**Title**
Chemical Characterization of Almond (Prunus dulcis) Varieties



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Chemical Characterization of Almond (*Prunus dulcis*) Varieties

By

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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. High consumption is due to its versatile usage in products such as gluten-free flour and dairy alternatives, as well as a source of protein in vegetarian diets. Almonds contain high concentrations of health-promoting compounds such as Vitamin E and has 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 meats produced in California alone in 2020 (USDA 2021) leading to a new emphasis on the valorization of coproducts (e.g., donhulls, shells, skins, and blanch water). This paper presents comparison of chemical characterization across sixty commercial and new experimental varieties of almonds cultivated in California, Spain, and Australia. The samples can be clustered in to seven sections, with UCD 1-232 standing out from other varieties. It also explores the chemical composition of almond kernels (e.g. macro-, and micronutrients, phenolic compounds, cyanogenic glycosides, and allergens) and current research exploring the valorization of almond coproducts.

# Chapter 1- Introduction

## History

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*). The fruit of 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 fruit, however with almonds it is the seed that is consumed. Almond hulls and shells are coproducts of almond processing and are primarily used for feed 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, Jordon (3000 BCE) and the tomb of Tutankhamen (1323 BCE), and Hippocrates (c.460-370 BCE) wrote of their medicinal use in ancient Greece (Mori et al. 2011)

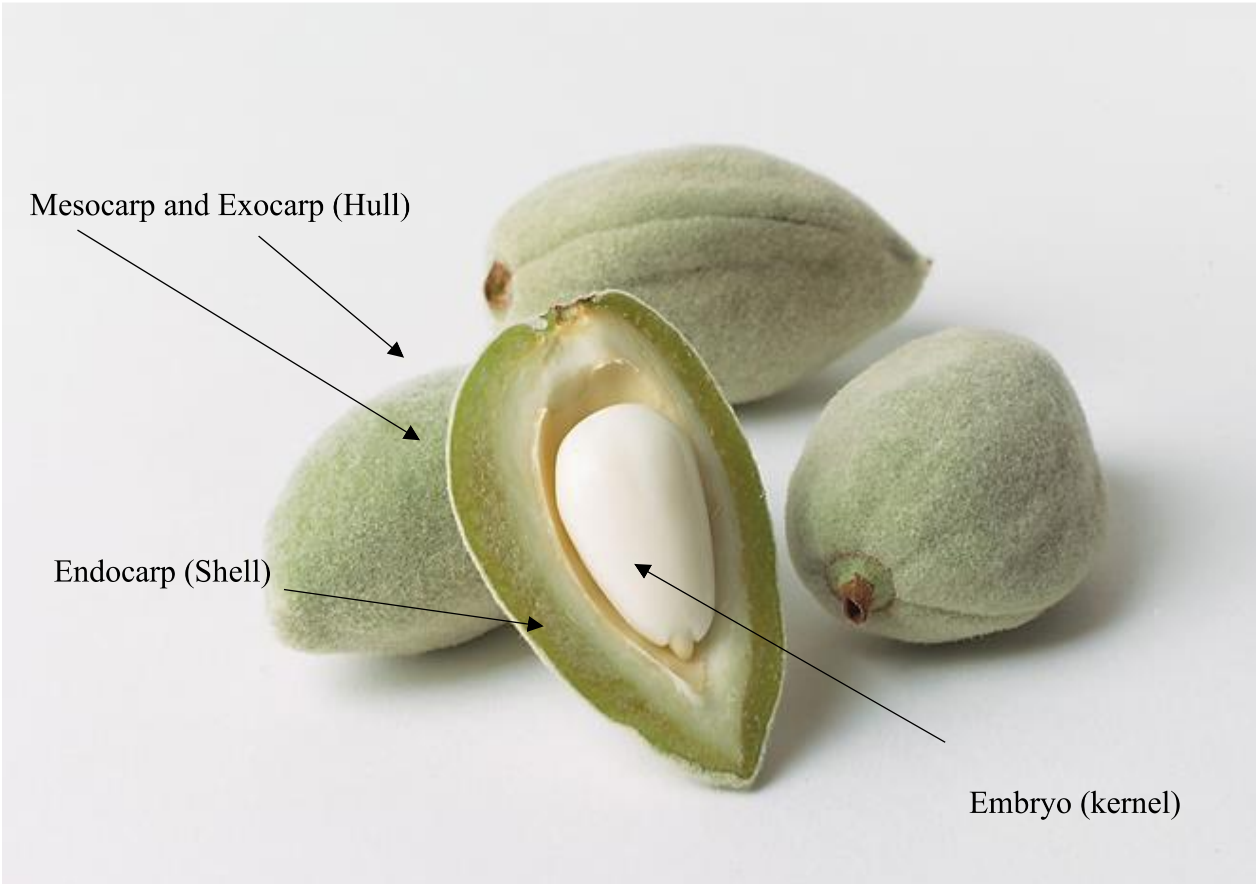


**Figure 1.** Anatomy of the developing almond. Mesocarp and exocarp (hull), endocarp (shell), and embryo (kernel) is displayed. The seedcoat has been removed in this image. Figure adapted with permission of the Almond Board of California.

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, due to it being more popular in certain regions of China and have adapted to more humid and uniform climates at slower elevation. In contrast, almonds thrived in Mediterranean climates of the Middle East. Almonds evolved to be self-incompatible when it comes to breeding, which promoted outbreeding and increased genetic diversity (Gradziel 2011).

**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 Sates, Spain, Australia, Morocco, Iran, Italy, Turkey, Tunisia, and Chile (Almond Board of California 2020a). California is the main producer of almonds worldwide producing 78% of the world production in 2019-2020 (Almond Board of California 2020a).

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 tree species, because of their low winter chilling requirement and fast response to warm spring temperatures (Mori et al. 2011). However, 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 endocarp (shell) and kernel inside allowing them 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 alongside the tree to allow for further drying to reach a kernel moisture content of < 6%. At this point, almonds are picked up and stockpiled until they can be processed at a huller/sheller facility. Stockpiled almonds exposed to post-harvest moisture, such as rain during wet harvest seasons, may experience damage that can limit shelf life (Rogel-Castillo et al. 2015, 2017).

**Figure 2.** In shell almonds showing hull split and exposed shells with pore morphology. Figure reproduced with permission of the Almond Board of California.

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

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 irrigation practices. In California, almonds are irrigated with ground or surface water, consume approximately nine percent of California's agricultural water, and require approximately one gallon of water to grow each almond kernel to maturity through irrigation watering methods (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 of California 2020b). Innovations to conserve water include identifying optimal irrigation levels that maximize production with minimal water input (Goldhamer & Fereres 2017), and on farm improvements such as micro-irrigation (used by 85 percent of California almond growers), demand-based irrigation, precision irrigation leaf monitoring systems (Almond Board of California 2020b), regulated deficit watering (Stewart et al, 2011), and water stress mapping and targeted watering using unmanned aerial vehicles (UAVs) 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, etc.,) 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.

**Almond Morphology**

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 of California 2020a). Valorization of these materials will improve industry sustainability through zero waste generation.

In general, the almond kernel (consisting of an embryo and a pair of cotyledons) has a symmetrical amygdaloidal shape. During fruit ripening the exocarp, mesocarp, endocarp and integument surround and protect the embryo and two cotyledons as they develop (**Figure 1**). The cotyledons grow from the tip of the almond and eventually fill almost the entire space inside the integument becoming the almond kernel. The integument 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 together with the exocarp will become the almond hull (**Figure 1**). The thickness and density of the almond hull varies 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 of the different almond varieties (Gradziel 2011). The shell helps protect the kernel from insects as it grows. The almond shell can be classified as hard, semi-hard 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 deep wrinkled surface (Monterey); a soft shell containing a medium flat shaped kernel with a smooth surface (Nonpareil); or have 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 mixture. In California, there are approximately thirty commercialized varieties grown, however the five major varieties grown in 2019-2020 were Nonpareil (41%), Monterey (18%), Butte/Padre (12%), Independence (6%), and Carmel (5%) (Almond Board of California 2020a). The top almond varieties in Spain include Marcona, Largueta, Ferragnes, Valencias and Guara. In Italy, ~90% of the almond orchards area located in Apulia and Sicily where varieties are classified based upon their place of origin [e.g. Tuono, Genco and Fragiulio (Apulia), Pizzuta, Fascionello, Romana and Bonifacio (Sicily)].

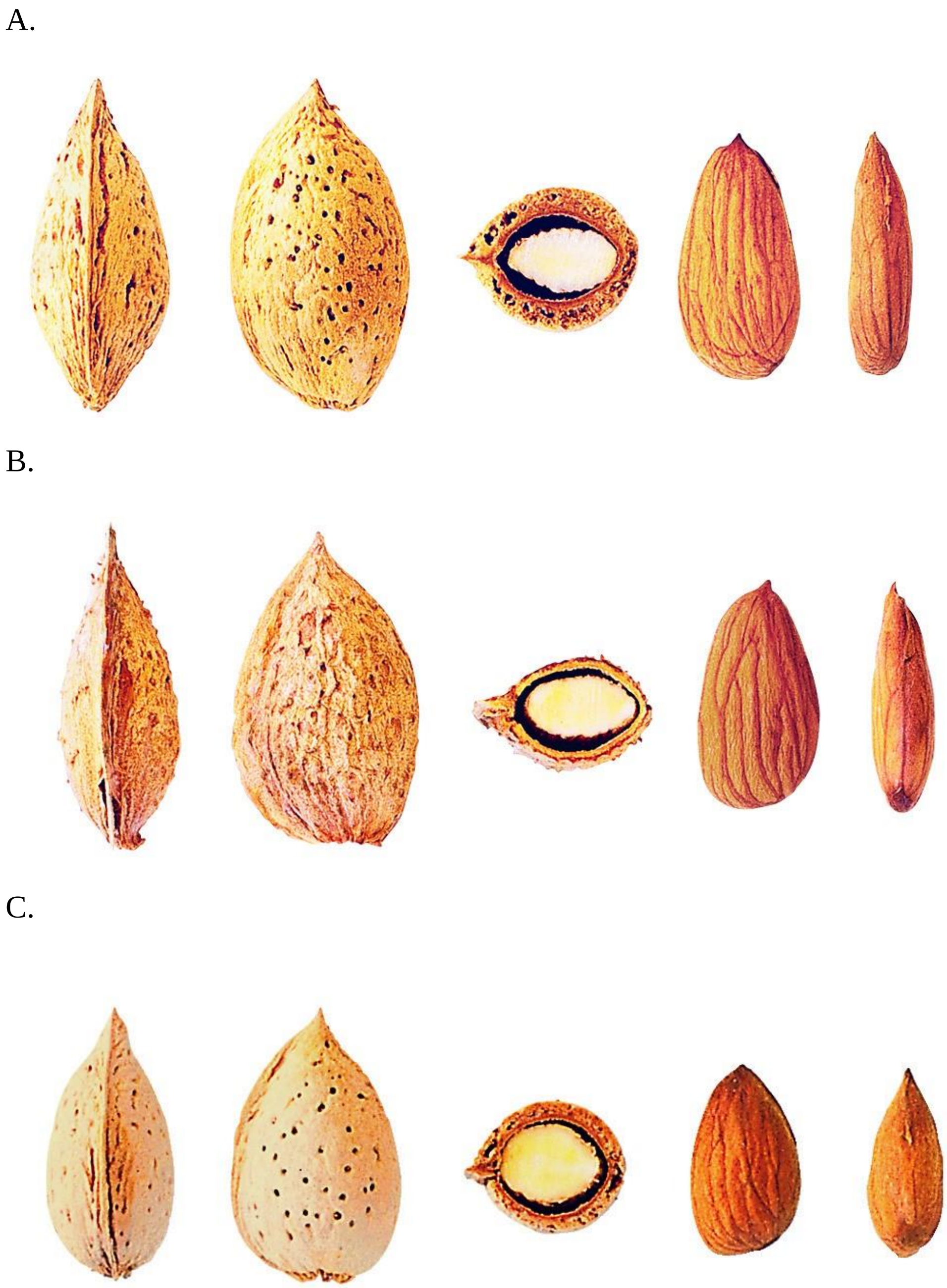


**Figure 3.** The morphology of the almond shell and kernel differ with variety. This figure show (A) Monterey almonds with a hard smooth shell containing a long narrow shaped kernel with a deep wrinkled surface; (B) Nonpareil almonds with a soft shell containing a medium flat shaped kernel with a smooth surface; and (C) Butte almonds with a semi-hard shell containing a small, short plump shaped kernel with a wrinkled surface.

