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**The Almond (*Prunus dulcis*):
 Chemical Properties,
 Utilization, and Valorization
 of Coproducts**

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Abstract

Almonds (*Prunus dulcis*) are one of the most consumed tree-nuts worldwide, with commercial production in arid environments such as California, Spain, and Australia. The high consumption of almonds is partly due to their versatile usage in products such as gluten-free flour and dairy alternatives as well as them being a source of protein in vegetarian diets. They contain high concentrations of health-promoting compounds such as Vitamin E and have demonstrated benefits for reducing the risk of cardiovascular disease and improving vascular health. In addition, almonds are the least allergenic tree nut and contain minute quantities of cyanogenic glycosides. Production has increased significantly in the past two decades with 3.12 billion pounds of kernel meat produced in California alone in 2020 (USDA 2021), leading to a new emphasis on the valorization of the coproducts (e.g., hulls, shells, skins, and blanch water). This article presents a review of the chemical composition of almond kernels (e.g., macro and micronutrients, phenolic compounds, cyanogenic glycosides, and allergens) and the current research exploring the valorization of almond coproducts.

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1. INTRODUCTION

The almond (*Prunus dulcis*) is a small deciduous tree in the family Rosaceae native to southwest Asia. It belongs to the subfamily Amygdaloideae, which includes apricots (*Prunus armeniaca*), cherries (*Prunus avium*), nectarines (*Prunus persica*), peaches (*Prunus persica*), and plums (*Prunus domestica*). These plants are drupes, or stone fruit, with each fruit consisting of a hull (the skin or exocarp and the flesh or mesocarp) that surrounds a single shell (the pit, or stone) of a hardened endocarp with a seed (kernel) inside (**Figure 1**). The exocarp and mesocarp are consumed in most stone fruits; however, with almonds, it is the seed that is consumed. Almond hulls and shells are co-products of almond processing and primarily used in the livestock industry; however, new uses are being evaluated that include novel food applications, biocomposites, and bioenergy.

Almonds were domesticated ~5,000 years ago in the Fertile Crescent region of the Middle East and are thought to be one of the oldest cultivated fruits (Ahmed & Vermna 2009, Delplancke et al. 2013, Gulati et al. 2017). Other fruit trees cultivated in this region include olive, fig, and date palm; however, almonds are thought to be the first to be cultivated. Introduction of cultivated almonds in the Eastern Mediterranean took place by 2000 BCE, and global dissemination of almonds began before 1300 BCE (Gradziel 2011). Almonds have been found in archaeological sites, including Numeria, Jordan (3000 BCE) and the tomb of Tutankhamen (1323 BCE), and Hippocrates (circa 460–370 BCE) wrote of their medicinal use in ancient Greece (Mori et al. 2011).

Almonds are taxonomically closest to the peach. They are thought to have originated in Asia from the same primitive species but evolved separately because they were physically separated by mountain ranges in Central Asia 10 million years ago (Gradziel 2011). It is thought that peaches evolved in East Asia and are more popular in certain regions of China and have adapted to more humid and uniform climates at lower elevations. In contrast, almonds thrived in the Mediterranean climates of the Middle East. Almonds evolved to be self-incompatible, which promoted outbreeding and increased genetic diversity (Gradziel 2011).

2. CULTIVATION

Almond production has increased worldwide from 1.03 million metric tons in 2014–2015 to 1.48 million metric tons in 2019–2020 (Shabandeh 2021). Almonds are grown commercially in the United States, Spain, Australia, Morocco, Iran, Italy, Turkey, Tunisia, and Chile (Almond Board Calif. 2020a). California is the main producer of almonds worldwide producing 78% of the world production in 2019–2020 (Almond Board Calif. 2020a).



Figure 1

Anatomy of the developing almond. Mesocarp and exocarp (hull), endocarp (shell), and embryo (kernel) are displayed. Figure adapted with permission of the Almond Board of California.



Figure 2

In-shell almonds showing hull split and exposed shells with pore morphology. Figure reproduced with permission of the Almond Board of California.

The almond blossom is fragile, which restricts production to areas with dry, warm Mediterranean climates, such as California, Chile, and Australia. In California, almond trees are dormant from November through January and bloom mid-February through March. Almonds are one of the earliest blooming of the deciduous fruit and nut trees because of their low winter chilling requirement and fast response to warm spring temperatures (Mori et al. 2011), although they are susceptible to spring frosts (Ahmed & Vermna 2009, Mori et al. 2011). Almonds mature and grow to full size from March through June. In July (variety dependent), the hull splits open and exposes the almond kernel inside, allowing it to begin to dry (**Figure 2**). When hulls turn a straw-yellow color and open completely (August–October), they are harvested mechanically using tree shakers. Almonds are dried on the orchard floor for 7–10 days and then swept into windrows to allow for further drying to reach a kernel moisture content of greater than 6%. At this point, almonds are picked up and stockpiled until they can be processed at a huller/sheller facility. Stockpiled almonds exposed to postharvest moisture may experience damage that can limit shelf life (Rogel-Castillo et al. 2015, 2017).

Because land with Mediterranean climates is limited, production has been increased by selecting varieties that thrive with dense planting to provide higher average productivity in tons per hectare of land. The most common commercial varieties grown in California include Nonpareil, Monterey, and Butte (Almond Board Calif. 2020a). The trees are usually planted from February to March in a square formation with equal spacing between rows. Almonds are generally not self-pollinating and require cross-pollination; therefore, squares include pollinizer trees (i.e., almond trees of a different variety) planted every third row.

Water is an increasingly important resource to consider in the production of all crops grown in Mediterranean climates. Global warming and drought have created an increasing need for innovations in watering practices. In California, almonds are irrigated with ground or surface water, consume nine percent of California's agricultural water, and are widely reported as requiring one gallon of water to grow each almond (Park & Lurie 2014). This perceived high-water usage has led to significant debate regarding the balance between environmental impacts of food production (e.g., water use), nutritional benefits, and public good (Reisman 2019). The California almond industry has long recognized the need for water conservation and has decreased the amount of water used to grow a pound (454 gm) of almonds by 33% over the past 20 years, with a goal of an additional 20% reduction by 2025 (Almond Board Calif. 2020b). Innovations

include identifying optimal irrigation levels that maximize production with minimal water input (Goldhamer & Fereres 2017) and on-farm improvements such as microirrigation (used by 85% of California almond growers), drip irrigation, demand-based irrigation, precision irrigation leaf monitoring systems (Almond Board Calif. 2020b), regulated deficit watering (Stewart et al. 2011), and water stress mapping and targeted watering using unmanned aerial vehicles for remote sensing (Zhao et al. 2017), among others. Innovations in artificial intelligence will continue and almond orchards are increasingly incorporating a range of precision farming technologies (e.g., in-field data, remote sensing, aerial imagery, satellites, weather information) to reduce water usage without compromising tree health or crop yield. For example, irrigation technology can be used to deliver different volumes of water to different parts of the same orchard in response to evapotranspiration rates, weather, and soil moisture sensors.

