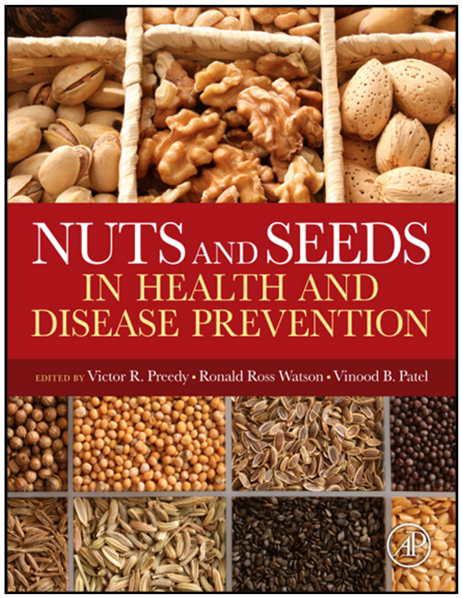
Antioxidants in Hazelnuts (Corylus avellana L.)

Chapter · December 2011

DOI: 10.1016/B978-0-12-375688-6.10072-6

Maria Teresa Frangipane
Tuscia University

Riccardo Massantini
Tuscia University



From Contini, M, Frangioane, M. T, Massantini, R. (2011). Antioxidants in Hazelnuts (Corylus avellana L.). In V. R. Preedy, R. R. Watson, V. B. Patel (Editors), Nuts & Seeds in Health and Disease Prevention (1st ed.) (pp 611-625). London, Burlington, San Diego: Academic Press is an imprint of Elsevier.
ISBN: 9780123756886

CHAPTER 72

Antioxidants in Hazelnuts (*Corylus avellana* L.)

Marina Contini, Maria Teresa Frangipane, Riccardo Massantini
Dipartimento di Scienze e Tecnologie Agroalimentari, Tuscia University, Viterbo, Italy

CHAPTER OUTLINE

LIST OF ABBREVIATIONS

BHA, butylated hydroxyanisole
BHT, butylated hydroxytoluene
DPPH, 2,2-diphenyl-1-picrylhydrazyl radical
MUFA, monounsaturated fatty acid
ORAC, oxygen radical absorbance capacity
Trolox, 6-hydroxy-2,5,7,8-tetra-methylchroman-2-carboxylic acid

INTRODUCTION

Endogenous or exogenous free radical compounds can damage biological molecules such as proteins, lipids, and DNA. The human body can neutralize them, but its own defense systems are not fully efficient; hence, as time proceeds, free radicals accumulate. Free radical load causes cell damage and body ageing, and has been postulated to induce a variety of pathological events, such as atherogenesis and carcinogenesis.

Hazelnuts contain a series of antioxidants that may cooperate in concert, providing the body with potential help in hindering the free radical threat, thus improving human well-being by countering the initiation and progression of oxidative stress-mediated disorders and diseases.

Nuts & Seeds in Health and Disease Prevention. DOI: 10.1016/B978-0-12-375688-6.10072-6

BOTANICAL DESCRIPTION

Hazel is the common name for the flowering plant genus *Corylus*, usually placed in the Betulacee family, although some botanists consider it a separate family, Corylaceae. The genus *Corylus* comprises about 15 species, including the European *Corylus avellana* L., the common commercially grown hazelnut. It is a monoecious species, growing as large shrubs or small trees, usually 2—5 m high.

The edible portion of the hazelnut is the roughly spherical to oval kernel of the seed, which is 1.0—2.5 cm long and 1.2—2.0 mm broad. The kernel is covered by a dark brown perisperm (skin or pellicle), varying in thickness and appearance between varieties, and protected by a smooth, hard, woody shell. The seed grows in a bristly leafy outer husk that opens in autumn, when it ripens (about 7—8 months after pollination).

The most popular commercial hazelnut varieties are Tombul (Turkey), Tonda Gentile (Italy), Negret (Spain), Barcellona and Segorbe (Portugal), and Ennis, Daviana, and Butler (USA).

HISTORICAL CULTIVATION AND USAGE

The hazelnut is reputedly native to Asia Minor. It has been known since prehistory, and extensively eaten since pre-agricultural times.

The hazelnut is also known as a filbert, probably because its harvesting began on Saint Philbert's Day, August 22. "Filbert" may also derive from "full beard," for its long, leafy husk.

Throughout Europe, the hazelnut has long been revered not only as a source of food but also as a plant with mystical and magical powers. The ancients thought hazelnuts had medicinal properties, using them as remedies for various disorders and diseases, including sore throat, phlegm, chronic cough, impotency, and baldness.