**Almond Composition**

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). They 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; Zibaeenezhad 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 sixty-four randomized controlled clinical trials concluded that 42.5 g / day intake of almonds significantly lowered LDL cholesterol and diastolic blood pressure (Dreher 2021). Interestingly, eating 42.5 g 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 (FMD) or vascular health (Dikariyanto et al. 2021). The current recommended daily intake of almonds is 30 to 50 g as part of a healthy diet (Gama et al. 2018). A 30 g serving is equivalent to about 23 almonds (variety dependent). Review of the relevant clinical trials associating almond consumption with health-promoting properties were recently summarized by Barreca et al. (2020) and Dreher (2021).

**Macronutrients**

Almonds are low in saturated fat, free of cholesterol and sodium, and are easily portable and relatively non-perishable. 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 of California). The nutrient composition of almonds is influenced by genotype (variety), agro-environmental factors, nut maturity, and by storage conditions after harvest (Agar et al. 1998; Nanos et al. 2002; Sanahuja et al. 2021; Yada et al. 2013). A summary of nutrient composition of almond kernels, hulls and shells of different varieties, which includes data from the U.S. 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) (Chen et al. 2006)and has good digestibility (Ahrens et al. 2005). The Protein Digestibility-Corrected Amino Acid Score (PDCAAS) of almonds ranges between 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 $\omega$-9 oleic acid (C18:1 $\omega$-9) whereas the $\omega$-7 and $\omega$-11 oleic acids constitute less than 2% of the total (Fernandes et al. 2017). The most abundant triacylglycerols are OLLN (27%), OLO (28 %) and OOO (13%). Although relatively stable, almonds, like all high-fat containing foods, are susceptible to oxidation and 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 $\beta$-sitosterol (56-95 mg/kg) and Δ5-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).

A 30 g serving of almond also provides approximately 6 g of carbohydrates, composed of soluble sugars (1.3 g), starch (0.2 g) and non-starch 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 100g serving of almonds contain 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 hinders the release of lipids from the kernel and thereby decreases their bio-accessibility for digestion (Ellis et al. 2004; Grundy et al. 2015). Limited bio-accessibility of lipids may help explain the paradoxical finding relating increased high-fat almond consumption with reduced risk of cardiovascular disease.

**Micronutrients**

Minerals and vitamins are important components of almonds. The major elements include potassium (465-1510 mg/100g), phosphorus (310-938 mg/100g), calcium (160-663 mg/100g), and magnesium (159-404 mg/100g) (**Table 1**). Almonds are also considered an excellent source of manganese (1.31-3.97 mg/100g) and a good source of copper (0.463-4.76 mg/100g) (**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/100g in kernels whereas β-tocopherol (0.012-0.8 mg/100g), γ-tocopherol (0.014-0.084 mg/100g) and δ-tocopherol (0.002-0.016 mg/100g) 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 among 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 18.2–32.9 mg/100g 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/100g α-tocopherol) is enough to meet current RDA for this vitamin. (Zamany et al. 2017).

**Table 1.** Nutritional content of almond kernels

| Macronutrients | Range (g/100g) | Average (g/100g) | Reference |
|---|---|---|---|
| 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. 2013a |
| 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. 2013a |
| 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. 2013a; 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. 2013a; 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. 2013a; 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. 2013a; 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/100g) | Average (mg/100g) | References |
|---|---|---|---|
| Potassium | 465 - 1510 | 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.

**Table 2.** The composition of almond hulls and shells.

| Analyte | Hulls Range (% wt) | Hulls Average (%wt) | Shells Range (%wt) | Shells Average (%wt) | Reference(s) |
|---|---|---|---|---|---|
| Dry Matter | 83.5-96.2 | 89.8 | N/A | N/A | DePeters et al. 2020; Jafari et al. 2015; Wang et al. 2021 |
| Crude Protein | 2.3-26.5 | 6.7 | N/A | N/A | DePeters et al. 2020; Jafari et al. 2015; Wang et al. 2021 |
| Carbohydrates | N/A | N/A | N/A | 56.1 | Queirós et al. 2020 |
| Sugars | 15.9-18.1 | 17 | N/A | N/A | 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 | N/A | 6714.2 | DePeters et al. 2020; Queirós et al. 2020; Wang et al. 2021 |
| Calcium | 0.2-0.4 | 0.3 | N/A | 1570 | DePeters et al. 2020; Jafari et al. 2015; Queirós et al. 2020; Wang et al. 2021 |
| Fiber | 12.1-26.4 | 16.1 | N/A | N/A | 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 | N/A | 6 | 19.7-35.2 | 26.8 | Deniz 2013; Holtman et al. 2015; Nabais et al. 2011; Wartelle & Marshall 2001 |
| Cellulose | N/A | 6.6 | 29.0-40.5 | 34 | Deniz 2013; Holtman et al. 2015; Nabais et al. 2011; Wartelle & Marshall 2001 |

Abbreviation: NA, not available

### Benzaldehyde and Volatile Compounds

Volatile compounds are the source of flavor properties of foods. The combination of these compounds gives foods the unique aroma perceived by olfactory neurons and is tied to overall liking and perception of the food. Volatile compounds found in raw almonds include aldehydes, ketones, alcohols, alkanes, acids, pyrazines, terpenes, sulfur containing compounds, and heterocyclic compounds (Xiao et al. 2014; Franklin 2019). Almond flavor is positively associated with benzaldehyde, phenylethyl alcohol, and benzyl alcohol while negatively associated with hexanal and pentanal (King et al. 2019). Benzaldehyde is the main volatile compound associated with almond flavor. This compound is a degradation product of the cyanogenic glycoside amygdalin that is released during chewing along with hydrogen cyanide (**Figure 4**). Synthetic almond flavor found in extracts and oils is from benzaldehyde, with the attributed flavor of marzipan. Although benzaldehyde can be found at high concentrations in almonds and play a major role in the almond flavor profile, other compounds play a role in the overall aroma of almonds. Franklin et. al (2017) conducted a sensory test looking at overall liking and amora qualities of common almond volatiles. They characterized aldehydes to be a penetrating aroma such as "grassy, cucumber, fatty, citrus peel, fruity, and floral" (Franklin et al. 2017). Alcohol compounds can give fermentative aromas, ketones can give an earthy tone such as mushroom-like flavor, and organic acids can have sweaty and cheesy aromas ranging to metallic (Franklin et al. 2017). The presence of hexane leads to development of oxidative off-flavors (Mexis et al. 2009).

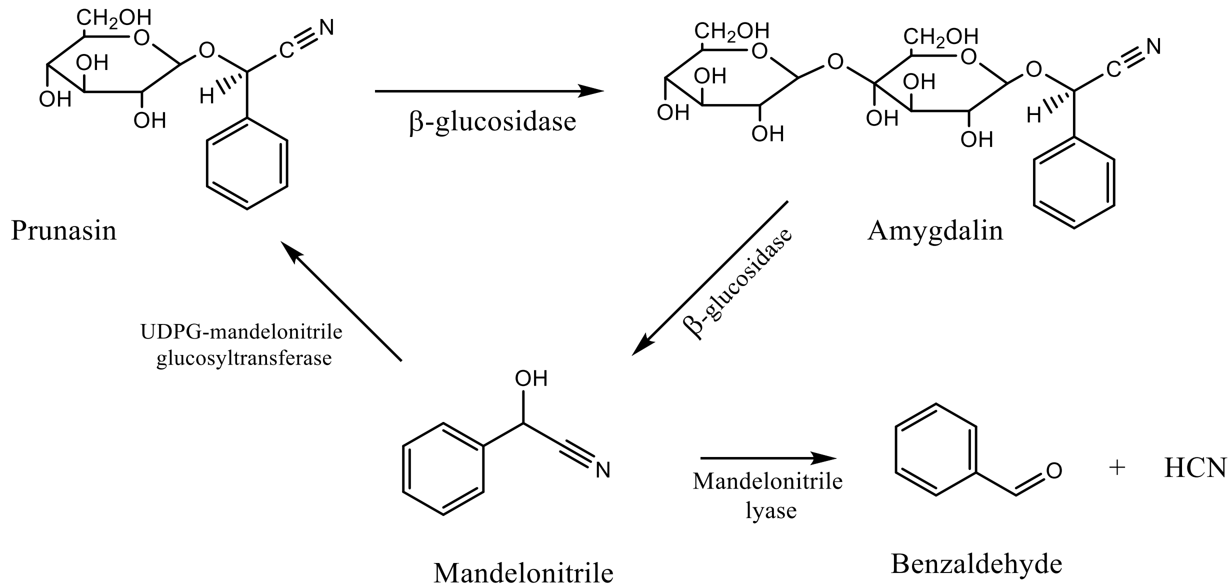


**Figure 4.** Synthesis of prunasin (D-mandelonitrile-*β*-D-glucoside) and hydrolysis of amygdalin (D-mandelonitrile-*β*-D-glucoside-6-*β*-D- glucoside) with formation of benzaldehyde and hydrogen cyanide.