3. ALMOND MORPHOLOGY

The morphological structure of the almond kernels is distinct from others in the *Prunus* spp. and is unique to each variety of almond. Unlike other *Prunus* spp. in which the shell and kernel are discarded, with almonds it is the kernel that is consumed while the hull and shell are discarded (**Figure 2**). In 2020, 1.8 billion kg of hulls and 0.72 billion kg of shells were produced in California alone (Almond Board Calif. 2020a). Valorization of these materials will improve industry sustainability through zero waste generation.

In general, the almond kernel (cotyledon) has a symmetrical amygdaloidal shape. During fruit ripening, the exocarp, mesocarp, endocarp, and tegument surround and protect the cotyledon as it develops (**Figure 1**). The cotyledon grows from the tip of the almond and eventually fills the entire space inside the tegument, becoming the almond kernel. The tegument becomes the brown skin covering the kernel. The endocarp, which is initially green and quite soft, turns brown and develops a woody texture to become the shell. The mesocarp and the exocarp become the almond hull (**Figure 1**). The thickness and density of the almond hull can vary depending on the variety of the almond. During maturation, the hull becomes dry and leathery, ultimately splitting to reveal the shell underneath. There are four different ways the hull can split, e.g., ventral split, ventral and dorsal split, four-way split, and dorsal split, which can be used to identify different almond varieties (Gradziel 2011). The shell helps protect the kernel from insects as it grows. The almond shell can be classified as hard, semihard, or soft, with the hardness correlating to the lignin content of the shell. The main constituents of almond shells include cellulose (~38%), hemicellulose (~29%), and lignin (30%) (Li et al. 2018). Almond shells have unique markings made by pores with varying sizes, shapes, and quantities as well as grooves that are unique to each variety. Shells can also be smooth or have channels or grooves (**Figure 2**).

The size and shape of the kernel are determined by genetics as well as environmental factors such as crop density, tree health, soil nutrition, and irrigation. Kernel growth occurs primarily in the spring, whereas kernel mass continuously increases until nut maturity is reached. Almonds come in a range of sizes, shapes, and shell characteristics. For example, almonds can have a hard smooth shell containing a long, narrow-shaped kernel with a deeply wrinkled surface (Monterey); a soft shell containing a medium, flat-shaped kernel with a smooth surface (Nonpareil); or a semi-hard shell containing a small, short, plump-shaped kernel with a wrinkled surface (Butte) (**Figure 3**).

There are hundreds of distinct almond varieties grown around the world, and each country possesses a particular varietal platform. In California, there are approximately 30 commercialized varieties grown; however, the five major varieties grown in 2019–2020 were Nonpareil (41%),

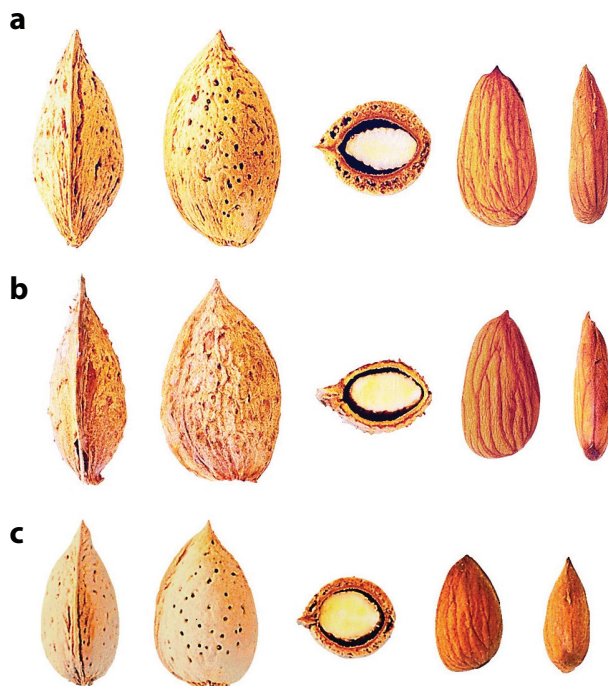


Figure 3

The morphology of the almond shell and kernel differ with variety. (a) Monterey almonds with a hard, smooth shell containing a long, narrow-shaped kernel with a deeply wrinkled surface. (b) Nonpareil almonds with a soft shell containing a medium, flat-shaped kernel with a smooth surface. (c) Butte almonds with a semi-hard shell containing a small, short, plump-shaped kernel with a wrinkled surface.

Monterey (18%), Butte/Padre (12%), Independence (6%), and Carmel (5%) (Almond Board Calif. 2020a). Top varieties in Spain include Marcona, Langueta, Ferragnes, Valencias, and Guara. In Italy, ~90% of the almond orchards are located in Apulia and Sicily. Here, varieties are classified based on their place of origin [e.g., Tuono, Genco, and Fragiulio (Apulia), Pizzuta, Fascionello, Romana, and Bonifacio (Sicily)].

4. ALMONDS AND HEALTH

Almonds are nutritionally dense and have been studied extensively for their positive impact on serum lipids (Bento et al. 2014, Hyson et al. 2002, Liu et al. 2018), heart health (Berryman et al. 2015, Jalali-Khanabadi et al. 2010, Jenkins et al. 2002), diabetes (Cohen & Johnston 2011, Jenkins et al. 2006, Li et al. 2011), and weight management (Dhillon et al. 2016) and are increasingly popular as a complementary protein in plant-based diets. The first study linking almond consumption to a reduced risk of coronary heart disease was published in 1998 (Spiller et al. 1998). Numerous other studies followed directly linking almond intake with improved markers of cardiovascular health, including lowering blood low-density lipoprotein (LDL) cholesterol (Bento et al. 2014, Berryman et al. 2015, Dikariyanto et al. 2020, Gulati et al. 2017, Hyson et al. 2002, Liu et al. 2018, Zibaenezhad et al. 2019). In 2003, the US Food and Drug Administration (FDA) granted almonds a qualified heart-health claim stating that “scientific evidence suggests, but does not prove, that eating 1.5 ounces (42.5 g) of most nuts, as part of a diet low in saturated fat and

cholesterol may reduce the risk of heart disease” (FDA 2003). In 2016, the US FDA categorized almonds as healthy based on updated FDA criteria for lipid content in foods. A recent review of 64 randomized controlled clinical trials concluded that almond intake of 42.5 g/day significantly lowered LDL cholesterol and diastolic blood pressure (Dreher 2021). Interestingly, eating 42.5 g of almonds daily was also shown as a cost-effective approach for preventing cardiovascular disease (Wang et al. 2020). Dietary surveys continue to show that consumption of whole almonds is associated with better diet quality, reduced risk of cardiovascular disease, and a significant improvement in flow-mediated dilation or vascular health (Dikariyanto et al. 2021). The current recommended daily intake of almonds is 30–50 g as part of a healthy diet (Gama et al. 2018). A 30 g serving is equivalent to about 23 almonds (variety dependent). The relevant clinical trials associating almond consumption with health-promoting properties were recently summarized by Barreca et al. (2020) and Dreher (2021).