PRESENT-DAY CULTIVATION AND USAGE

The world production of unshelled hazelnut amounts to nearly 1 million tonnes per year. Turkey is the leading producer and exporter, accounting for about 70% of world production, followed by Italy, with around 13%. The USA is third (about 4%), and Spain fourth (near 3%). Other minor producers are Azerbaijan, Georgia, Iran, China, Greece, and France.

About 90% of the world crop is absorbed by the food industry. Shelled hazelnuts are commercialized mainly after roasting, which provides a more intense, pleasant typical flavor and a crisper texture, in addition to allowing for removal of the slightly bitter and astringent skin. Hazelnuts are available in many forms (whole, chopped, crumbled, ground into a paste) and are extensively employed in confectionery. Hazelnut oil is used not only as food, but also in cosmetics, for its astringent and emollient properties, or as a carrier in aromatherapy.

APPLICATIONS TO HEALTH PROMOTION AND DISEASE PREVENTION

Nutrient and nutraceutical compounds in hazelnut and hazelnut oil

Hazelnuts are well known and appreciated for their organoleptic properties; in addition, they are very nutritious and healthful because of their favorable composition of nutrients and nutraceutical compounds.

Hazelnuts are a very rich source of fat (about 60%) and fiber (around 10%), as well as a good source of protein and carbohydrates; the major minerals are potassium, phosphorus, calcium, and magnesium, while significant amounts of copper, manganese, and selenium are also present (Table 72.1). The selenium content given in Table 72.1 (2.4—4.1 μg/100 g) is much lower than that reported by Dugo *et al.* (2003), which in Italian (Sicilian) hazelnuts was about 90 μg/100 g.

TABLE 72.1 Proximate Composition and Micronutrient Content in 100 g of Hazelnuts

Proximates	Unit	Dry Roasted	Unroasted	Blanched, Unroasted
Water	g	2.52	5.31	5.79
Protein (N × 5.3)	g	15.03	14.95	13.70
Total lipid (fat)	g	62.40	60.75	61.15
Ash	g	2.45	2.29	2.36
Carbohydrate, by difference	g	17.60	16.70	17.00
Fiber, total dietary	g	9.4	9.7	11.0
Sugars, total	g	4.89	4.34	3.49
Sucrose	g	4.75	4.20	3.35
Glucose (dextrose)	g	0.07	0.07	0.07
Fructose	g	0.07	0.07	0.07
Starch	g	1.10	0.48	0.93
Energy	kcal	646	628	629
Energy	kJ	2703	2629	2630
Minerals				
Potassium	mg	755	680	658
Phosphorous	mg	310	290	310
Magnesium	mg	173	163	160
Calcium	mg	123	114	149
Manganese	mg	5.550	6.175	12.650
Iron	mg	4.38	4.70	3.30
Zinc	mg	2.50	2.45	2.20
Copper	mg	1.750	1.725	1.600
Selenium	μg	4.1	2.4	4.1
Vitamins				
Vit E (α-tocopherol)	mg	15.28	15.03	17.50
β-Tocopherol	mg	0.33	0.33	0.35
γ-Tocopherol	mg	0	0	2.15
δ-Tocopherol	mg	0	0	0.14
Vit. C (total ascorbic acid)	mg	3.8	6.3	2.0
Niacin	mg	2.050	1.800	1.550
Pantothenic acid	mg	0.923	0.918	0.815
Vit B_6	mg	0.620	0.563	0.585
Thiamin	mg	0.338	0.643	0.475
Riboflavin	mg	0.123	0.113	0.110
Folate, total	μg	88	113	78
Vit A, RAE[a]	μg RAE	3	1	2
Vit A, IU[b]	IU	61	20	40
β-carotene	μg	36	11	23
α-carotene	μg	1	3	2
Choline, total	mg	n.r.	45.6	n.r.
Betaine	mg	n.r.	0.4	n.r.
Lutein + zeaxanthin	μg	n.r.	92	n.r.
Vitamin K (phylloquinone)	μg	n.r.	14.2	n.r.

Source: United States Department of Agriculture (USDA) National Nutrient Database for Standard Reference, Release 22 (2009), www.nal.usda.gov/fnic/foodcomp/search.

[a] *RAE, Retinol Activity Equivalent;*

[b] *IU, Internationan Unit; n.r., not reported.*

Selenium, though not an antioxidant itself, has an essential role in constructing the endogenous antioxidant defense system, protecting the human body against oxidative disorders and diseases, including cancer (Awad & Bradford, 2005).

Hazelnuts also contain appreciable amounts of vitamins (Table 72.1); in particular, they are an excellent source of α-tocopherol (over 15 mg/100 g), a fat-soluble phenolic compound that is very important for human health because of both its vitamin E function and its powerful biological antioxidant properties.