The types and concentration of volatiles can vary with cultivar and growing regions (Beltrán Sanahuja et al. 2011). Beltrán Sanahuja et al. (2011) found that Spanish cultivars Marcona and Guara had higher volatile content when compared with the California cultivar Butte and concluded composition of aroma is directly related to the type of cultivar. Out of common varieites grown in California, King et al. (2019) and Luo et al. (2018) found that Aldrich and Fritz were higher in total flavor intensity, specifically with marzipan/benzaldehyde flavor. This correlates with findings of higher amygdalin concentrations in these two varieties (Luo et al. 2018; Lee et al. 2013), along with finding that amygdalin varied with growing regions (Lee et al. 2013). Aldrich also had high benzaldehyde concentration in the analyzed headspace (17995.00 ± 5886.65 ng/g) when compared with other varietals (Luo et al. 2018). Mexis et al. (2009) found thirteen volatiles with benzaldehyde as a dominant compound at a concentration of 1839200 ± 84100 ng/g. Xiao et al. (2014) found fourty-one volatiles including thirteen carbonyls, one pyrazine, twenty alcohols and seven additional volatiles. Benzaldehyde was also found at high concentration in this study with 2934.6 ± 272.5 ng/g (Xiao et al. 2014). Two terpene compounds, α-pinene, and limonene were detected at low concentration $<17$ ng/g (Xiao et al. 2014).

**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 bio-accessibility. Phenolic compounds have numerous applications in foods, beverages and personal care products as antioxidants, sunscreens, nutraceuticals, and cosmeceuticals. 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. hydrolysable tannins [$(C_6C_1)_5$], condensed tannins or proanthocyanidins [$(C_6C_3C_6)_{n\,=\,2\text{-}20}$] and lignins [$(C_6C_3)_{n\,>\,100}$].

Almonds provide a range of phenolic compounds concentrated in the skin (20-100% 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/100g) (Mandalari et al. 2010b) and hulls with an average of 3,385 mg/100g of dry matter (Jafari et al. 2015). The amount of phenolic compounds present in the blanch water can vary depending on the temperature and time of the blanching process (Hughey et al. 2012). To date, about 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). In skin, the predominant phenolic compounds are chlorogenic acid (9.5 mg/100g), catechin (11.04 mg/100g), epicatechin (12.47 mg/100g) and isorhamnetin-3-O-rutinoside (48.5 mg/100g) (**Table 3**). The most abundant phenolic compounds in whole almonds are proanthocyanidins (67.1–257 mg/100g), hydrolyzable tannins (72.9-91.5 mg/100g), and flavonoids (13.0-93.8 mg/100g) (Bolling 2017). Hydrolyzable tannins in almonds include ellagitannins (53-57 mg/100 g), gallotannins (20-34 mg/100g) and ellagic acid (0.51 mg /100g) respectively (Xie et al. 2012). Phenolic acids and aldehydes range from 5.12 to 12.2 mg/100g in whole almonds, with the most abundant being protocatechuic acid, aldehyde, chlorogenic acid, ferulic acid, *p*-hydroxybenzoic acid, *p*-courmaric acid and gallic acid (Bolling 2017). Almond proanthocyanins consist of (−)-epicatechin and (+)-catechin with mainly B-type interfalvan 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).

**Table 3.** Phenolic content in almond skins.

| Phenolic Compounds | Range (µg/g) | Average (µg/g) | Reference(s) |
|---|---|---|---|
| **Benzoic acids** | | | |
| *p*-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 |
| Protocachuic | 2.9-62.0 | 25.3 | Bolling et al. 2009; Mandalari et al. 2010b; Pasqualone et al. 2018 |
| **Cinnamic Acids** | | | |
| Chlorogenic | N/A | 95.7 | Mandalari et al. 2010b |
| *p*-Courmaric | N/A | 3.7 | Mandalari et al. 2010b |
| **Flavonoids** | | | |
| Catechin | 7.3-366.3 | 110.4 | Bolling et al. 2009; Hughey et al. 2012b; Mandalari et al. 2010b; Pasqualone et al. 2018; Valdés et al. 2015 |
| Epicatchin | 1.3-724.0 | 124.7 | Bolling et al. 2009; Hughey et al. 2012b; 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 | N/A | 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. 2012b; 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

**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 generation of hydrogen cyanide (HCN). To date, ~sixty different cyanogenic glycosides have been identified in plants and levels can vary depending upon genetic factors and environmental pressures. Cyanogenic glycosides are sequestered in vacuoles. When plant tissues are disrupted (e.g., chewing, physical damage, etc.) 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 a 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-$\beta$-D-glucoside-6-$\beta$-D-glucoside) and prunasin (D-mandelonitrile-$\beta$-D-glucoside (**Figure 4)**. Amygdalin and prunasin possess a nitrile group which gives them a bitter characteristic. Amygdalin levels are relatively low in sweet almond (0.0631 mg $g^{-1}$) when compared to bitter almond (40.06 ± 0.78 mg $g^{-1}$) (Lee et al. 2013) and vary with variety (Luo et al. 2018). 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 (integument) 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 integument 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 these trees, as it confers protection to the trees from potential pests.

Amygdalin is a pharmaceutically interesting compound demonstrating antibacterial, anti-atherosclerotic, anti-asthmatic and anti-cancer activity in *in vitro* cell culture studies however, is also toxic due to the enzymatic production of hydrogen cyanide (HCN) (Jaszczak-Wilke et al.

2021). Acute cyanide toxicity can occur in humans at doses between 0.5 and 3.5 mg kg-1 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.

**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 haves 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 with 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 allergies are 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 y-conglutin) however only six are currently recognized by WHO-IUIS (WHO/IUIS Allergen Nomenclature Sub-Committee) 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 almond (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 almond, 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).

### Almond Production and Coproduct Valorization

Almond production involves growing, hulling and shelling and the manufacture of almond products. The process 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 un-ripened almonds (almond oysters) and are becoming popular with chefs in gourmet restaurants and cuisines.

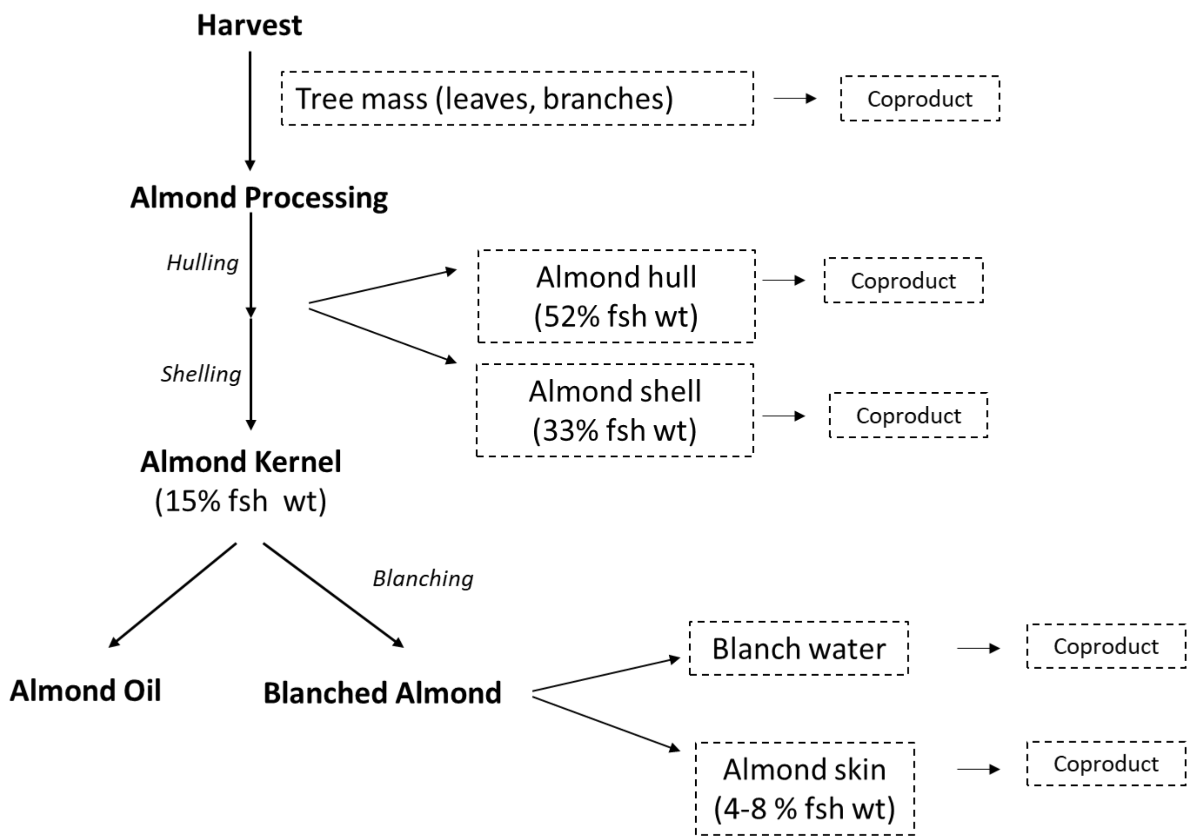


**Figure 5.** A flow diagram demonstrating coproducts generated through almond harvesting and processing. The processing includes almond whole nut, almond oil, and blanching.

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 of California 2020a). Hulls and shells are primarily used in livestock and biofuel production, whereas skins and blanch water are primarily disposed of, yet 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 productive lives can be ground up and mixed back into the soil to promote soil health and increase water holding capacity (Jahanzad 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* nematodes 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).

**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 in to bio-char through torrefaction and added to post-consumer 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 in to the groundwater when applied to the soil | CASFS 2019 |
| | Source of Antioxidant | Phenolic compounds recovery from alkali hemicellulose extractions | Ebringerova et al. 2015 |
| | Source of Bioactive Compounds | Extraction of betulinic, oleanolic and ursolic acid for anti-cancer 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. 2010 |
| | Growth Medium | Alternative to traditional peat moss for mushroom cultivation | California 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 | Mandalari et al. 2010b; Prgomet et al. 2017 |

| | | | |
|---|---|---|---|
| | | care products and supplements | |
| | Food Supplement | Added to baked products to increase fiber, fats, phenolic compounds, 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 |

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 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, the 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 post-blanching 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 to 35.2%,) and crude lignin (7.5 to 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 (bio-char). 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) (Valdés García et al. 2014)(Garcia et al. 2020). The fortification of existing plastic is an important first step, however the goal is to completely eliminate petroleum based, non-sustainable 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 over polymeric membranes, and the use of almond waste can 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 used as 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 1/3 of the mass of almond shells (Nabarlatz et al. 2005). Xylo-oligosaccharides produced enzymatically from xylan rich hemicellulose can be used as a low-calorie sweetener and a source of soluble fiber (Nabarlatz 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 acid can be extracted from 1 kg of almond hulls (Spatafora 2012). These three acids are known for their anti-cancer and/or anti-HIV properties (Cichewicz & Kouzi 2004; Dar et al. 2016; Zhao et al. 2012; Zhu et al. 2010) and can be used as phytoceuticals, in supplements or food products.

To summarize, the chemical composition of almonds is complex and contain many beneficial compounds (e.g. vitamins, phenolic compounds) when consumed. Additionally, there is high potential for the reutilization of processing coproducts. Valorization of almond coproducts can provide feedstocks and a natural source of nutritional compounds in order to add value to food products and reduce food waste.