5. ALMOND COMPOSITION

5.1. Macronutrients

Almonds are low in saturated fat, free of cholesterol and sodium, and easily portable and relatively nonperishable. The nutrient content of a 28 g serving of almonds is considered an excellent source (containing > 20% US Daily Value) of vitamin E (50%), riboflavin (25%), and magnesium (20%) and is a good source (containing 10–20% US Daily Value) of dietary fiber (13%) (Almond Board Calif. 2016). The nutrient composition of almonds is influenced by genotype (variety), agro-environmental factors, nut maturity, and storage conditions after harvest (Agar et al. 1998, Nanos et al. 2002, Sanahuja et al. 2021, Yada et al. 2013). A summary of the nutrient composition of almond kernels, hulls, and shells of different varieties, which includes data from the US Department of Agriculture (USDA) National Nutrient Database for Standard Reference (USDA 2019) can be found in **Tables 1** and **2**. Almonds contain 10–29% protein by weight (avg. 21%) with one 30 g serving providing around 6.3 g of protein (**Table 1**). Almond protein contains a high relative percentage of arginine (2.465 g/100 g protein) and has good digestibility (Yada et al. 2011). The Protein Digestibility-Corrected Amino Acid Score (PDCAAS) is 44.3–47.8 (House et al. 2019) and free amino acid levels are ≤ 200 mg/100 g in ripe kernels (Soler et al. 1989).

Although the almond kernel is composed of 32–66% total fat (**Table 1**), the fat is primarily monounsaturated fats and therefore possesses high oxidative stability (Fernandes et al. 2017). The most abundant unsaturated fatty acids in almonds are oleic acid (O-18:1, 50–81%), linoleic acid (L-18:2, 6–37%), linolenic acid (Ln-18:3, 0–11%), and palmitoleic acid (16:1, 0.1–2.5%), and the most abundant saturated fatty acid is palmitic acid (C16:0, 5–16%) (Fernandes et al. 2017). The main fatty acid isomer is the ω -9 oleic acid (C18:1 ω -9), whereas the ω -7 and ω -11 oleic acids constitute less than 2% of the total (Fernandes et al. 2017). The most abundant triacylglycerols are O-L-Ln (27%), O-L-O (28%), and O-O-O (13%). Although relatively stable, almonds, like all high-fat foods, are susceptible to oxidation and the formation of a range of acids, alcohols, aldehydes, and ketones associated with off-aromas and consumer rejection (Franklin & Mitchell 2019, Franklin et al. 2017).

Phytosterols are lipophilic steroid alcohols (sterols and stanols) similar to cholesterol and are well known for their ability to lower cholesterol levels by preventing cholesterol reabsorption. A daily dose of 2–3 g of phytosterols has been shown to reduce LDL cholesterol levels by 5–15% (Demonty et al. 2009, MacKay & Jones 2011). The main phytosterols in almonds include β -sitosterol (56–95 mg/kg) and Δ 5-avenasterol (8.5–28 mg/kg) (Fernandes et al. 2017). Significant genotypic effects are observed for phytosterol content and concentration in kernels (Fernández-Cuesta et al. 2012, Yada et al. 2013).

Table 1 Nutritional content of almond kernels

Macronutrients	Range (g/100 g)	Average (g/100 g)	References
Moisture	1.68–6.53	4.25	Barreira et al. 2012, Chung et al. 2013, King et al. 2019, Simsek et al. 2018, Summo et al. 2018, USDA 2019, Yada et al. 2013
Carbohydrate	14–26.63	21	Barreira et al. 2012, Chung et al. 2013, Summo et al. 2018, USDA 2019
Protein	10–29	21	Barreira et al. 2012, Chung et al. 2013, Drogoudi et al. 2013, King et al. 2019, Kodad et al. 2013, Özcan et al. 2011, Simsek et al. 2018, Summo et al. 2018, USDA 2019, Yada et al. 2013
Total lipids	31.72–66.1	52.3	Barreira et al. 2012, Chung et al. 2013, Gama et al. 2018, Gouta et al. 2021, King et al. 2019, Kodad et al. 2013, Simsek et al. 2018, USDA 2019, Yada et al. 2013, Zamany et al. 2017
SFAs	3.2–11.98	7.1	Barreira et al. 2012, Chung et al. 2013, Gouta et al. 2021, King et al. 2019, USDA 2019, Yada et al. 2013, Zamany et al. 2017
MUFAs	26.6–82.54	55.9	Barreira et al. 2012, Chung et al. 2013, Gouta et al. 2021, King et al. 2019, USDA 2019, Yada et al. 2013, Zamany et al. 2017
PUFAs	8.35–29.92	15.53	Barreira et al. 2012, Chung et al. 2013, Gouta et al. 2021, King et al. 2019, USDA 2019, Yada et al. 2013, Zamany et al. 2017
Sugar	2.1–6.5	4.1	Gouta et al. 2021, King et al. 2019, Simsek et al. 2018, USDA 2019
Micronutrients	Range (mg/100 g)	Average (mg/100 g)	References
Potassium	465–1,510	831.0	Drogoudi et al. 2013, Gama et al. 2018, King et al. 2019, Özcan et al. 2011, Simsek et al. 2018, USDA 2019, Yada et al. 2013
Calcium	160–663	271	Drogoudi et al. 2013, Gama et al. 2018, King et al. 2019, Özcan et al. 2011, Simsek et al. 2018, USDA 2019, Yada et al. 2013
Magnesium	159–404	304.0	Drogoudi et al. 2013, Gama et al. 2018, King et al. 2019, Özcan et al. 2011, Simsek et al. 2018, USDA 2019, Yada et al. 2013
Phosphorus	310–938	597	Drogoudi et al. 2013, Gama et al. 2018, King et al. 2019, Özcan et al. 2011, Simsek et al. 2018, USDA 2019, Yada et al. 2013
Copper	0.463–4.76	1.76	Gama et al. 2018, King et al. 2019, Özcan et al. 2011, Simsek et al. 2018, USDA 2019, Yada et al. 2013
Manganese	1.31–3.97	2.66	Gama et al. 2018, King et al. 2019, Özcan et al. 2011, Simsek et al. 2018, USDA 2019, Yada et al. 2013
α -Tocopherol	13.91–38	25	Barreira et al. 2012, Chung et al. 2013, King et al. 2019, Stuetz et al. 2017, USDA 2019, Yada et al. 2013, Zamany et al. 2017
Riboflavin (Vitamin B2)	0.46–2.26	1.25	USDA 2019, Yada et al. 2013