It is well recognized that a diet high in MUFAs (especially oleic acid) and phytosterols (especially β-sitosterol) tends to improve the cholesterol balance and triglyceride levels, reducing the risk of atherosclerosis and coronary heart disease. The hazelnut lipid fraction is close to that of olive oil; it has a high content of MUFAs (about 80%, essentially comprising oleic acid) and phytosterols, mainly β-sitosterol (almost 1 mg/g oil) (Table 72.2), the most active among phytosterols in reducing serum LDL cholesterol levels. Moreover, many epidemiologic/experimental studies have provided evidence that dietary phytosterols may offer protection against certain typologies of cancer, such as colon, breast, and prostate cancer (Awad & Bradford, 2005).

It has been demonstrated that hazelnut supplementation favorably changes plasma lipid profiles (VLDL cholesterol, triacylglycerol, and apolipoprotein B reduction; HDL cholesterol increase) in hypercholesterolemic adult men (Mercanligil *et al.*, 2007). In young, healthy humans, a hazelnut-enriched diet was found to be beneficial in lowering total cholesterol and LDL cholesterol levels, elevating HDL cholesterol, and significantly increasing the HDL/LDL ratio; in addition, an enhancement in the plasma antioxidant potential and a reduction in plasma lipidic peroxidation levels were noted (Durak *et al.*, 1999). In rabbits fed on a high cholesterol diet, Hatipoğlu *et al.* (2004) observed that hazelnut oil administration not only lowered aortic cholesterol accumulation, but also reduced plasma, liver, and aortic peroxide levels. These findings suggested that hazelnut bioactive substances (i.e., phytosterols, tocopherols, and/or other antioxidants) were able to ameliorate the cellular antioxidant defenses, thus improving the cardioprotective effects of the MUFA-rich hazelnut lipids.

Among five different nuts (hazelnut, macadamia, peanut, walnut, and almond), hazelnuts and macadamias were by far the best sources of squalene (186.4 and 185.0 μg/g oil, respectively); furthermore, hazelnut and almond oils were found to have very high vitamin E contents, mainly α-tocopherol (310.1 and 439.5 μg/g oil, respectively) (Table 72.2). Gordon and colleagues found 161 ± 6 mg/kg oil of phenolics (as caffeic acid equivalents) in the polar fraction of unrefined hazelnut commercial oils; myricetin and chrysin were tentatively identified as minor components, but the main phenolic compounds could not be recognized (Gordon *et al.*, 2001).

Antioxidant characteristics of hazelnut and hazelnut oil

Recently, Arranz and colleagues found that hazelnut and pistachio oils exhibit a high antioxidant capacity, close to that of extra virgin olive oil, and higher than those of walnut, almond, and peanut oils (Arranz *et al.*, 2008). They observed that after methanolic extraction of the polar fraction, a noticeable reduction of antioxidant capacity was recorded in the remaining nut oils. The authors found good correlation between the DPPH-scavenging activity of the stripped nut oils and tocopherol content, while proving that the antioxidant activity registered in the methanolic fraction was essentially due to phospholipids, the contribution of phenolics being negligible.

Currently hazelnut oil is mainly employed in the cosmetic and sometimes in the confectionery industry, but it is becoming increasingly popular as an edible oil, owing to its beneficial nutritional composition and health-promoting characteristics. It can be found on the market in both crude and refined forms. Cold-pressed hazelnut oil may be conveniently employed for cooking or frying, due to its high resistance to oxidative degradation, which is close to that of

TABLE 72.2 Total Oil of Five Edible Nuts, and Relative Content of Squalene, Tocopherols, and Phytosterols in Oils

Nut	Total Oil (g/100 g)	Squalene (μg/g oil)	Tocopherols[a]			Phytosterols			
			α-Tocopherol (μg/g oil)	*γ-Tocopherol (μg/g oil)*	*Sum of Tocopherols (μg/g oil)*	*β-Sitosterol (μg/g oil)*	*Campesterol (μg/g oil)*	*Stigmasterol (μg/g oil)*	*Sum of Phytosterols (μg/g oil)*
Hazelnut	49.2 ± 1.6	186.4 ± 11.6	310.1 ± 31.1	61.2 ± 29.8	371.3	991.2 ± 73.2	66.7 ± 6.7	38.1 ± 4.0	1096.0
Macadamia	59.2 ± 1.5	185.0 ± 27.2	122.3 ± 24.5	Trace	122.3	1506.7 ± 140.5	73.3 ± 8.9	38.3 ± 2.7	1618.3
Peanut	37.9 ± 1.8	98.3 ± 13.4	87.9 ± 6.7	60.3 ± 6.7	148.2	1363.3 ± 103.9	198.3 ± 21.4	163.3 ± 23.8	1724.9
Walnut	50.8 ± 1.4	9.4 ± 1.8	20.6 ± 8.2	300.5 ± 31.0	321.1	1129.5 ± 124.6	51.0 ± 2.9	55.5 ± 11.0	1236.0
Almond	40.8 ± 2.5	95.0 ± 8.5	439.5 ± 4.8	12.5 ± 2.1	452.0	2071.7 ± 25.9	55.0 ± 10.8	51.7 ± 3.6	2178.4