# Chapter 2 Chemical Characterization of New Almond Varietals for Commercialization

## Introduction

The Almond Board of California (ABC) has been funding almond varietal development since the early 1970s. On-going research includes long-term and multilocational Regional Varietal Trials (RVTs) to test the performance of potential new varieties across different growing locations and environmental conditions. Varieties developed at universities, the USDA, commercial nurseries and by private breeders are important in introducing new almond varieties and must be observed in large-scale variety trials to understand commercial viability. Climate change, increasing population, and a rising demand for almonds presents an on-going need for improving production and quality of new varieties that can be grown on less land and use less water.

In 2019, the ABC hosted what was called a "Crack-Out" event. This event brought together stake-holders integral to the production of almonds from across the globe. The participants included public and private breeders, growers and handlers, hullers/shellers, University of California Cooperative Extension (UCCE) researchers, farm advisors, and nursery representatives for an opportunity to sample current varieties that are being grown in the RVTs and identify new potential varietals for future RVTs. The RVTs always contain a mixture of new potential varieties as well as established commercial varieties for comparison. This event was aimed at identifying new high-yield, disease resistant almonds that have excellent nutritional and flavor characteristics. The samples included over sixty varieties from UC Davis and USDA breeding programs, private breeders, nurseries in California, and varieties from Australia, Spain and Israel.

This research focused on quantifying and comparing the chemical and physical attributes of sixty almond varieties being grown in the current RVTs or imported from Australia, Spain, and Israel in support of the "Crack-out" event. Data obtained will help support identification of new experimental almond varieties with excellent flavor and nutritional profiles. Maintaining good quality characteristics, in new experimental varieties, is critical to the success of this commodity. The characteristics evaluated herein include L*a*b* color values, moisture content, texture, as well as levels of amygdalin, benzaldehyde and other volatile organic compounds, tocopherol, and fatty acid methyl esters (FAME). Visual characteristics are important for appealing to consumers, especially the vibrance of color in almonds. Color is the first parameter consumers utilize to evaluate quality of a food item. The L*a*b* color values helps with identifying colors and comparing colors of items by quantifying the lightness/darkness as well as the red, green, blue, and yellow values. Texture and moisture content are related to the likeability of a product by contributing to mouthfeel (hardness and crunch) when biting into the almond kernels. Texture was analyzed based on work and maximum force reached (Fmax). The chemical make-up of the almonds is important for flavor development as well as for the associated nutritional benefits and for storage stability. Benzaldehyde and volatiles, as well as fatty acid are key parameters related to the aroma of almonds. Tocopherols are the key antioxidants associated with oxidative stability and is important for shelf life of the almonds. Each of these compounds were analyzed for concentration in ground almonds and extracted almond oil.

## Materials and Methods

### Chemical Reagents

Acetonitrile LC/MS Optima, methanol LC/MS Optima, methyl tert-butyl ether (MTBE) HPLC grade, alpha tocopherol standard, gamma tocopherol standard, toluene, hydrochloric acid (HCl), and acetic acid (99.7%) were obtained from Thermo Fischer Scientific (Waltham, MA). Delta tocopherol standard, FAME standard, hexane HPLC grade, and amygdalin standard were obtained from MilliporeSigma (Burlington, MA). Deionized water was obtained from a Milli-Q system (Millipore, Burlington, MA) with a resistance of 18.2 MΩcm at 25℃. Sodium sulfate in anhydrous form was acquired from Research Product International (Mt. Prospect, IL) while volatile standard including n-hexyl-$d_{13}$ alcohol, benzaldehyde-$d_6$, and 2-nonanone-1, 1, 1, 3, 3-$d_5$ were from CDN Isotopes (Pointe-Claire, Quebec Canada).

### Almond Samples

Raw kernels of sixty almond varieties harvested in 2019 were obtained through the Almond Board of California. 1 kg of kernels of each cultivars that was grown and harvested in California, Spain, or Australia was obtained for conducting these analyses. The names and characteristics of the varieties analyzed are summarized in **Table 5**. The samples were stored in two layers of Ziploc bags at 0ºC/33ºF with no light and no humidity control until analysis.

Some analysis required extraction from ground (pulverized) almonds. This was prepared by lightly crushing almonds with a hammer then grinding them in a food blender Model 51BL30 (Waring Commercial, Torrington, CT). The blender was set on low speed and the almond pieces were pulverized for a total of 9 seconds in 3 second intervals with rests in between. The pulverized almonds were passed through a 20-mesh sieve prior to all analyses. A sample of devolatilized almonds (blank) was prepared in the same manner as above for the GC analysis, however, these samples were heated at 55°C in a vacuum oven for least 3 days to remove present volatiles.

Almond oil required for some analyses was obtained through hydraulic pressing. Approximately 50 g of whole almonds were lightly crushed with a hammer and placed in a Carver press unit model 3912 (Carver Inc., Wabash, IN, USA). The expelled oil was stored in amber vials with the headspace replaced by $N_2$ gas and at -20 °C until analysis.

**Table 5.** The 60 varieties of almonds studied with the characteristics of kernel weight (g), kernel shape and texture, and shell texture (personal communication with Dr. DeJong and Dr. Gradziel at UC Davis).

| Variety Name | Ave Kernel Weight (g) | Kernel Shape | Kernel Texture | Shell Texture |
|---|---|---|---|---|
| 1. Aldrich | 1.00 | Narrow | Light-medium wrinkle | Soft |
| 2. Bennett | 1.11 | Flat | Light wrinkle | Soft |
| 3. Booth | 1.26 | Long, flat | Deep wrinkle | Soft |
| 4. Butte | N/A | Short, wide | Light wrinkle | Semi-hard |
| 5. Capitola | 1.16 | Average | Deep wrinkle | Soft |
| 6. Carmel | N/A | Long | Slightly wrinkled | Soft |
| 7. Durango | 1.21 | Long average | Light wrinkle | Soft |
| 8. Eddie | 1.46 | Long,flat | Light wrinkle | Soft |
| 9. Folsom | 1.09 | Average | Medium wrinkle | Soft |
| 10. Independence | N/A | Long, flat | Light wrinkle | Semi-hard |
| 11. Jenette | 1.18 | Round | Medium-deep wrinkle | Soft |
| 12. Kester (2-19E) | 1.02 | Small average | Deep wrinkle | Soft |
| 13. Mission | N/A | Flat | Medium-deep wrinkle | Semi-hard |
| 14. Monterey | N/A | Long thin | Deep wrinkle | Semi-hard |
| 15. Nonpareil | 1.21 | Flat | Smooth | Soft |
| 16. Peerless | N/A | Short, wide | Smooth-light wrinkle | Semi-hard |
| 17. Pyrenees | N/A | Long | Smooth-light wrinkle | Semi-hard |

| | | | | |
|---|---|---|---|---|
| 18. Self Fruit P13.019 | 1.19 | N/A | Medium wrinkle | Soft |
| 19. Self Fruit P16.013 | 1.28 | Flat | Smooth | Soft |
| 20. Shasta | N/A | Large, flat | Smooth | Soft |
| 21. Sonora | N/A | Long, narrow | Smooth | Soft |
| 22. Sterling | 1.04 | Long | Smooth | Soft |
| 23. Sweetheart | 1.04 | Round | Medium wrinkle | Soft |
| 24. UCD-1-16 | 1.11 | Long | Smooth-light wrinkle | Soft |
| 25. UCD 1-232 | 1.23 | Semi-long | Medium wrinkle | Soft |
| 26. UCD 1-271 | 1.30 | Long, semi-flat | Smooth | Soft |
| 27. UCD 3-40 | 1.57 | Flat | Light wrinkle | Soft |
| 28. UCD 7-159 | 1.58 | Long | Smooth-light wrinkle | Soft |
| 29. UCD 8-27 | 1.09 | Average | Smooth | Soft |
| 30. UCD 8-160 | 1.48 | Long | Light-medium wrinkle | Soft |
| 31. UCD 8-201 | 1.08 | Long, oval | Light wrinkle | Soft |
| 32. UCD 18-20 | 1.29 | Long | Light-medium wrinkle | Soft |
| 33. Winters | 1.10 | Long | Light wrinkle | Soft |
| 34. Y116-161-99 | 1.32 | Flat | Light wrinkle | Soft |
| 35. Y117-86-03 | 1.13 | Long | Light wrinkle | Soft |
| 36. Y117-91-03 | 1.00 | Oval | Smooth-light wrinkle | Soft |
| 37. Y121-42-99 | 0.9 | Small average | Medium wrinkle | Soft |
| 38. Capella | 1.33 | Oval | Deep wrinkle | Hard |
| 39. Carina | 1.34 | Oval | Smooth-light wrinkle | Semi-Hard |
| 40. Maxima | 1.81 | Cordate | Light-medium wrinkle | Semi-Hard |
| 41. Mira | 1.28 | Cordate | Smooth | Semi-Hard |
| 42. Rhea | 1.28 | Cordate | Smooth-light wrinkle | Soft |
| 43. Vela | 1.70 | Cordate | Smooth-light wrinkle | Soft |
| 44. Constanti | 1.20 | Flat, round | Light wrinkle | Hard |
| 45. Marinada | 1.30 | Cordate | Light wrinkle | Hard |

| | | | | |
|---|---|---|---|---|
| 46. Tarraco | 1.70 | Elliptical | Light wrinkle | Hard |
| 47. Selection 29-148 | 1.30 | Cordate | Light-medium wrinkle | Semi-hard |
| 48. Selection 30-297 | 1.60 | Cordate | Medium-deep wrinkle | Hard |
| 49. Guara | N/A | Flat | Smooth-light wrinkle | Hard |
| 50. Mardia | 1.20 | Cordate | Deep wrinkle | Hard |
| 51. Soleta | 1.30 | Elliptical | Smooth | Hard |
| 52. Vialfas | 1.20 | Elliptical, cordate | Deep wrinkle | Hard |
| 53. Antoneta | 1.50 | Flat cordate | Medium wrinkle | Hard |
| 54. Makako | 1.20 | Elliptical | Medium wrinkle | Hard |
| 55. Marta | 1.20 | Elliptical, flat | Medium wrinkle | Hard |
| 56. Penta | 1.00 | Elliptical | Smooth to deep wrinkle | Hard |
| 57. Selection D00-360 | 1.00 | Teardrop | Deep wrinkle | Semi-hard |
| 58. Selection D01-188 | 1.40 | Elliptical | Medium wrinkle | Soft |
| 59. Selection D06-795 | 1.20 | Elliptical | Medium-deep wrinkle | Soft |
| 60. Matan | 1.48 | Long, flat | Smooth-light wrinkle | Semi-hard |

Abbreviation: NA, not available

**Color**

Two samples of 10 whole almond kernels were selected for each variety. The kernels chosen were selected to have no discoloration or damage. The almonds were allowed to reach room temperature before analysis. The 10 kernels were placed into a clear container and the L*a*b* color values were measured using a ColorFlex colorimeter (HunterLab, Reston, VA).

The observed lighting was set to D65/10 with 10º observation port. The varieties were run in duplicate.

### Moisture

The moisture content was obtained on approximately 5 g of pulverized almonds by Sartorius Mark3 Moisture Analyzer (Sartorius, Göttingen, Germany). The varieties were run in duplicate.