Abbreviations: MUFAs, monounsaturated fatty acids; PUFAs, polyunsaturated fatty acids; SFAs, saturated fatty acids.

A 30 g serving of almonds also provides approximately 6 g of carbohydrates composed of soluble sugars (1.3 g), starch (0.2 g), and nonstarch polysaccharides or dietary fiber (4 g). Like lipids and other nutrients, carbohydrate levels vary across cultivars and growing regions; however, at harvest, the primary sugar is sucrose (90%). The dietary fiber of almonds and almond skins has also been shown to have prebiotic effects on gut microbiota (Liu et al. 2014, Mandalari et al. 2010a). A 100 g serving of almonds contains 14.0–26.6 g of dietary fiber (**Table 1**), which provides about 15% of the daily requirement of dietary fiber. The major source of dietary fiber is the cell walls of the seed, which are high in arabinose-rich polysaccharides and phenolic compounds (Ellis et al. 2004). Cell wall encapsulation of lipids has been shown to hinder the release of lipids from the kernel and thereby decrease their bioaccessibility for digestion (Ellis et al. 2004, Grundy et al. 2015). Limited bioaccessibility of lipids may help explain the paradoxical finding relating increased almond (high in fat) consumption with reduced risk of cardiovascular disease.

Table 2 Composition of almond hulls and shells

Analyte	Hulls		Shells		Reference(s)
	Range (% wt)	Average (% wt)	Range (% wt)	Average (% wt)	
Dry matter	83.5–96.2	89.8	NA	NA	DePeters et al. 2020, Jafari et al. 2015, Wang et al. 2021
Crude protein	2.3–26.5	6.7	NA	NA	DePeters et al. 2020, Jafari et al. 2015, Wang et al. 2021
Carbohydrates	NA	NA	NA	56.1	Queirós et al. 2020
Sugars	15.9–18.1	17	NA	NA	Wang et al. 2021
Ash	3.5–12.8	7.8	0.7–1.1	0.9	Deniz 2013, DePeters et al. 2020, Holtman et al. 2015, Jafari et al. 2015, Nabais et al. 2011, Queirós et al. 2020, Wang et al. 2021
Potassium	2.5–4.0	3.2	NA	6,714.2	DePeters et al. 2020, Queirós et al. 2020, Wang et al. 2021
Calcium	0.2–0.4	0.3	NA	1,570	DePeters et al. 2020, Jafari et al. 2015, Queirós et al. 2020, Wang et al. 2021
Fiber	12.1–26.4	16.1	NA	NA	DePeters et al. 2020, Wang et al. 2021
Lignin	7.0–12.8	9.6	24.8–30.0	27.7	Deniz 2013, DePeters et al. 2020, Holtman et al. 2015, Nabais et al. 2011, Queirós et al. 2020, Wartelle & Marshall 2001
Hemicellulose	NA	6	19.7–35.2	26.8	Deniz 2013, Holtman et al. 2015, Nabais et al. 2011, Wartelle & Marshall 2001
Cellulose	NA	6.6	29.0–40.5	34	Deniz 2013, Holtman et al. 2015, Nabais et al. 2011, Wartelle & Marshall 2001

Abbreviation: NA, not available.

5.2. Micronutrients

Minerals and vitamins are important components of almonds. The major elements include potassium (465–1,510 mg/kg), phosphorus (310–938 mg/kg), calcium (160–663 mg/kg), and magnesium (159–404 mg/kg), and almonds are considered an excellent source of manganese (1.31–3.97 mg/100 g) and a good source of copper (0.463–4.76 mg/100 g) (**Table 1**). The mineral composition of almonds depends on agronomic and regional factors due to uptake from soil, water, and fertilizers (Piscopo et al. 2010) and also varies with genotype (Özcan et al. 2011). This leads to variability in the mineral content of almonds depending on geographical location and agricultural practices (Drogoudi et al. 2013).

Almonds have a high content of vitamin E tocopherols (α , β , γ , δ) and riboflavin (vitamin B2). The levels of tocopherols are higher in almonds relative to other tree nuts (Fernandes et al. 2017) and decrease slowly during storage (Franklin et al. 2017). α -Tocopherol is the main isomer and has been shown to range from 8.5–84.0 mg/100 g in kernels, whereas β -tocopherol (0.012–0.8 mg/100 g), γ -tocopherol (0.014–0.084 mg/100 g), and δ -tocopherol (0.002–0.016 mg/100 g) are found at lower levels (Kodad et al. 2018). The tocopherols impart significant antioxidant stability to almond oil along with their health benefits, although composition varies significantly between the genotypes studied (Kodad et al. 2006, Yada et al. 2013, Zamany et al. 2017) and with temperature differences and water application (Kodad et al. 2011). For example, α -tocopherol levels were found to range between 18.2 and 32.9 mg/100 g in seven commercial almond varieties grown in California (Yada et al. 2013). It was recently shown that daily consumption of 50 g of Afghan almonds (average 30 mg/100 g α -tocopherol) is enough to meet the current RDA for this vitamin (Zamany et al. 2017).

5.3. Phenolic Compounds

Phenolic compounds are found in most edible plant tissues, including tree nuts. They are secondary plant metabolites synthesized through the shikimic acid, pentose phosphate, and phenylpropanoid pathways. In plants, phenolic compounds function as antioxidants, structural polymers (lignin), pollinator attractors (anthocyanidins), UV protectants (flavonoids), antioxidants (flavonoids), signaling compounds (flavonoids), and defense response chemicals (tannins). Epidemiology studies suggest numerous health benefits associated with the consumption of phenolic compounds, especially in the context of reducing the incidence of chronic disease such as cancer (Del Rio et al. 2013). However, it should be noted that *in vivo*, values of antioxidant capacity have no relevance to the effects of specific bioactive compounds on human health. This is because these compounds undergo extensive metabolism during digestion and metabolism and undergo food–matrix interactions that influence their bioaccessibility. Phenolic compounds have numerous applications in foods, beverages, and personal care products as antioxidants, sunscreens, nutraceuticals, and cosmeceuticals.