Hazelnut oil emerges as having high squalene and tocopherol (mainly α-tocopherol) contents; phytosterols (mainly β-sitosterol) are present in consistent amounts, although at lower concentrations than in all the other nuts.
Results are the mean ± SEM from three independent experiments.
Source: Maguire, O'Sullivan, Galvin, O'Connor, and O'Brien (2004), *Intl J. Food Sci. Nutr.* 55, 171–178.
[a] *Traces of δ-tocopherol were detected in all nuts (data not shown).*

extra virgin olive oil (Contini *et al.*, 1997). Of the five nut oils, hazelnut oil showed the best oxidative stability (Rancimat test) (Arranz *et al.*, 2008).

Plant phenolics are not nutrients for humans. Nevertheless, their inclusion in the diet is beneficial, because many could potentially play a major role in human health promotion and disease risk reduction. Many phenolic compounds exhibiting antioxidant properties have been studied and proposed for protection against numerous pathologies associated with oxidative damage. Plant phenols have been reported to show anticarcinogenic, anti-atherogenic, anti-ulcer, antithrombotic, anti-inflammatory, anti-allergic, immune modulating, antimicrobial, vasodilatatory, and analgesic effects (Wollgast & Anklam, 2000). Wu and colleagues (2004) found that one serving (28.4 g) of hazelnuts contained about 237 mg of total phenols (as gallic acid equivalent) and had a total antioxidant capacity (ORAC test) of 2739 μmol Trolox equivalent. Interestingly, the principal fraction responsible for antioxidant capacity was not the lipophilic fraction (comprising tocopherols), but the hydrophilic counterpart. Oliveira *et al.* (2008) demonstrated that boiling-aqueous extracts of hazelnut showed DPPH-radical scavenging ability and antioxidant activity in the β-carotene/linoleate model system, but their efficiency was much lower with respect to reference antioxidants; contrarily, the extracts showed a better reducing power than BHA and α-tocopherol. It was recently shown that consistent amounts of tree nut phenolics exist in a non-soluble (bound) form; in particular, the bound fraction accounted for close to 93% of the total phenols in hazelnuts (Yang *et al.*, 2009). Therefore, both the content and antioxidant activity of nut phenolics are probably underestimated in the literature.

Antioxidant characteristics of hazelnut skin

Most of the hazelnut phenolics are located in the seed skin (Shahidi *et al.*, 2007); this evidence suggested exploiting the hazelnut skin by-product (the industrial residue of pellicle removal) as a source of natural and efficient antioxidants. With respect to other hazelnut by-products, it was demonstrated that the skin waste provides a much higher yield of phenolic extract, which has a very high phenolic content and multiple antioxidant properties – i.e., DPPH-radical, hydrogen peroxide, and superoxide radical scavenging activities; reducing and chelating powers; the ability to inhibit oxidation of human LDL-cholesterol; and the capability to reduce DNA damage induced by hydroxyl radical (Shahidi *et al.*, 2007; Contini *et al.*, 2008; Contini *et al.*, 2009). In particular, hazelnut skin phenolic extract showed high Fe^{3+} reducing activity and excellent radical scavenging ability (DPPH test) (Figure 72.1A, 72.1B); moreover, an *in vivo* test demonstrated that it was biologically active in rats (Figure 72.1C) (Contini *et al.*, 2009).

Hazelnut skin extract was found to be very rich in tannins (over 60% of total phenols) (Contini *et al.*, 2008). Historically, tannins were considered to be antinutrients, but recently the recognition of their very effective antioxidative capacity and probable protective actions (such as cardioprotective, anticarcinogenic, gastroprotective, anti-inflammatory) has led to second thoughts towards their effect on human health (Santos-Buelga & Scalbert, 2000). Tannins resulted in much more powerful antioxidants than simple monomeric phenols, and may have unique roles in the human digestive metabolism, both as preservers of other biological antioxidants and as protectors of nutrients from oxidative damage. In particular, non-absorbed high polymerized tannins may exert important local activities in the gastrointestinal tract, especially in the colon (Halliwell, 2007), which, being particularly exposed to oxidizing agents, is prone to several pathologies, such as inflammation and cancer.