### Texture

A sample of 10 whole almond kernels were obtained per variety. Each kernel was measured for 10 duplicates per variety. Kernels chosen were checked for lack of damage or cracks, and ideally symmetrical. The samples were allowed to reach room temperature before analysis. A TA.XT2 texture analyzer (Texture Technology Corp., Scarsdale, NY) with a compression test was used to determine the texture of each almond kernels using a 50.8 mm compression disk TA-25 with a load cell of 50 kg. The pre-test speed was set at 0.5 mm/sec, test speed at 1 mm/sec, and post-test speed at 10 mm/sec. The test type strain was set at 50% with a target mode "Strain" and trigger force of 5 g. Work (N*mm) and maximum force (N) was measured. Maximum force was determined to be the point reached by the highest peak, while work

### Amygdalin

Amygdalin was analyzed in a 25 g sample of pulverized almonds of each variety. 50 ± 0.1 mg of a pulverized sample was placed in a 15 ml centrifuge tube with 1 ml of 0.1 % acetic acid in methanol. The tubes were placed in a shaker at 250 rpm for 15- 24 hours at room temperature. The tubes were then centrifuged at 4000 rpm for 15 minutes. The supernatant was collected into a 2 ml centrifuge tube and concentrated to dryness under a speed vac at 40ºC for 40-60 minutes.

The dry material was reconstituted with 1 ml of 0.1% acetic acid in Milli-Q water, vortexed for 20 seconds and rested for at least 10 minutes. The samples were cleaned using solid-phase extraction (SPE) column (Hypersep C18, 500 mg/3ml from Thermo Scientific, Waltman, MA, USA) preconditioned with 2 ml of methanol followed by 2 ml of Milli-Q water. The samples were loaded on the SPE column and another 1 ml of 0.1% acetic acid Milli-Q water was used to remove residuals in the tube which is loaded on to the column. The column was flushed with 2 ml of 0.1% acetic acid in Milli-Q water. Amygdalin was eluted from the column with 4 ml of 40:60 methanol:Milli-Q water v/v into a glass tube. The tube was vortexed for 20 seconds and passed through 0.2 µm filter (EMD Millipore, Billerica, MA, USA) into a vial before analysis. Two 25 g sample aliquots were prepared for duplicate measurements.

Amygdalin analysis was performed on an Agilent 1290 Infinity ultra high-pressure liquid chromatography system (UHPLC) interfaced with a 6460 triple-quadrupole mass spectrometer (QQQ MS/MS) via an electrospray ionization (ESI) with Jet Stream Technology (Agilent Technologies, Santa Clara, CA, USA). The UHPLC was equipped with an autosampler (G4226A), a binary pump (G4220A) with an integrated vacuum degasser, and a column compartment (G1316C) with a thermostat (G1330B). The column used for separation was the ZORBAX Eclipse Plus C18 (2.1x100mm 1.8-micron, Agilent Technologies, Santa Clara, CA, USA) kept at a column temperature of 45ºC. The mobile phase consisted of (A) 0.1% acetic acid in water and (B) 0.1% acetic acid in acetonitrile and followed a time table of 5% B for 0-1 minutes at 0.3 ml/min; 5-20% B for 1-6 minutes at 0.3 ml/min; 20-95% B for 6-7.5 minutes at 0.5 ml/min, held 7.5-10 minutes at 0.5 ml/min; and 95-5% B for 10-11 minutes at 0.3 ml/min. The injection volume was 10 µl. For the source, negative ESI with gas temperature of 300°C and gas flow rate of 8.0 L/min was used. The sheath gas temperature was at 350°C and sheath gas flow rate was 11.0 L/min. The nebulizer gas pressure, capillary voltage, fragmentor voltage, and dwell time were 45 psi, 3500 V, 160 V, and 200 ms, respectively. The analysis of amygdalin was done through the multiple reaction monitoring (MRM) mode and quantified through the use of an external calibration curve based on the peak areas obtained from the amygdalin standard. The standards were diluted in 40:60 methanol:Milli-Q water v/v. The curve was built off the peak area of 456 m/z (precursor ion) to 323 m/z (product ion). Two more transactions (qualifier ions) were also observed: 456 m/z (precursor ion) to 179 m/z (product ion), and 456 m/z (precursor ion) to 119 m/z (product ion). Samples that exceeded the maximum of the linear range of the standard curve were diluted and the dilution factor factored in for calculation.

**Tocopherols**

The sample preparation for this assay was adapted from Puspitasari-Nienaber et al (Source). A 0.5 ± 0.02 g sample of oil was added to an 8 ml amber borosilicate glass vial. A 5 ml aliquot of high performance liquid chromatography (HPLC) -grade methanol and MTBE in a 1:1 ratio was added to the vial. The vial was capped with a PTFE lined cap and agitated for 20 seconds. The sample was filtered through a 0.2 µm nylon filter before analysis. The varieties were prepared in duplicate.

Tocopherol was analyzed utilizing Agilent 1260 infinity HPLC system with a fluorescence detector (Agilent Technologies). The method was adjusted from a method released by Phenomenex (Aquel & Lomas 2015). Four isomers were separated through this method; beta, delta, gamma, and alpha. The column used was a reverse phase Kinetex F5 column (3.0mm ID, 150mm, 2.6µm) 100 Å from Phenomenex kept at 45ºC. The mobile phase consisted of (A) filtered water and (B) methanol and followed a time table of 85% B for 0-1 minutes; 85-94% B for 1-9 minutes; 94-100% B for 9-9.5 min and hold for 9.5-12 minutes; 100-85% B for 12-13 minutes and hold for 4 minutes. Injection volume was 4 µl and flow rate was kept constant at 0.62 ml/min. The fluorescence detection was set at an excitation wavelength of 293 nm and emission at 325 nm. The concentration of tocopherol isomers was calculated using external calibration. Pure standards of alpha, delta, gamma tocopherols were diluted in methanol:MTBE (1:1) and serial dilution was made to create the standard calibration curve. Relative quantification of the beta tocopherol was achieved using the gamma tocopherol standard.

**Fatty Acid Methyl Esters**

A 10 µl sample of oil was added to an 8 ml amber glass vial. The samples were transesterified by a modified method of Ichihara and Fukubayashi (Ichihara & Fukubayashi 2010). The vial containing the sample was dissolved with 400 µl of toluene. Then 3 ml of 100% methanol and 600 µl of 8% : 92% v/v HCl:methanol were added in that order. The vials were placed on a heating block at 90 ºC for 30 minutes, then placed in an ice bath for 5 minutes. A 1 ml aliquot of hexane, followed by 1 ml aliquot of Milli-Q water, were added to the vial and rested for 10 to 15 minutes. After the separation of hexane and water layer, 600 µl of the upper hexane layer was transferred into a micro-centrifuge tube with 2 small scoops of sodium sulfate (drying agent). The tube was inverted several times to absorb any residual water from the hexane layer. The tube was rested for the sodium sulfate to gravitate to the bottom. Then 400 µl of the hexane layer was transferred into a vial for analysis. Analysis of each variety was performed in duplicates.

Fatty acid methyl esters were analyzed utilizing an Agilent 7820A GC (Agilent Technologies, Santa Clara, CA, USA), with flame ionization detection (FID). An Agilent DB-23 column (30m length, 0.25mm ID, 0.25 mm film) was used for separation. Helium was used for carrier gas at 2.5 ml/min. At the inlet, 10:1 split ratio was used with a split flow rate of 25 ml/min and injector temperature of 275 ºC. The oven temperature program went as follows: start at 90 ºC and hold for 2 minutes. Then ramp up 45 ºC/min until 140 ºC, followed by a ramp up 10 ºC/min to 190 ºC and hold for 2 minutes. Finally, ramp up at 25 ºC/min to 240 ºC and hold for 2 minutes. The FID gas composition was $N_2$ 25 ml/min, $H_2$ 30 ml/min, and air 400 ml/min. The detector temperature was at 300 ºC. The sample injection volume was 1 µl. Fatty acid identification was based on the retention times obtained through the FAME standard. The FAME standard was diluted in hexane. Quantification was achieved using external standardization and authentic standards.

**Benzaldehyde and Volatile Organic Compounds**

The method for volatile analysis was adapted from Xiao et al (2014). A 5 ± 0.02 g sample of pulverized almonds was placed in a 20 ml glass headspace vial. Vials used for blank or building the standard curve utilized 5 ± 0.02 g of devolatilized almonds. Glass inserts were inserted to hold the 1µl glass capillary tubes holding standards or methanol for blanks. Deuterated standards of benzaldehyde-$d_6$, 2-nonanone-1,1,1,3,3-$d_5$, and n-hexyl-$d_{13}$ alcohol were prepped in cold methanol. All vials were immediately sealed with an aluminum pressure release seal top and left to equilibrate in room temperature for at least 6 hours before analysis. The varieties were prepared in duplicate.

Agilent 7890 gas chromatography (GC) systems with 5975C MS was used for volatile analysis. Agilent DB-WAX column (30 m length, 0.25 mm ID, 0.25 µm film) and Divinylbenzene/Carboxen/Polydimethylsiloxane solid phase microextraction (SPME) fiber (Supelco Inc., Belefonte, PA) was utilized. The incubation time was optimized at 25 minutes at 40℃ and 500 rpm. Extraction time was optimized at 30 minutes at 250 rpm with fiber exposure of 22 mm. Desorption at the inlet was set to splitless mode at 250℃ for 0.9 minutes, then changed to split at 50:1 for a total of 10 minutes injection time. Source temperature was set to 230℃ while quadrupole temperature was set to 150℃. Oven temperature ramp went as follows: initial temperature was set to 35ºC with a 1 minute hold, followed by a 3ºC/min ramp to 65ºC, 6 ℃/min ramp to 180℃, then 30 ºC/min ramp to 240℃ held for 5 minutes. Air flow for helium was 1.2 ml/min. Ion chromatogram of the MS scanned from 22 to 300 m/z with a fixed electron energy of 70.3 eV. Compound identification was made through the NIST 17 library with a match score of 85% and above. Quantification was done through an external standard curve based off peak areas obtained from n-hexyl-$d_{13}$ alcohol, benzaldehyde-$d_6$, and 2-nonanone-1, 1, 1, 3, 3-d5 deuterated standards.

**Statistical Analysis**

Statistical analysis was performed using RStudio v.1.2.5001 (RStudio, Boston, MA). The significant differences of color, moisture content, texture, amygdalin, volatiles, tocopherol, and FAME content between the almond cultivars were determined using a one-way analysis of variance (ANOVA) with post-hoc Tukey's HSD test if there was a significant difference. The α-value was set at 0.05. Samples were organized into clusters by variety. The cluster dendrogram was created from compiled data for each variety, and the number of clusters was assessed. Principal component analysis (PCA) was performed to make the comparison across varieties and attributes.

## Results and Discussion

Individual data measured for each variety is summarized in **Table 6**, **7**, **8** and **9**.

### Color

The average reading for L*a*b* color values were L* = 41.04 ± 2.99, a* = 13.93 ± 1.07, and b* = 26.53 ± 2.02. Mission had the lowest average L* value of 35.94 ± 1.54 indicating it was the darkest colored variety. Mira with the highest average L* value of 46.62 ± 1.79 was the lightest variety (**Table 6**). Statistical analysis showed that there were significant differences ($p < 0.001$) with L*, a* and b* values among the varieties.