Almonds provide a range of phenolic compounds concentrated in the skin (70–100% of total phenolic compounds) where they contribute to almond color and astringency (Garrido et al. 2008). They are also found in almond blanch water (1.389 mg/100 g) (Mandalari et al. 2010b) and hulls with an average of 3,385 mg/100 g of dry matter (Jafari et al. 2015). The number of phenolic compounds present in the blanch water can vary depending on the temperature and time of the blanching process (Hughes et al. 2012). To date, approximately 130 phenolic compounds have been identified in almonds, but many still elude quantification due to a lack of authentic standards. Climate and agro-environmental factors can result in seasonal variation in the phenolic content of almonds (Bolling et al. 2010).

Phenolic compounds can be placed into eight different main categories based on their carbon skeleton: the simple phenolics (e.g., hydroxybenzoic acids [C_6C_1] and hydroxycinnamic acids [C_6C_3]), dimeric phenolics (e.g., stilbenes [$C_6C_2C_6$], flavonoids [$C_6C_3C_6$] and lignans [$(C_6C_3)_2$]) and oligomeric or polymerized phenolic compounds (e.g., hydrolyzable tannins [$(C_6C_1)_5$], condensed tannins or proanthocyanidins [$(C_6C_3C_6)_n = 2-20$], and lignins [$(C_6C_3)_n > 100$]).

In skin, the predominant phenolic compounds are chlorogenic acid (9.5 mg/100 g), catechin (11.04 mg/100 g), epicatechin (12.47 mg/100 g), and isorhamnetin-3-O-rutinoside (48.5 mg/100 g) (**Table 3**). The most abundant phenolic compounds in whole almonds are proanthocyanidins (67.1–257 mg/100 g), hydrolyzable tannins (72.9–91.5 mg/100 g), and flavonoids (13.0–93.8 mg/100 g) (Bolling 2017). Hydrolyzable tannins in almonds include ellagitannins (53–57 mg/100 g), gallotannins (20–34 mg/100 g), and ellagic acid (0.51 mg/100 g) (Xie et al. 2012). Phenolic acids and aldehydes range from 5.12 to 12.2 mg/100 g in whole almonds, with the most abundant being protocatechuic acid, aldehyde, chlorogenic acid, ferulic acid, *p*-hydroxybenzoic acid, *p*-coumaric acid, and gallic acid (Bolling 2017).

Almond proanthocyanins consist of (–)-epicatechin and (+)-catechin with mainly B-type interflavan bonds at C4 to C6 or C8 (Gu et al. 2003). The main proanthocyanidin dimers include B1, B2, B3, B5, and B7 (De Pascual-Teresa et al. 1998). The average degree of polymerization is 12.7 (Gu et al. 2003).

5.4. Cyanogenic Glycosides

Cyanogenic glycosides are glycosides of α -hydroxynitriles (cyanohydrins) common to plants in the Rosaceae family. Cyanogenic glycosides provide plants with immediate chemical defense against herbivores and pathogens via the generation of hydrogen cyanide (HCN). To date, ~60 different cyanogenic glycosides have been identified in plants and levels can vary depending on

Table 3 Phenolic content of almond skins

Phenolic compounds	Range (μg/g)	Average (μg/g)	Reference(s)
Benzoic acids			
<i>p</i> -Hydroxybenzoic	3.9–12.3	7	Bolling et al. 2009, Pasqualone et al. 2018
Vanillic	3.1–58.1	24	Barreca et al. 2020, Mandalari et al. 2010b
Protocatechuic	2.9–62.0	25.3	Bolling et al. 2009, Mandalari et al. 2010b, Pasqualone et al. 2018
Cinnamic acids			
Chlorogenic	NA	95.7	Mandalari et al. 2010b
<i>p</i> -Coumaric	NA	3.7	Mandalari et al. 2010b
Flavonoids			
Catechin	7.3–366.3	110.4	Bolling et al. 2009, Hughey et al. 2012, Mandalari et al. 2010b, Pasqualone et al. 2018, Valdés et al. 2015
Epicatechin	1.3–724.0	124.7	Bolling et al. 2009, Hughey et al. 2012, Mandalari et al. 2010b, Pasqualone et al. 2018, Valdés et al. 2015
Quercetin	0.01–2.14	1.23	Bolling et al. 2009, Mandalari et al. 2010b
Quercetin-3-O-glucoside	NA	33.8	Mandalari et al. 2010b
Quercetin-3-O-galactoside	8.8–13.7	11.9	Bolling et al. 2009, Mandalari et al. 2010b
Quercetin-3-O-rhamnoside	10.3–32.0	17.5	Bolling et al. 2009, Mandalari et al. 2010b
Kaempferol-3-O-rutinoside	1.0–238.7	128.1	Bolling et al. 2009, Hughey et al. 2012, Mandalari et al. 2010b, Pasqualone et al. 2018, Valdés et al. 2015
Kaempferol-3-O-glucoside	19.6–37.7	30.1	Bolling et al. 2009, Pasqualone et al. 2018
Isorhamnetin	7.8–45.4	19.3	Bolling et al. 2009, Mandalari et al. 2010b, Pasqualone et al. 2018
Isorhamnetin-3-O-glucoside	2.0–169.4	67.6	Bolling et al. 2009, Mandalari et al. 2010b, Valdés et al. 2015
Isorhamnetin-3-O-rutinoside	26.5–756.5	485.1	Bolling et al. 2009, Pasqualone et al. 2018, Valdés et al. 2015

Abbreviation: NA, not available.

genetic factors and environmental pressures. Cyanogenic glycosides are segregated in vacuoles. When plant tissues are disrupted (via, e.g., chewing or physical damage), damaged vacuoles allow the cyanogenic glycosides to come into contact with β-glucosidases (E.C. 3.2.1.117) and hydroxynitrile lyase (E.C. 4.1.2.10) enzymes. Hydrolysis by β-glucosidase results in the release of sugar(s) and a cyanohydrin. The resulting cyanohydrin is relatively unstable and spontaneously degrades (pH < 6.0) or can be enzymatically cleaved by hydroxynitrile lyase to produce HCN and an aldehyde or ketone (Thodberg et al. 2018). β-Glucosidase enzymes are also found in the human small intestine as well as in many common foods and are important in the bioavailability of dietary flavonoids (Németh et al. 2003).