Because of their potential antioxidant and nutraceutical properties, phenolic extracts obtained from hazelnut skin might satisfy the demand for new natural phenolic antioxidants, useful in the food industry alongside or as a substitute for synthetic antioxidants, or as ingredients in the preparation of innovative foods with a high dietetic/functional value. One outcome of these findings is that it would be better to eat hazelnuts with intact skins, and the industry/consumer preference for peeled kernels should be revised.

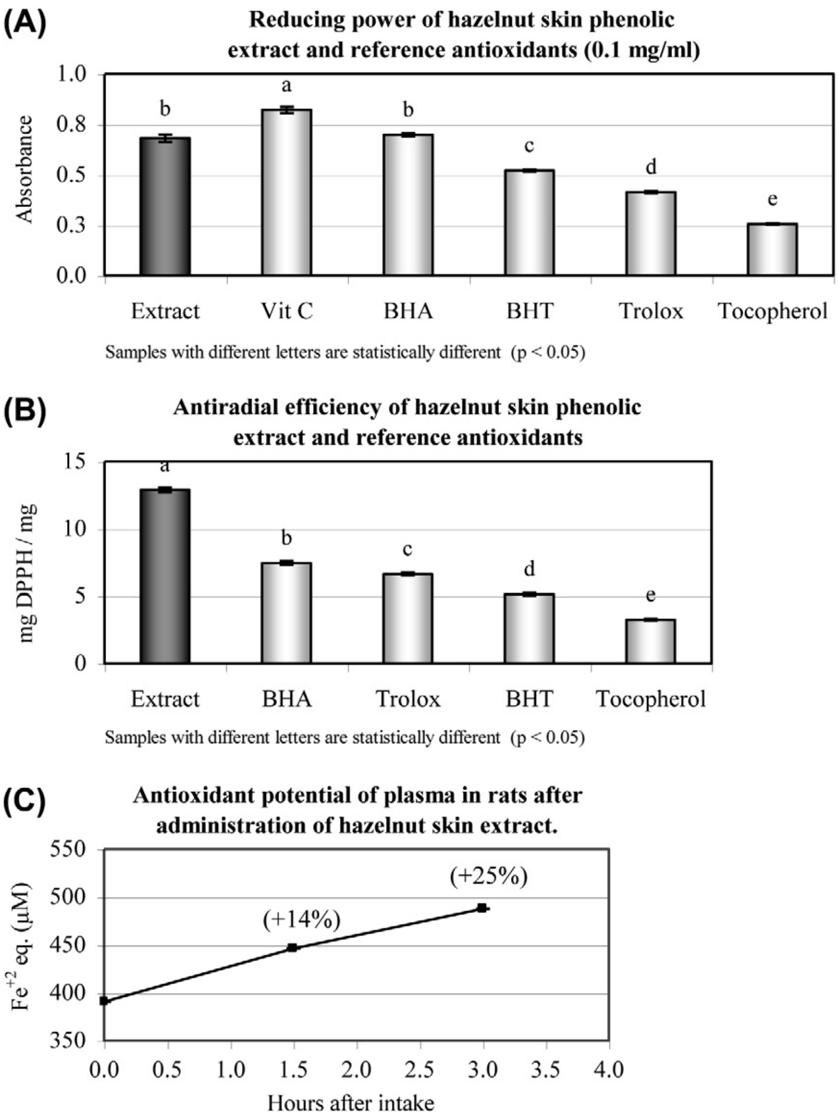


FIGURE 72.1
***In vitro* and *in vivo* antioxidant power of hazelnut skin crude phenolic extract.** The extract showed ferric reducing activity similar to that of BHA (butylated hydroxyanisole), superior to that of BHT (butylated hydroxytoluene), Trolox (6-hydroxy-2,5,7,8-tetra-methylchroman-2-carboxylic acid) and α-tocopherol, and inferior only to ascorbic acid (A); its activity against the DPPH (2,2-diphenyl-1-picrylhydrazyl) radical was better than the reference antioxidants, including α-tocopherol (B). Plasma antioxidant potential of rats which consumed 10 mg of extract increased by 14% and 25% at 1.5 and 3 hours after administration, respectively (C). Reprinted from Contini *et al.* (2009), *Acta Hortic.*, *845*, 717–722, with permission.