### Moisture

The average moisture content for almond kernel was 5.23 ± 0.77 % wet basis (wb). The variety with highest average moisture content was Antoneta at 6.38 ± 0.01 % and the lowest average was Aldrich at 3.98 ± 0.01 % (**Table 6**). Antoneta is a self-compatible late flowering almond cultivar that matures in mid-September, which may help explain the higher moisture content. Statistical analysis showed that there are significant differences ($p < 0.001$) in moisture content among the varieties. The average percentage of moisture content found in the samples was higher than the average of 4.25% found in literature, but still within the range of 1.68 to 6.53% (**Table 1**). However, it must be noted that the moisture content of almonds will depend upon external environmental factors and all almonds are dried to < 6 % moisture to avoid damage during the hulling and shelling process.

### Texture

Force value of the first force breakdown can be related to hardness, crispiness and crunchiness (Contador et al. 2015). Work relates to the area under the curve during a texture analysis. Across varieties, the average maximum force was 335.02 ± 74.87 N and average work was 676.83 ± 132.75 N*mm. The lowest average maximum force was observed in Penta (185.21 ± 28.11 N) and the highest average maximum force was observed in UCD 3-40 (505.55 ± 46.52 N). Penta did the lowest work at 409.17 ± 52.91 N*mm while UCD 3-40 had the highest at 1007.39 ± 116.32 N*mm (**Table 6**). Nonpareil regression analysis of percent moisture to maximum force (N) indicated only a weak correlation ($R_2$ = 0.2915) as can be seen in **Figure 6**.

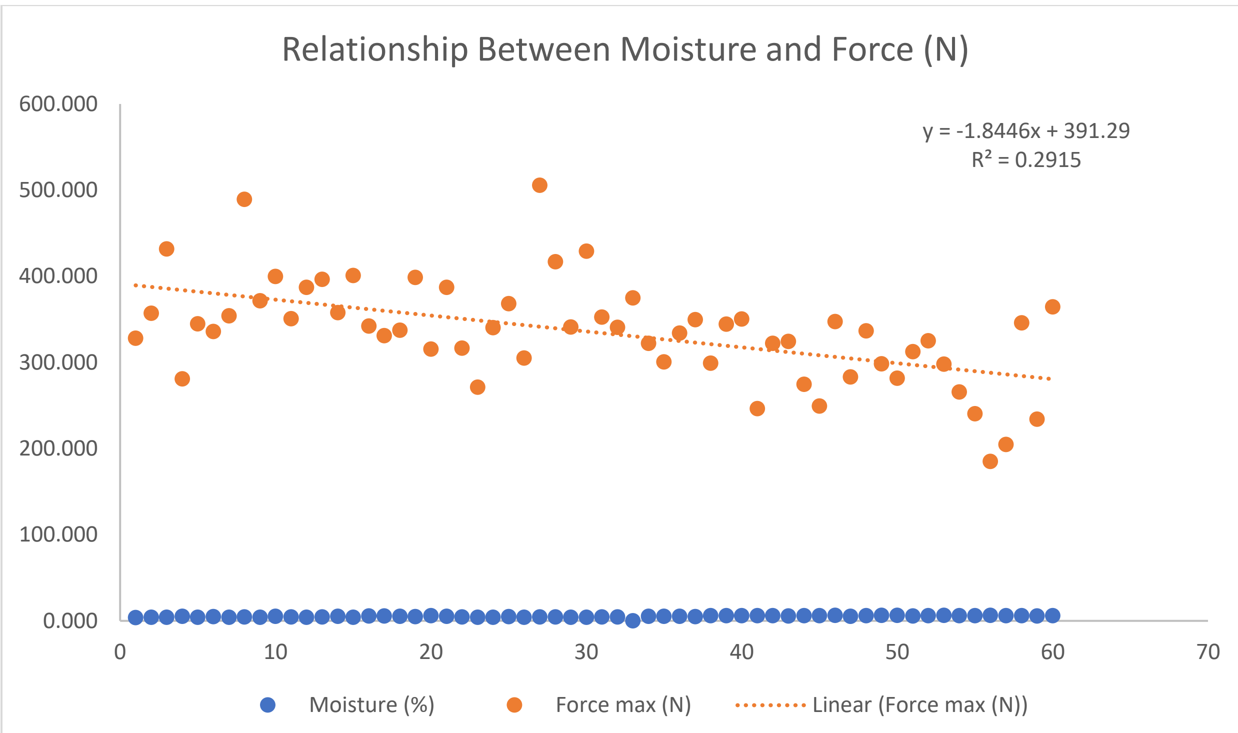


**Figure 6.** Correlation between moisture content (%) and maximum force (N) on variety Nonpareil. There is weak correlation at $R_2$ = 0.2915.

Statistical analysis showed that there were significant differences (p<0.001) with maximum force and work among the varieties. These results can be useful for identifying high-yield varieties with desirable texture attributes of crispiness and crunchiness as these attributed are related to the fracture properties of foods which correlate to the force value of a food.

**Amygdalin**

The average amygdalin concentration among all varieties was 24.194 ± 57.832mg/kg. The highest average concentration was found in Rhea at 402.294 ± 34.471 mg/kg while the lowest average concentration was in Selection D01-188 (0.085 ± 0.044 mg/kg) (**Table 7**). Statistical analysis showed that there are significant differences ($p < 0.001$) in amygdalin concentration among the varieties. The concentration found in Rhea was significantly higher than levels found in other varieties (402.294 ± 34.471 mg/kg), and higher than the average concentration of amygdalin (63.13 mg/kg) in 14 commercial non-bitter almonds grown in California (Lee et al., 2013).

The varieties Aldrich (80.3-172.8 mg/kg) and Fritz (89.2-141.2 mg/kg) consistently demonstrate the highest levels of amygdalin in commercialized California almonds (private communication with Almond Board of California). These levels correlate with < 1-10.8 PPM (Aldrich) and 2.2-3.2 PPM (Fritz) of hydrogen cyanide equivalents. The EU Food Safety Authority is proposing (2022) a new limit of 30-35 ppm HNC for almonds. The highest level detected in these almonds is below the proposed EU limit (~25 ppm in Rhea).

**Fatty Acid Methyl Esters**

The FAMEs found in almond oil samples were palmitic acid methyl ester (C16:0), stearic acid methyl ester (C18:0), oleic acid methyl ester (C18:1 cis), and linoleic acid methyl ester (18:2 cis). The average concentrations of FAMEs were as follows: palmitic 49.127 ± 9.238, stearic was 11.619 ± 2.667, oleic 499.452 ± 62.286, and linoleic 154.458 ± 46.420 mg/ml of oil. The range of FAMEs was found from 29.409 ± 19.350 (Pyrenees) to 68.716 ± 16.030 (Booth) mg/ml of oil for palmitic, 7.226 ± 1.139 (UCD 8-27) to 18.091 ± 3.153 (Y121-42-99) mg/ml of oil for stearic, 371.020 ± 76.782 (UCD 1-232) to 628.307 ± 83.469 (Y121-42-99) mg/ml of oil for oleic, and 68.070 ± 14.281 (Matan) to 244.889 ± 3.699 (UCD 8-201) mg/ml of oil for linoleic (Table 7). Statistical analysis showed that there were significant differences at $p<0.001$ with palmitic, stearic, and linoleic FAME concentrations among the varieties. There was a significant difference at $p < 0.01$ with oleic FAME concentrations.

**Table 6.** Average moisture content, color L*a*b* values, force maximum (N) and work (N*mm) for 60 almond varieties (average ± SD, n=2 for moisture content and color, n=10 for texture).

| Varietal Name | **Moisture Content** | **Color** | | | **Texture** | |
|---|---|---|---|---|---|---|
| | (% wb) | L* | a* | b* | Force max (N) | Work (N*mm) |
| Aldrich | 3.98 ± 0.01 | 38.23 ± 0.39 | 12.84 ± 0.30 | 25.21 ± 0.19 | 328.05 ± 45.22 | 670.66 ± 84.55 |
| Bennett | 4.22 ± 0.13 | 44.22 ± 0.21 | 13.41 ± 0.06 | 25.83 ± 0.01 | 356.91 ± 52.05 | 697.68 ± 101.35 |
| Booth | 4.30 ± 0.31 | 39.96 ± 0.33 | 12.59 ± 0.16 | 24.11 ± 0.80 | 431.83 ± 46.09 | 849.65 ± 97.87 |
| Butte | 5.29 ± 0.21 | 39.85 ± 2.62 | 14.21 ± 0.18 | 27.54 ± 0.95 | 280.89 ± 45.46 | 592.87 ± 99.10 |
| Capitola | 4.10 ± 0.04 | 37.19 ± 0.14 | 13.54 ± 0.60 | 24.01 ± 0.23 | 344.96 ± 79.86 | 688.04 ± 105.61 |
| Carmel | 5.10 ± 0.03 | 39.29 ± 1.32 | 13.67 ± 0.25 | 26.26 ± 0.47 | 335.80 ± 45.01 | 631.40 ± 73.69 |
| Durango | 4.37 ± 0.05 | 43.44 ± 0.98 | 13.50 ± 0.02 | 27.79 ± 0.26 | 353.95 ± 30.46 | 705.17 ± 60.35 |
| Eddie | 4.51 ± 0.26 | 43.83 ± 0.28 | 14.90 ± 0.28 | 26.45 ± 0.22 | 489.33 ± 43.22 | 910.76 ± 76.28 |
| Folsom | 4.09 ± 0.04 | 39.31 ± 2.15 | 11.86 ± 0.34 | 23.96 ± 0.71 | 371.46 ± 41.13 | 694.11 ± 104.44 |
| Independence | 5.31 ± 0.15 | 43.9 ± 2.16 | 14.13 ± 1.06 | 26.44 ± 1.36 | 399.84 ± 56.82 | 804.10 ± 88.90 |
| Jenette | 4.47 ± 0.21 | 41.84 ± 3.71 | 12.67 ± 0.36 | 25.63 ± 2.23 | 350.91 ± 38.58 | 711.85 ± 123.16 |
| Kester (2-19E) | 4.25 ± 0.28 | 40.00 ± 0.52 | 13.97 ± 0.03 | 24.80 ± 0.81 | 387.15 ± 41.34 | 683.68 ± 57.68 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Mission | 4.44 ± 0.21 | 35.94 ± 1.54 | 13.11 ± 0.15 | 23.85 ± 1.00 | 396.52 ± 63.17 | 845.26 ± 122.12 |
| Monterey | 5.19 ± 0.28 | 40.42 ± 0.04 | 15.40 ± 0.53 | 29.05 ± 0.45 | 357.67 ± 45.31 | 636.41 ± 84.06 |
| Nonpareil | 4.25 ± 0.13 | 45.82 ± 2.13 | 13.33 ± 0.22 | 27.65 ± 1.47 | 400.94 ± 50.47 | 735.08 ± 85.50 |
| Peerless | 5.50 ± 0.22 | 39.54 ± 0.09 | 15.95 ± 0.37 | 28.25 ± 0.88 | 342.15 ± 38.46 | 651.76 ± 76.65 |
| Pyrenees | 5.80 ± 0.13 | 41.48 ± 1.04 | 15.71 ± 0.11 | 30.09 ± 0.11 | 331.12 ± 47.84 | 638.33 ± 109.19 |
| Self Fruit P13.019 | 5.44 ± 0.12 | 38.48 ± 3.71 | 14.52 ± 0.50 | 26.64 ± 2.23 | 337.33 ± 47.4 | 640.18 ± 81.68 |
| Self Fruit P16.013 | 4.76 ± 0.18 | 42.29 ± 0.33 | 14.01 ± 0.21 | 26.15 ± 0.33 | 398.82 ± 55.23 | 712.39 ± 85.30 |
| Shasta | 5.96 ± 0.09 | 38.89 ± 0.61 | 14.17 ± 0.08 | 24.31 ± 0.62 | 315.60 ± 23.83 | 655.3 ± 51.88 |
| Sonora | 5.22 ± 0.09 | 45.44 ± 0.74 | 14.69 ± 0.39 | 29.80 ± 0.96 | 387.24 ± 56.52 | 761.55 ± 75.78 |
| Sterling | 4.39 ± 0.24 | 43.26 ± 3.39 | 13.65 ± 0.09 | 27.91 ± 0.98 | 316.54 ± 34.27 | 591.27 ± 65.63 |
| Sweetheart | 4.29 ± 0.00 | 42.17 ± 1.99 | 12.98 ± 0.35 | 26.22 ± 1.04 | 271.14 ± 52.78 | 576.74 ± 113.46 |
| UCD-1-16 | 4.36 ± 0.08 | 41.22 ± 0.25 | 14.23 ± 0.11 | 27.75 ± 0.09 | 340.39 ± 51.53 | 669.49 ± 89.11 |
| UCD 1-232 | 4.79 ± 0.14 | 39.08 ± 0.26 | 12.60 ± 0.54 | 23.44 ± 0.04 | 368.07 ± 66.81 | 695.26 ± 106.91 |
| UCD 1-271 | 4.36 ± 0.04 | 40.27 ± 2.06 | 12.49 ± 0.67 | 23.77 ± 1.42 | 305.23 ± 43.46 | 592.49 ± 90.38 |
| UCD 3-40 | 4.74 ± 0.03 | 42.86 ± 2.27 | 11.76 ± 0.74 | 22.76 ± 1.58 | 505.55 ± 46.52 | 1007.39 ± 116.32 |
| UCD 7-159 | 4.44 ± 0.03 | 40.54 ± 0.84 | 13.57 ± 0.28 | 25.61 ± 0.33 | 416.81 ± 44.77 | 889.48 ± 171.22 |