In almonds, the primary cyanogenic glycosides are amygdalin (D-mandelonitrile-β-D-glucoside-6-β-D-glucoside) and prunasin (D-mandelonitrile-β-D-glucoside) (**Figure 4**). Amygdalin and prunasin possess a nitrile group that gives them a bitter characteristic. Amygdalin levels are relatively low in sweet almond (0.0631 mg/g) compared to bitter almond (40.06 ± 0.78 mg/g) (Lee et al. 2013) and vary with variety (Luo et al. 2018).

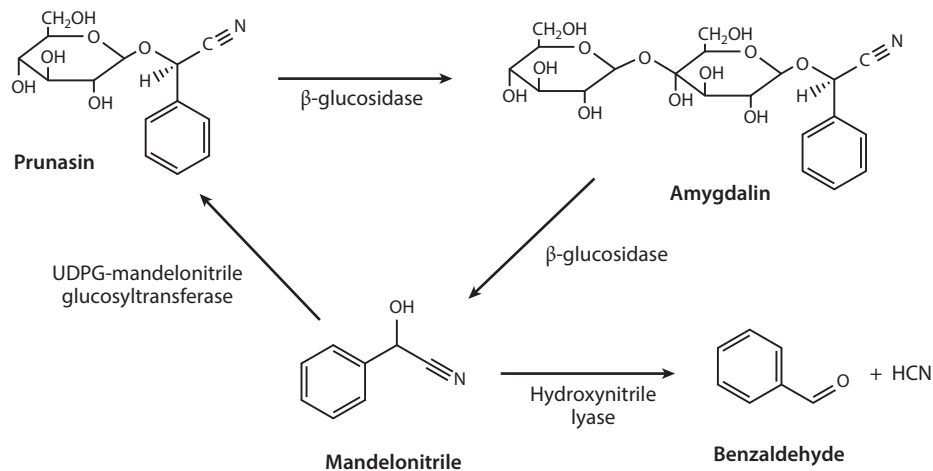


Figure 4

Synthesis of prunasin (D-mandelonitrile-β-D-glucoside) and hydrolysis of amygdalin (D-mandelonitrile-β-D-glucoside-6-β-D-glucoside) with formation of benzaldehyde and hydrogen cyanide (HCN).

Abbreviation: UDPG, uridine diphosphate glucose.

The synthesis and degradation of prunasin and amygdalin in almond kernels were first described by Sánchez-Pérez et al. (2008) (**Figure 4**). Prunasin is biosynthesized from phenylalanine in the seed coat (tegument) of almonds. Sánchez-Pérez et al. (2019) and Thodberg et al. (2018) demonstrated that the first two enzymes in the prunasin biosynthetic pathway are the cytochrome P450 monooxygenases PdCYP79D16 and PdCYP71AN24, which are poorly expressed in the tegument of sweet genotypes relative to bitter genotypes. A single point mutation in the transcription factor results in the formation of a P450 that can no longer catalyze the conversion of phenylalanine into the oxime and then to the prunasin precursor mandelonitrile. A lack of mandelonitrile limits prunasin synthesis and results in the sweet almond phenotype. To date, prunasin has been found in all vegetative parts of the almond tree, including roots, leaves, and developing kernels; however, only bitter genotypes accumulate amygdalin in the kernel (Dicenta et al. 2002). The prunasin levels in vegetative tissues are independent of the amygdalin content in kernels and, therefore, cannot predict kernel bitterness (Dicenta et al. 2002, Sánchez-Pérez et al. 2008). Although amygdalin levels are very low in sweet almond kernels, it is still found in the leaves and bark of the trees, as it confers protection from potential pests.

Amygdalin is a pharmaceutically interesting compound demonstrating antibacterial, anti-atherosclerotic, antiasthmatic, and anticancer activity in *in vitro* cell culture studies; however, it is also toxic due to the enzymatic production of HCN (Jaszczak-Wilke et al. 2021). Acute cyanide toxicity can occur in humans at doses between 0.5 and 3.5 mg/kg body weight. Levels of amygdalin in commercial sweet almonds are well below the threshold for any public health concern due to their consumption (Lee et al. 2013). Consumption of bitter almonds is not recommended due to the potential of cyanide toxicity.

5.5. Allergens

A food allergy is an adverse health effect arising from a specific immune response that occurs reproducibly upon exposure to a given food. Allergies to foods have been on the increase for many years; however, early introduction of allergenic foods is an important way forward to help reduce

the prevalence and severity of food allergies (Gupta 2019, Gupta et al. 2019). Almonds are the least allergenic of all tree-nuts (Gupta 2019); however, like all nuts, they require allergen labeling in the United States and European Union (Xiong et al. 2019). Food allergens are usually proteins, and each identified allergen is given a distinct name by the World Health Organization (WHO) and International Union of Immunological Societies (IUIS) Allergen Nomenclature Subcommittee. The naming contains the first three letters of the genus, followed by the letters of the species and a numeric number indicating the identification order of the allergen in the species. For example, the first identified almond (*Prunus dulcis*) allergen is named Pru du 1.

Although almond allergy is considered rare (0.7% prevalence of tree nut allergies), numerous proteins have been identified as potential allergens in almonds (i.e., Pru du 1, Pru du 2 and 2S, Pru du 3, 4, 5, 6, 9, 10, vicilin, and γ -conglutin); however, only six are currently recognized by WHO-IUIS (<http://www.allergen.org/>) as being allergenic and include Pru du 3, 4, 5, 6, 8, and 10 (Gupta 2019, Gupta et al. 2019).

Pru du 3 is a member of the subfamily of nonspecific lipid transfer proteins. This protein produces systemic and life-threatening symptoms (Mandalari & Mackie 2018). Pru du 4 (profilin) is an actin-binding protein that produces only mild symptoms limited to the oral cavity (Mandalari & Mackie 2018). The amount of profilin compared to other storage proteins found in almonds is considered minute (Zhang et al. 2014). Little information is available about Pru du 5, a ribosomal protein found in almonds (Abolhassani & Roux 2009), and more studies are needed to understand the immunological and biochemical properties of this protein. Pru du 6, also known as amandin, is one of the most widely studied allergens in almonds. It is a major seed storage protein accounting for ~65% of the total almond protein, and ingestion can result in severe IgE allergic-type reactions (Mandalari & Mackie 2018). This allergen is a promising candidate as an almond allergen marker (Kabasser et al. 2020). Pru du 8 is the first disulfide-rich antimicrobial peptide/protein to be determined as a food allergen (Che et al. 2019). Although expressed as an allergen in almonds, further studies are needed to confirm that other Pru du 8 orthologs in other foods are also food allergens. Pru du 10, the newest member of the allergen database, is a mandelonitrile lyase and is recognized as an almond-specific allergen (Kabasser et al. 2020). Potential allergenic almond proteins without WHO-IUIS-recognized names include Pru du 1 and Pru du 2, which are adaptive stress proteins and seed storage proteins (Costa et al. 2012), and Pru du vicilin and Pru du γ -conglutin, which are storage proteins (Zhang & Jin 2020).