Phenolic compounds of hazelnut kernel and skin

Some works have been published reporting the chemical composition of phenolics in hazelnut kernel and skin. A comprehensive bibliographic data compilation in this respect is summarized in Tables 72.3–72.5. The hazelnut has elevated contents of flavan-3-ols, especially highly polymerized ones (tannins over decamers). In addition to high amounts of flavan-3-ol monomers and dimers, tannin forms mainly consisting of B-type proanthocyanidins up to nonamers were detected (but not quantified) in roasted hazelnut skin. Alasalvar *et al.* (2009) were the first to show that the tannin fraction isolated from roasted hazelnut skin phenolic extract manifested the highest antioxidant activity (DPPH test) with respect to both the crude phenolic extract and the low molecular weight phenolic fraction. Several phenolic acids, such as benzoic acid and cinnamic acid derivatives, were also found in hazelnut and its skin. Regarding flavonols, myricetin, kaempferol, and quercetin were identified in the skin by-product, while the presence of quercetin in the kernel is controversial. A single anthocyanin (cyanidin) was found, but just in the kernel. Furthermore, some phytoestrogens (isoflavones, lignans and coumestrol) were found in the kernel. Phytoestrogens are phenolics that have important antioxidant properties which are thought able to protect against a wide range of diseases (Cornwell *et al.*, 2004).

TABLE 72.3 Phenolic Compounds Identified in Hazelnuts

	Reference	Yurttas *et al.*, 2000	Gu *et al.*, 2003	Gu *et al.*, 2004; USDA, 2004	Alasalvar *et al.*, 2006		Harnly *et al.*, 2006; USDA, 2007	Shahidi *et al.*, 2007	Amarowicz *et al.*, 2008	Prosperini *et al.*, 2009	
	Extraction solvent	MeOH/H_2O (2 : 1)	Acetone/H_2O/ acetic acid (70 : 29.5 : 0.5)	Acetone/H_2O/ acetic acid (70 : 29.5 : 0.5)	EtOH/H_2O (80 : 20) or acetone/H_2O (80 : 20)		None	EtOH/H_2O (80 : 20)	Acetone/H_2O (80 : 20)	EtOH/H_2O (80 : 20) or acetone/H_2O (80 : 20), at different temperatures	
	Treatment[a]	Acid hydrolysis	Sephadex LH-20 column, then HPLC analysis before and after thiolytic degradation	Sephadex LH-20 column, then HPLC analysis before and after thiolytic degradation	Partition in diethyl ether	Basic hydrolysis plus partition in diethyl ether	Acid hydrolysis	Partition in diethyl ether before and after basic hydrolysis	Oxidative depolymeri- zation (n- butanol/HCl)	Partition in diethyl ether	Basic hydrolysis plus partition in diethyl ether
	Analytical technique	HPLC-UV	HPLC-MS/ MS	HPLC-MS/ MS	HPLC/DAD	HPLC/DAD	HPLC/DAD	HPLC/DAD	HPLC/DAD	HPLC/DAD	HPLC/DAD
	Phenolic class analyzed	Simple phenolics	Flavan-3-ols	Flavan-3-ols	Free phenolic acids	Esterified phenolic acids	Flavan-3-ols; anthocyanins	Phenolic acids	Flavan-3-ols	Free phenolic acids	Esterified phenolic acids
	Unit	Qualitative data[b,c]	Qualitative data[b]	mg/100 g of kernel	µg/g of extract	µg/g of extract[d]	mg/100 g of kernel	µg/g of extract	Qualitative data[b]	µg/g of extract[e]	µg/g of extract[e]
Phenolic acids	p-OH benzoic acid	✓									
	Caffeic acid	✓[f]			n.d	n.d		81		n.d.	0–2.18
	p-coumaric acid				5[g]	13 (21)		208		0–5.14	0–3.71
	Ferulic acid				n.d.	n.d.		105		0–8.10	n.d.
	Gallic acid	✓			n.d.	158 (204)		127		0–34.50	0–18.40
	Sinapic acid	✓			n.d.	39 (52)		93		0–9.09	0–7.70
	Total phenolic acids				**0–5**	**210 (277)**		**614**		**0–39.64**	**7.31–18.40**
Flavonols	Quercetin	✓					n.d.				
Antho cyanins	Cyanidin						6.7				

Flavan-3-ols monomers and polymers (condensed tannin)	**(+) catechin**						1.2				
	(−) epicatechin	✓[f]					0.2				
	Epigallo-catechin						2.8				
	Epigallo-catechin gallate						1.1				
	Gallocatechin gallate						0.4				
	Proantho-cynidins (B-type)		✓								
	Procyanidins[h]		✓[i]	✓[j]					✓		
	Prodel-phinidins[k]		✓	✓[j]					✓		
	(epi)catechin glycoside		✓								
	Monomers			9.8							
	DP[l]										
	2			12.5							
	3			13.6							
	4–6			67.7							
	7–10			74.6							
	> 10			322.4							
	Average DP[m]		14.0								
	Total flavan-3-ols			**500.7**			**5.7**				
Total phenols quantified				500.7	0–5	210 (277)	12.4	614		0–39.64	7.31–18.40