| | | | | | | |
|---|---|---|---|---|---|---|
| UCD 8-27 | 4.35 ± 0.00 | 36.29 ± 1.41 | 12.58 ± 0.27 | 22.29 ± 1.17 | 341.01 ± 44.92 | 668.92 ± 71.68 |
| UCD 8-160 | 4.22 ± 0.03 | 43.15 ± 1.42 | 12.70 ± 0.62 | 26.08 ± 1.39 | 429.18 ± 47.06 | 839.96 ± 82.64 |
| UCD 8-201 | 4.45 ± 0.13 | 42.36 ± 1.32 | 12.57 ± 0.20 | 27.39 ± 0.86 | 352.51 ± 57.27 | 657.18 ± 108.47 |
| UCD 18-20 | 4.48 ± 0.20 | 39.21 ± 0.30 | 13.78 ± 0.42 | 25.55 ± 0.04 | 340.81 ± 56.36 | 692.42 ± 161.20 |
| Winters | 5.32 ± 0.13 | 38.69 ± 2.29 | 13.13 ± 0.37 | 23.39 ± 0.98 | 374.91 ± 56.32 | 737.95 ± 99.14 |
| Y116-161-99 | 5.19 ± 0.20 | 46.03 ± 1.48 | 13.64 ± 0.28 | 28.66 ± 0.51 | 322.14 ± 49.88 | 686.31 ± 107.04 |
| Y117-86-03 | 5.19 ± 0.04 | 42.23 ± 0.59 | 13.20 ± 0.86 | 26.61 ± 1.26 | 300.65 ± 82.09 | 654.29 ± 126.09 |
| Y117-91-03 | 5.30 ± 0.01 | 44.38 ± 2.60 | 12.23 ± 0.81 | 25.41 ± 2.20 | 334.19 ± 66.30 | 633.29 ± 97.39 |
| Y121-42-99 | 4.98 ± 0.23 | 42.26 ± 1.00 | 13.79 ± 0.26 | 26.32 ± 1.14 | 349.74 ± 36.47 | 634.33 ± 59.66 |
| Capella | 6.13 ± 0.04 | 43.44 ± 2.06 | 15.39 ± 0.20 | 30.58 ± 1.51 | 299.12 ± 35.09 | 654.94 ± 71.14 |
| Carina | 5.97 ± 0.07 | 46.30 ± 0.84 | 14.72 ± 0.66 | 27.56 ± 0.67 | 344.30 ± 42.32 | 653.87 ± 52.52 |
| Maxima | 5.93 ± 0.07 | 46.47 ± 1.58 | 14.35 ± 0.77 | 27.54 ± 0.11 | 350.40 ± 46.13 | 705.19 ± 78.69 |
| Mira | 5.87 ± 0.01 | 46.62 ± 1.79 | 15.33 ± 0.21 | 30.06 ± 1.07 | 246.50 ± 43.53 | 650.94 ± 61.45 |
| Rhea | 6.05 ± 0.08 | 42.10 ± 1.05 | 15.08 ± 0.09 | 28.96 ± 0.25 | 322.18 ± 69.67 | 702.25 ± 121.30 |
| Vela | 5.78 ± 0.08 | 40.60 ± 0.31 | 16.64 ± 0.12 | 25.70 ± 0.47 | 324.41 ± 63.43 | 734.72 ± 68.06 |
| Constanti | 6.20 ± 0.08 | 38.55 ± 2.24 | 14.38 ± 0.44 | 26.57 ± 0.61 | 274.66 ± 21.05 | 519.44 ± 66.44 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Marinada | 5.87 ± 0.14 | 40.55 ± 1.73 | 15.39 ± 0.14 | 28.79 ± 0.35 | 249.34 ± 28.68 | 531.65 ± 58.89 |
| Tarraco | 6.25 ± 0.08 | 37.61 ± 0.49 | 14.70 ± 0.71 | 27.90 ± 1.10 | 347.37 ± 55.25 | 720.05 ± 86.20 |
| Selection 29-148 | 5.48 ± 0.08 | 43.20 ± 0.77 | 15.19 ± 0.11 | 29.23 ± 0.68 | 283.00 ± 40.63 | 688.99 ± 102.78 |
| Selection 30-297 | 5.93 ± 0.13 | 40.70 ± 2.17 | 14.59 ± 1.17 | 28.63 ± 2.22 | 336.45 ± 47.01 | 759.67 ± 73.18 |
| Guara | 6.36 ± 0.16 | 39.69 ± 0.54 | 14.63 ± 0.16 | 27.50 ± 0.04 | 298.26 ± 51.81 | 642.89 ± 91.42 |
| Mardia | 6.33 ± 0.12 | 41.44 ± 0.57 | 14.25 ± 0.49 | 27.88 ± 1.55 | 281.64 ± 43.06 | 538.53 ± 71.98 |
| Soleta | 5.65 ± 0.23 | 40.26 ± 1.98 | 14.78 ± 0.15 | 27.26 ± 1.41 | 312.42 ± 52.02 | 557.76 ± 85.01 |
| Vialfas | 5.95 ± 0.03 | 44.16 ± 2.31 | 14.56 ± 0.23 | 28.46 ± 1.39 | 325.01 ± 30.69 | 619.58 ± 88.90 |
| Antoneta | 6.38 ± 0.01 | 41.56 ± 1.04 | 13.80 ± 0.08 | 27.51 ± 0.41 | 298.07 ± 35.48 | 634.52 ± 69.16 |
| Makako | 6.08 ± 0.13 | 37.74 ± 0.28 | 14.00 ± 0.59 | 25.82 ± 0.07 | 265.71 ± 36.64 | 598.52 ± 81.66 |
| Marta | 5.97 ± 0.16 | 36.44 ± 0.28 | 13.86 ± 0.25 | 25.17 ± 0.13 | 240.57 ± 49.68 | 574.76 ± 95.10 |
| Penta | 6.23 ± 0.05 | 36.91 ± 0.72 | 13.27 ± 0.24 | 24.82 ± 0.64 | 185.21 ± 28.11 | 409.17 ± 52.91 |
| Selection D00-360 | 6.22 ± 0.13 | 36.18 ± 0.91 | 14.06 ± 0.88 | 26.47 ± 0.60 | 204.84 ± 36.58 | 519.91 ± 89.02 |
| Selection D01-188 | 6.11 ± 0.37 | 41.91 ± 1.47 | 13.50 ± 0.14 | 26.50 ± 0.91 | 346.08 ± 32.05 | 727.51 ± 62.80 |
| Selection D06-795 | 5.69 ± 0.30 | 38.17 ± 1.76 | 13.84 ± 0.80 | 26.25 ± 1.14 | 234.24 ± 29.50 | 583.85 ± 63.11 |
| Matan | 6.05 ± 0.04 | 38.87 ± 1.77 | 14.49 ± 0.45 | 25.42 ± 0.60 | 364.35 ± 51.33 | 737.89 ± 104.24 |

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|---|---|---|---|---|---|---|
| Total Average | 5.23 ± 0.77 | 41.01 ± 2.99 | 13.93 ± 1.07 | 26.53 ± 2.02 | 335.02 ± 74.87 | 676.83 ± 132.75 |

**Table 7.** Average amygdalin and FAME concentrations for 60 almond varieties (average ± SD, n=2).

| Varietal Name | Amygdalin | Fatty Acid Methyl Esters | | | |
|---|---|---|---|---|---|
| | (mg/kg almond) | C16:0 (mg/ml oil) | C18:0 (mg/ml oil) | C18:1 CIS (mg/ml oil) | C18:2 CIS (mg/ml oil) |
| Aldrich | 160.969 ± 14.145 | 60.541 ± 6.193 | 12.274 ± 2.420 | 611.649 ± 61.925 | 193.308 ± 16.235 |
| Bennett | 52.395 ± 6.984 | 47.125 ± 1.706 | 8.325 ± 0.428 | 470.573 ± 7.744 | 148.592 ± 5.759 |
| Booth | 0.829 ± 0.118 | 68.716 ± 16.030 | 9.047 ± 0.737 | 499.575 ± 48.630 | 174.427 ± 7.073 |
| Butte | 34.325 ± 9.880 | 58.526 ± 2.422 | 10.306 ± 0.992 | 514.480 ± 39.634 | 235.482 ± 7.116 |
| Capitola | 3.848 ± 0.555 | 56.433 ± 0.926 | 11.968 ± 0.017 | 551.789 ± 4.626 | 195.066 ± 4.392 |
| Carmel | 3.504 ± 0.704 | 57.759 ± 12.368 | 10.799 ± 2.962 | 549.497 ± 96.951 | 217.908 ± 61.132 |
| Durango | 80.438 ± 1.647 | 54.061 ± 1.250 | 10.355 ± 0.081 | 568.307 ± 53.535 | 168.658 ± 19.124 |
| Eddie | 2.130 ± 1.138 | 60.457 ± 0.046 | 10.534 ± 0.132 | 565.703 ± 5.286 | 215.314 ± 0.848 |
| Folsom | 32.836 ± 2.898 | 42.593 ± 1.040 | 7.635 ± 0.282 | 460.393 ± 11.767 | 147.214 ± 4.508 |
| Independence | 2.223 ± 0.340 | 51.108 ± 0.711 | 11.494 ± 0.157 | 502.370 ± 9.931 | 163.005 ± 6.502 |