6. ALMOND PRODUCTION AND COPRODUCT VALORIZATION

Almond production involves growing, hulling, and shelling and the manufacture of almond products. Almond production generates large amounts of coproducts, including hulls, shells, skins, and blanch water (**Figure 5**). The hulls on average account for ~52% of the total fresh weight, and the shells and kernel (including skin) account for ~32.0% and 15.0% of the total fresh weight, respectively (Godini 1984). Processing can also include dry or oil roasting, slicing, chopping, and conversion into marzipan paste (bitter almonds) or flavorings. The majority of almonds are consumed as snacks or as ingredients in manufactured goods. Almond flour and almond milk are increasingly popular as gluten-free and dairy alternatives. Green almonds are unripened almonds (almond oysters) and are becoming popular with chefs in gourmet restaurants and cuisines.

6.1. Almond Coproduct Valorization

With increasing almond production, there is also an increase in the amount of coproduct created. In 2019–2020, 1.645 billion pounds of shells and 4.031 billion pounds of hulls were created in California alone (Almond Board Calif. 2020a). Hulls and shells are primarily used in livestock and

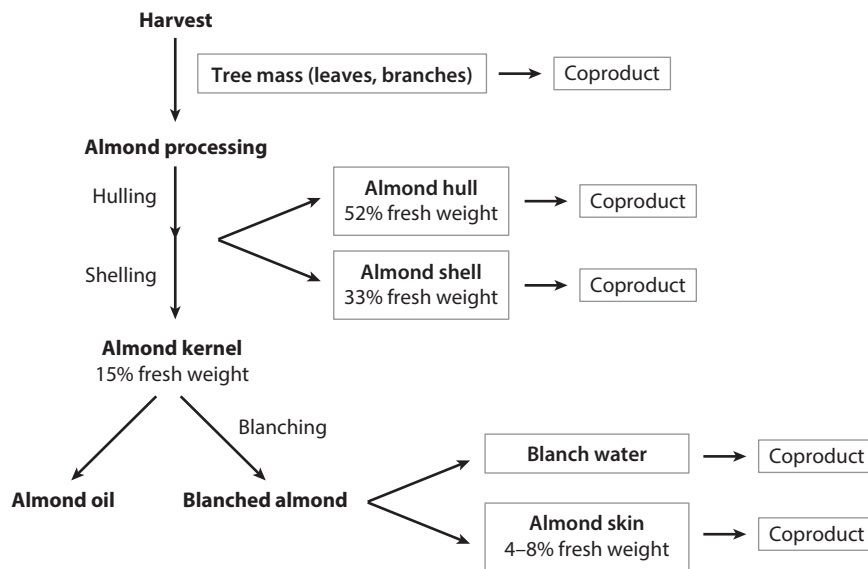


Figure 5

A flow diagram demonstrating coproducts generated through almond harvesting and processing. The processing includes almond whole nut, almond oil, and blanching.

biofuel production, whereas skins and blanch water are primarily disposed of but can be a source of value-added phenolic compounds and used in food upcycling (Pasqualone et al. 2020). A large percentage of hulls are purchased by dairy and poultry farmers to increase the nutritional and fiber content of animal feed. Almond shells are also used as animal bedding and as feedstock for green energy production (Table 4). Anaerobic digestion of hulls and shells can produce biogas (e.g., methane) and heat and is increasingly being used to manage almond coproducts (Mandalari et al. 2010b, Vandermeersch et al. 2014). Coproducts can also be applied back into almond orchards. For example, almond shells can be used as bioenergy feedstock for green energy production of biochar for soil conditioning using an anaerobic digester (Kaur et al. 2020). Additionally, almond trees that are at the end of their production lives can be ground up and mixed back into the soil to promote soil health and increase water-holding capacity (Jahanzaad et al. 2020). Biosolarization is an alternative technology to soil fumigation that relies on a combination of solar radiation and organic matter application to soil to kill agricultural pests and bacteria. Amendments used for biosolarization may contain endogenous compounds toxic to pests (e.g., organic acids, phenolics) or can be subjected to fermentation by soil microbiota to form toxic metabolites. Almond shells and hulls can be used as materials for the amendments needed for biosolarization (Shea et al. 2020, 2021). For example, a recent study demonstrated that almond hulls and a hull and shell mixture were suitable amendments for controlling *Pratylenchus vulnus* and potentially other soil agricultural pests in simulated biosolarization experiments (Fernandez-Bayo et al. 2020). The application of high-carbon natural materials such as almond shells to the soil has the added benefit of preventing nitrogen leaching into the groundwater (CASFS 2019).

6.2. Valorization of Almond Coproducts

The purpose of valorization is to repurpose coproducts generated during food manufacturing and redirect them from landfills. Reducing coproduct materials discarded in landfills will help reduce

Table 4 Alternative uses for almond coproducts: shell, hulls, skins, and blanch water