Hazelnuts contain mainly flavan-3-ols, especially highly polymerized (tannins over decamers). Several phenolic acids and cyanidin were also found, while the presence of quercetin is controversial.
n.d., not detected.
[a]*Treatment of sample/phenolic extract before analysis;*
[b]*✓, reported presence;*
[c]*tentative identification;*
[d]*first value, ethanolic extract; second value (in brackets), acetonic extract;*
[e]*min and max amount dosed, depending on the solvent and temperature of extraction;*
[f]*unresolved peaks;*
[g]*present only in the acetonic extract;*
[h]*(epi)catechin polymers;*
[i]*presence of 3-O-gallate;*
[j]*types of flavan-3-ols found;*
[k]*(epi)gallocatechin polymers;*
[l]*DP, degree of polymerization;*
[m]*excluding monomers.*

TABLE 72.4 Phenolic Compounds Identified in Hazelnut Skin

	Reference	Senter *et al.*, 1983	Coisson *et al.*, 2002	Travaglia *et al.*, 2006	Shahidi *et al.*, 2007	Monagas *et al.*, 2009	
	Sample	Skin	Skin by-product	Skin from roasted kernel	Skin by-product	Skin by-product	
	Extraction solvent	MeOH-HCl	MeOH	Several polar solvents	$EtOH/H_2O$ (80 : 20)	$Acetone/H_2O$ (80 : 20)	
	Treatment[a]	Acid hydrolysis	None	None	Partition in diethyl ether before and after basic hydrolysis	None	Sephadex LH-20 column
	Analytical technique	GLC/MS	HPLC/UV	LC/MS	HPLC/DAD	LC-DAD-Fluorescence; LC-DAD/ESI-MS	MALDI-TOF MS
	Phenolic class analyzed	Phenolic acids	Simple phenolics	Simple phenolics	Phenolic acids	Flavan-3-ols	
	Unit	µg/g of skin	µg/g of extract	Qualitative data[b]	µg/g of extract	µg catechin equivalent/g of extract	Qualitative data[b]
Phenolic acids	p-OH benzoic acid	tr	453.6	n.d.			
	Caffeic acid	tr		n.d.	tr		
	Chlorogenic acid		49.4				
	p-coumaric acid		6.9		231		
	Ferulic acid	n.d.	n.d.		124		
	Gallic acid	tr	472.4	✓	387		
	Protocatechuic acid	0.36	183.5	✓			
	Sinapic acid				124		
	Vanillic acid	tr	11.3				
	Total phenolic acids	**0.36**	**1177.1**		**866**		
Flavonols	Myricetin		91.2	✓			
	Kaempferol		66.3	✓			
	Quercetin		52.2	✓			
	Total flavonols		**209.7**				

Flavan-3-ols monomers and polymers (condensed tannins)	(+) catechin	993.2	✓	1168.00	
	(−) epicatechin	342.2	✓	n.d.	
	Dimer B3			104.62	
	Unknown dimer B			28.37	
	Trimers[c]				
	3(epi)catechin (2B)				✓
	2(epi)catechin, 1(epi) gallocatechin (1A,1B)				✓
	2(epi)catechin, 1(epi) gallocatechin (2B)				✓
	1(epi)catechin, 2(epi) gallocatechin (1A,1B)				✓
	1(epi)catechin, 2(epi) gallocatechin (2B)				✓
	3(epi)catechin, 1gallate (2B)				✓
	Tetramers[c]				
	4(epi)catechin (3B)				✓
	3(epi)catechin, 1(epi) gallocatechin (3B)				✓
	2(epi)catechin, 2(epi) gallocatechin (3B)				✓
	3(epi)catechin, 1(epi) gallocatechin, 1gallate (3B)				✓
	Pentamers[c]				
	5(epi)catechin (4B)				✓
	4(epi)catechin, 1(epi) gallocatechin (4B)				✓
	3(epi)catechin, 2(epi) gallocatechin (4B)				✓
	4(epi)catechin, 1(epi) gallocatechin, 1gallate (4B)				✓
	Hexamers[c]				
	6(epi)catechin (5B)				✓
	5(epi)catechin, 1(epi) gallocatechin (5B)				✓
	4(epi)catechin, 2(epi) gallocatechin (5B)				✓

Continued

TABLE 72.4 Phenolic Compounds Identified in Hazelnut Skin—continued

	Reference	Senter *et al.*, 1983	Coisson *et al.*, 2002	Travaglia *et al.*, 2006	Shahidi *et al.*, 2007	Monagas *et al.*, 2009
	Heptamers[c]					
	7(epi)catechin (6B)					✓
	6(epi)catechin, 1(epi) gallocatechin (6B)					✓
	5(epi)catechin, 2(epi) gallocatechin (6B)					✓
	Octamers[c]					
	7(epi)catechin, 1(epi) gallocatechin (7B)					✓
	6(epi)catechin, 2(epi) gallocatechin (7B)					✓
	Nonamers[c]					
	7(epi)catechin, 2(epi) gallocatechin (8B)					✓
	Total flavan-3-ols		**1335.4**			**1300.99**
Other phenols	Pyrocatechol		119.8			
	Total phenols quantified	**0.36**	**2842.0**		**866**	**1300.99**

Hazelnut skin emerges as having very high contents of (+) catechin and (−) epicatechin. Flavan-3-ol polymers (tannins) were also found, but not quantified. Several phenolic acids and flavonols (myricetin, kaempferol, quercetin) are also present.

