liver, kidney disorders, fever, infections and in promoting lactation [12].

Composition and Antioxidant Effects of the Bioactive Compounds in Rice

The bioactive compounds are concentrated in the outer bran layers of the rice grain [2, 6]. Bioactive compounds in rice include phenolic compounds, γ-oryzanol, tocopherols, tocotrienols, *β*-sitosterol, γ- campesterol and vitamins like thiamine, riboflavin and niacin. Bran from thicker kernels (>1.84 mm) contains a higher content of oryzanol, tocopherols, and tocotrienols [13] that have strong antioxidant properties. *γ*-tocotrienol contributes the most to the total tocol content (27–63%), followed by *α*-tocopherol (10–30%), *α*-tocotrienol (9–19%), *γ*-tocopherol (9–14%), *δ*-tocotrienol (2–6%), *β*-tocotrienol (1–4%), *β*-tocopherol (1–2%), and *δ*-tocopherol (1–2%) [3]. Japonica varieties contain a higher content of total tocopherol, total tocotrienol and γ-oryzanol than indica varieties [14]. The phenolic compounds in rice comprise of phenolic acids and flavonoids. The dominant phenolic acids in rice are ferulic acid and *p*-coumaric acid [15]. Other phenolic acids include sinapic, protocatechuic, chlorogenic, vanillic, syringic, caffeic and gallic acids [16]. Among the four types of rice ranked by color, black rice varieties exhibit the highest antioxidant activities, followed by purple, red, and brown rice varieties. Furthermore, insoluble compounds appear to constitute the major fraction of phenolic acids and proanthocyanidins in rice, but not of flavonoids and anthocyanins [2, 3]. Njavara, the medicinal rice variety contains about 50% higher soluble and insoluble forms of ferulic ester than non-medicinal rice [2]. Among the flavonoids, tricin, tricinin and anthocyanins are prominent. The pigmented varieties contain higher levels of anthocyanins than the non pigmented rice. Anthocyanins are group of red to purple water soluble flavonoids.

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