Almond coproduct	Use	Description	Reference(s)
Shell	Energy production	Feedstock for anaerobic digestion for production of heat and biogas	Vandermeersch et al. 2014
	Strengthen available polymers	Shells are turned into biochar through torrefaction and added to postconsumer plastics	Chiou et al. 2016, Garcia et al. 2020, McCaffrey et al. 2018
	Bioplastics	Cellulose is converted to cellulose acetate for bioplastics	Mostafa et al. 2018
	Ceramic membranes	Lignin, hemicellulose, and cellulose in powdered shells are used for making microfiltration membranes	Ahmed & Mir 2021
	Source of antioxidants	Phenolic compounds recovery from alkali hemicellulose extractions	Ebringerova et al. 2015
	Source of lignin	Feedstock for renewable materials and reinforced biocomposites	de Hoyos-Martínez et al. 2018
	Source of xylooligosaccharides	Source of low-degree polymerized xylooligosaccharides for prebiotic and antioxidant purposes and low-calorie sweetener	Nabarlatz et al. 2005, Singh et al. 2019
	Green construction material	Activator in alkali-activated cement	Soriano et al. 2021
Hull	Livestock feed	Supplement to feed for nutrients and fiber	Aguilar et al. 1984
	Energy production	Feedstock for anaerobic digestion for production of heat and biogas	Vandermeersch et al. 2014
	Biosolarization material	Applied to the soil to create a healthy microbiome, beneficial for fighting agricultural pests	Fernandez-Bayo et al. 2020; Shea et al. 2020, 2021
	Green construction material	Material for low-cost panels that can be used for interior walls, floorings, and furniture	Ferrandez-Villena et al. 2019, Pirayesh & Khazaeian 2012
	Soil amendment	Prevent nitrogen leaching into the groundwater when applied to the soil	CASFS 2019
	Source of antioxidant	Phenolic compound recovery from alkali hemicellulose extractions	Ebringerova et al. 2015
	Source of bioactive compounds	Extraction of betulinic, oleanolic, and ursolic acid for anticancer and/or anti-HIV properties for foods, drugs, and supplements	Cichewicz & Kouzi 2004, Dar et al. 2016, Spatafora 2012, Zhao et al. 2012, Zhu et al. 2001
	Growth medium	Alternative to traditional peat moss for mushroom cultivation	Almond Board Calif. 2018
Skin	Energy production	Feedstock for anaerobic digestion for production of heat and biogas	Mandalari et al. 2010b, Vandermeersch et al. 2014
	Food preservation, nutritional supplements	Phenolic compounds for addition to food, personal care products, and supplements	Mandalari et al. 2010b, Prgomet et al. 2017
	Food supplement	Added to baked products to increase fiber, fats, and phenolic and antioxidant compounds	Pasqualone et al. 2020
Blanch water	Food preservation, nutritional supplements	Phenolic compounds for addition to food, personal care products, and supplements	Mandalari et al. 2010b, Prgomet et al. 2017

greenhouse gas emissions, which contributes to global warming. Valorization uses a combination of green chemical, physical, and/or enzymatic extraction methods to obtain essential compounds that can be utilized to add value to food products or produce sustainable options for current materials. Almond coproducts are a rich source of many valuable compounds that can be extracted and reutilized (**Table 4**). For example, almond skin is an excellent source of dietary fiber, soluble

dietary fiber, lipids, and proteins (Mandalari et al. 2010a). It also contains a high content of phenolic compounds (60–80% of the total phenolic content of almonds) (Prgomet et al. 2017). Blanch water, used to remove the skin, also contains a high percentage of the phenolic compounds leached out during the blanching process (Mandalari et al. 2010b). Precipitated postblanching water has been shown to contain a range of nonpolar phenolic aglycones, partially insoluble glycosides, and water-soluble catechins (Hughey et al. 2012). The antioxidants and phenolic compounds extracted from almond skins and blanch water can be used in food and personal care products as antioxidants and preservatives. To stabilize phenolic compounds and reduce degradation, the compounds can be encapsulated (Prgomet et al. 2017). Spray drying is the most common and rapid method to encapsulate phenolic compounds (Munin & Edwards-Lévy 2011).

Almond hulls and shells are an additional source of material for value-added ingredients. The shell is composed of cellulose, hemicellulose, and lignin (Ledbetter 2008). Although the hull composition can vary greatly based on genetic and agro-environmental factors (Prgomet et al. 2017), it contains a high percentage of cellulose (20.6–35.2%), and crude lignin (7.5–15.6%) (Homedes et al. 1993).

There are numerous studies investigating the extraction and application of fibers found in plant materials to create more sustainable packaging and plastics. Torrefaction is a simple yet energy-intensive method used to convert almonds shells into a charcoal-like material (biochar). Torrefaction involves heating almond shells to between 200 and 300°C under inert conditions to remove moisture and volatile components and produce a stable, high-density product that can be used in plastics. This material adds strength and stability to the available plastics, reducing the need to produce new plastics (Chiou et al. 2016). Almonds have potential use as a source of biofibers as filler and to reinforce polymer composites (biocomposites) (Garcia et al. 2020, Valdés García et al. 2014). The fortification of existing plastic is an important first step, but the goal is to completely eliminate petroleum-based, nonsustainable plastics. Almond shells can be used in other materials such as in the formation of ceramic membranes for microfiltration. For example, powdered almond shells, used as a pore-forming agent for ceramic membranes, resulted in a product with good chemical stability and low production costs (Ahmed & Mir 2021). Ceramic membranes have better stability than polymeric membranes, and the use of almond waste will make the production of these membranes economical and sustainable. Ground almond hulls can also be used to make low-cost panels that can be used in the production of interior walls, floorings, and furniture (Ferrandez-Villena et al. 2019, Pirayesh & Khazaeian 2012).

The carbohydrate component of shells and hulls can be applied to food products as well. For example, after extracting hemicellulose using NaOH, the water-soluble portion of the hemicellulose fraction contains antioxidant compounds, with antioxidant activity supported by DPPH testing (Ebringerova et al. 2015). This would provide a polysaccharide-based antioxidant applicable to food products. Almond shells also have the capacity to be a source of low-degree polymerized xylooligosaccharides as prebiotics (Singh et al. 2019) for use in polysaccharide-based antioxidants for food, supplements, and personal care products. The hemicellulose can also provide xylan, which accounts for one-third of the mass of almond shells (Nabarlantz et al. 2005). Xylooligosaccharides produced enzymatically from xylan-rich hemicellulose can be used as a low-calorie sweetener and a source of soluble fiber (Nabarlantz et al. 2005). There are components of almond coproducts other than fibers that are beneficial to the food industry. For example, 700 mg of betulinic acid and a total of 4 g of oleanolic and ursolic acids can be extracted from 1 kg of almond hulls (Spatafora 2012). The three acids are known for their anticancer and/or anti-HIV properties (Cichewicz & Kouzi 2004, Dar et al. 2016, Zhao et al. 2012, Zhu et al. 2001) and can be used as phytochemicals in supplements or food products.

7. CONCLUSIONS

Almonds are the least allergenic tree nut, are low in cyanogenic glycosides, and contain many valuable nutrients and phytochemicals. Studies continue to support an association between almond consumption and healthier serum lipids, decreased cardiovascular risk, and improved vascular health and weight management. Sustainability in almond production includes improved use of water through new technologies, zero-waste generation, and valorizing coproducts and reduces carbon emissions, among others. Building a circular economy that utilizes on-farm biomass and coproduct materials as a source of biofuels, bio-based chemicals, and other bioproducts is of great value and necessary for ensuring a low carbon footprint and industry sustainability. A better understanding of the composition of the coproducts is still needed for identifying new uses and optimizing and valorizing existing materials.

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Errata

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