[a] *Treatment of phenolic extract before analysis;*

[b] *✓, reported presence;*

[c] *in brackets, linkage; tr, traces; n.d., not detected.*

TABLE 72.5 Phytoestrogens (μg/100 g) in Hazelnuts

	Reference	Liggins *et al.*, 2000		Thompson *et al.*, 2006
		Dry weight	*Wet weight*	*Wet weight*[a]
Isoflavones	Formononetin			1.2
	Daidzein	5.8	5.52	3.6
	Genistein	19.4	18.47	24.8
	Glycitein			0.5
	Total isoflavones	**25.2**	**23.99**	**30.2**
Lignans	Matairesinol			1.2
	Lariciresinol			14.3
	Pinoresinol			1.1
	Secoisolariciresinol			60.5
	Total lignans			**77.1**
Coumestan	Coumestrol			0.3
	Total phytoestrogens			**107.5**

The major hazelnut phytoestrogens are lignans (mainly secoisolariciresinol); genistein is the major isoflavone. Small amounts of coumestrol are also present.
[a]*Hazelnut with skin (specified by the authors).*

Studies on the composition and *in vitro* antioxidant activity of hazelnut phenolics are intensifying, symptomatic of the great interest of the scientific community regarding their potential beneficial effects. However, more research is needed to fully identify and characterize hazelnut phenolics, to evaluate their bioavailability, to establish the *in vivo* antioxidant action and metabolism of tannin and non-tannin fractions, as well as to elucidate the relationships between antioxidant properties and health benefits.

ADVERSE EFFECTS AND REACTIONS (ALLERGIES AND TOXICITY)

Like other tree nuts, hazelnuts can induce allergic reactions. The allergic responses depend strongly on individual sensitivity, ranging from mild symptoms to severe, life-threatening anaphylactic forms. Hazelnut Cor a 1 (a protein that shows high homology to the major birch pollen allergen Bet v 1) and Cor a 2 (porphyrin) are responsible for mild oral syndromes correlated to pollen sensitivity. More severe clinical symptoms (dermal, abdominal, respiratory, and cardiovascular) are manifestations of non-pollen related allergies involving other hazelnut protein allergens (Cor a 8, Cor a 9, Cor a 11, 2S albumin, and oleosin) (Flinterman *et al.*, 2008).

Nuts, including hazelnuts, are liable to infestation by aflatoxin-producing *Aspergillus*. Mould development may occur during crop growth, but mainly takes place during storage under unhygienic, unventilated, hot, humid conditions. The major aflatoxins produced by the mould are designated B_1, B_2, G_1, and G_2; among them, B_1 is by far the most toxic. The intense carcinogenicity of aflatoxin B1 is related to its oxidation to highly reactive products inducing DNA, RNA, and protein modifications. Thus, aflatoxin contamination is an important issue in the areas of food safety and international trade. To protect consumer health, the maximum aflatoxin content is rigorously controlled by national and international regulations, with limits varying in regulations for different countries.

SUMMARY POINTS

- Hazelnuts are very nutritious and healthful.
- The oil fraction is rich in oleic acid, phytosterols (mainly β-sitosterol), vitamin E, and squalene; this special composition may help diminish the risk of coronary and oxidative stress-induced diseases.

- The nut contains a precious mix of synergistically acting antioxidants, among which are tocopherols (mainly α-tocopherol) and phenolics (especially tannins, essentially located in the brown skin); phytoestrogens, selenium, and squalene contribute towards improving the antioxidant network efficiency.
- The hazelnut skin by-product, being remarkably rich in phenolics, is proposed as an excellent source of natural and powerful antioxidants.
- Dietary antioxidants counteract free radicals, promoters of oxidative deteriorations; the assumption is that hazelnut antioxidants might be a valuable aid against oxidative stress-mediated disorders and diseases, such as inflammatory, cardiovascular, and neurodegenerative diseases, and cancer.
- Because of their richness in nutrients and bioactive health-promoting compounds, there are good reasons for profitably including hazelnuts as part of a nutritious and functional diet.

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