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|---|---|---|---|---|---|
| Jenette | 1.218 ± 0.086 | 55.170 ± 8.588 | 11.080 ± 1.058 | 517.639 ± 55.476 | 210.232 ± 16.749 |
| Kester (2-19E) | 4.457 ± 3.975 | 54.332 ± 8.630 | 10.547 ± 1.838 | 550.081 ± 66.946 | 168.684 ± 39.742 |
| Mission | 31.370 ± 3.620 | 46.485 ± 2.633 | 9.894 ± 0.171 | 471.715 ± 33.744 | 151.207 ± 12.710 |
| Monterey | 35.804 ± 1.094 | 45.887 ± 0.403 | 12.926 ± 0.145 | 464.769 ± 15.718 | 182.011 ± 2.962 |
| Nonpareil | 9.929 ± 0.427 | 62.691 ± 3.190 | 11.671 ± 0.264 | 617.715 ± 4.459 | 195.805 ± 14.638 |
| Peerless | 7.595 ± 2.956 | 52.971 ± 7.107 | 10.183 ± 0.396 | 514.586 ± 42.102 | 202.399 ± 22.970 |
| Pyrenees | 87.141 ± 9.098 | 29.409 ± 19.350 | 7.903 ± 4.305 | 524.094 ± 14.860 | 129.869 ± 1.925 |
| Self Fruit P13.019 | 28.987 ± 0.174 | 57.637 ± 8.632 | 14.546 ± 2.989 | 553.320 ± 80.361 | 205.146 ± 32.366 |
| Self Fruit P16.013 | 0.709 ± 0.110 | 60.866 ± 4.360 | 14.407 ± 1.063 | 564.872 ± 16.170 | 220.168 ± 10.044 |
| Shasta | 0.920 ± 0.060 | 43.730 ± 8.126 | 10.598 ± 0.830 | 496.823 ± 54.952 | 169.994 ± 17.640 |
| Sonora | 1.077 ± 0.056 | 60.543 ± 4.943 | 11.679 ± 0.744 | 543.383 ± 37.134 | 218.817 ± 20.567 |
| Sterling | 7.495 ± 0.485 | 45.165 ± 3.011 | 8.578 ± 1.161 | 430.811 ± 38.366 | 145.463 ± 7.571 |
| Sweetheart | 5.687 ± 0.354 | 53.293 ± 1.748 | 9.753 ± 0.549 | 511.843 ± 23.973 | 173.087 ± 1.705 |
| UCD-1-16 | 8.885 ± 7.010 | 48.705 ± 1.331 | 11.515 ± 1.213 | 511.046 ± 53.572 | 159.589 ± 5.419 |
| UCD 1-232 | 1.052 ± 0.241 | 43.122 ± 6.168 | 10.233 ± 1.524 | 371.020 ± 76.782 | 150.530 ± 8.135 |
| UCD 1-271 | 1.234 ± 1.226 | 52.153 ± 5.744 | 11.505 ± 1.028 | 462.907 ± 68.326 | 164.425 ± 13.686 |

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|---|---|---|---|---|---|
| UCD 3-40 | 0.965 ± 0.050 | 48.319 ± 2.377 | 8.435 ± 0.842 | 403.070 ± 31.088 | 174.025 ± 7.222 |
| UCD 7-159 | 5.118 ± 0.116 | 43.632 ± 1.164 | 8.642 ± 0.026 | 413.499 ± 19.172 | 143.134 ± 7.807 |
| UCD 8-27 | 0.646 ± 0.078 | 47.684 ± 6.009 | 7.226 ± 1.139 | 453.138 ± 66.886 | 137.144 ± 21.662 |
| UCD 8-160 | 0.661 ± 0.537 | 55.535 ± 0.336 | 11.610 ± 1.415 | 537.776 ± 16.425 | 199.331 ± 3.364 |
| UCD 8-201 | 12.886 ± 0.757 | 64.49 ± 3.070 | 13.936 ± 0.983 | 539.738 ± 32.325 | 244.889 ± 3.699 |
| UCD 18-20 | 29.672 ± 0.117 | 54.252 ± 14.655 | 11.551 ± 3.345 | 540.646 ± 134.023 | 181.971 ± 53.090 |
| Winters | 1.682 ± 1.302 | 49.031 ± 8.641 | 8.382 ± 1.391 | 437.514 ± 65.973 | 170.196 ± 30.324 |
| Y116-161-99 | 1.552 ± 0.292 | 46.743 ± 3.649 | 12.038 ± 1.232 | 423.564 ± 44.456 | 162.669 ± 5.437 |
| Y117-86-03 | 26.563 ± 4.254 | 49.688 ± 1.876 | 17.203 ± 1.487 | 511.497 ± 3.556 | 170.556 ± 5.803 |
| Y117-91-03 | 1.195 ± 0.424 | 57.185 ± 4.627 | 13.700 ± 1.389 | 537.373 ± 31.589 | 184.943 ± 30.022 |
| Y121-42-99 | 57.284 ± 17.206 | 63.150 ± 6.467 | 18.091 ± 3.153 | 628.307 ± 83.469 | 203.911 ± 17.187 |
| Capella | 109.631 ± 4.802 | 50.339 ± 2.297 | 13.797 ± 2.035 | 508.697 ± 16.958 | 157.445 ± 7.259 |
| Carina | 1.402 ± 0.638 | 46.215 ± 9.370 | 11.913 ± 1.161 | 480.793 ± 84.611 | 151.714 ± 35.434 |
| Maxima | 0.531 ± 0.044 | 49.077 ± 8.188 | 14.586 ± 2.056 | 463.848 ± 48.230 | 162.820 ± 28.154 |
| Mira | 64.969 ± 5.422 | 54.046 ± 8.455 | 12.305 ± 0.576 | 467.082 ± 61.657 | 187.352 ± 28.827 |
| Rhea | 402.294 ± 34.471 | 47.291 ± 3.005 | 9.964 ± 0.804 | 483.376 ± 21.846 | 142.956 ± 18.203 |

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|---|---|---|---|---|---|
| Vela | 0.294 ± 0.058 | 42.403 ± 4.447 | 17.002 ± 4.194 | 509.520 ± 54.005 | 140.647 ± 20.140 |
| Constanti | 0.346 ± 0.078 | 43.815 ± 0.241 | 11.765 ± 0.985 | 499.069 ± 17.332 | 95.895 ± 4.755 |
| Marinada | 0.776 ± 1.102 | 41.931 ± 5.264 | 9.699 ± 1.561 | 478.662 ± 38.043 | 113.533 ± 12.330 |
| Tarraco | 1.030 ± 0.438 | 47.102 ± 4.282 | 13.034 ± 1.339 | 473.379 ± 1.224 | 124.631 ± 20.762 |
| Selection 29-148 | 0.706 ± 1.065 | 43.259 ± 11.220 | 12.097 ± 2.945 | 560.471 ± 138.087 | 93.326 ± 20.610 |
| Selection 30-297 | 0.166 ± 0.036 | 43.585 ± 7.034 | 12.074 ± 1.306 | 528.919 ± 90.908 | 97.652 ± 2.687 |
| Guara | 133.714 ± 2.445 | 41.408 ± 7.324 | 15.150± 0.421 | 451.240 ± 31.344 | 101.590 ± 15.579 |
| Mardia | 1.674 ± 0.802 | 38.407 ± 0.645 | 12.088 ± 0.206 | 456.167 ± 3.870 | 90.258 ± 10.113 |
| Soleta | 1.521 ± 1.506 | 45.572 ± 4.852 | 15.148 ± 1.846 | 482.192 ± 58.213 | 139.140 ± 14.340 |
| Vialfas | 0.417 ± 0.040 | 37.713 ± 0.740 | 12.309 ± 1.855 | 457.710 ± 15.812 | 77.772 ± 4.194 |
| Antoneta | 24.054 ± 1.097 | 38.536 ± 3.215 | 16.369 ± 3.046 | 461.656 ± 25.760 | 94.526 ± 9.546 |
| Makako | 0.783 ± 0.672 | 42.962 ± 2.473 | 10.732 ± 0.777 | 475.771 ± 12.420 | 82.431 ± 4.527 |
| Marta | 77.703 ± 6.802 | 37.812 ± 5.124 | 11.761 ± 1.310 | 480.148 ± 20.689 | 87.605 ± 14.741 |
| Penta | 2.534 ± 3.096 | 46.378 ± 2.065 | 13.628 ± 0.054 | 503.832 ± 19.461 | 107.807 ± 11.076 |
| Selection D00-360 | 9.518 ± 15.909 | 46.664 ± 0.474 | 12.635 ± 1.196 | 519.093 ± 1.166 | 106.317 ± 4.216 |
| Selection D01-188 | 0.085 ± 0.044 | 40.960 ± 2.102 | 9.976 ± 0.811 | 457.588 ± 17.466 | 89.641 ± 4.985 |

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|---|---|---|---|---|---|
| Selection D06-795 | 0.283 ± 0.123 | 38.464 ± 1.101 | 9.474 ± 0.533 | 495.319 ± 22.241 | 75.211 ± 2.484 |
| Matan | 0.477 ± 0.651 | 34.505 ± 4.616 | 9.094 ± 1.149 | 445.483 ± 32.326 | 68.070 ± 14.281 |
| Total Average | 24.194 ± 57.832 | 49.127 ± 9.238 | 11.619 ± 2.667 | 499.452 ± 62.286 | 154.458 ± 46.420 |

**Table 8.** Average tocopherol isomer (delta, beta, gamma, and alpha) concentrations for 60 almond varieties (average ± SD, n=2).

| Varietal Name | **Tocopherols (Vitamin E)** | | | | |
|---|---|---|---|---|---|
| | Delta (mg/kg oil) | Beta (mg/kg oil) | Gamma (mg/kg oil) | Alpha (mg/kg oil) | Total (mg/kg oil) |
| Aldrich | 0.814 ± 0.167 | 9.823 ± 1.551 | 27.466 ± 3.278 | 966.914 ± 56.076 | 1005.017 ± 57.970 |
| Bennett | 0.637 ± 0.054 | 7.842 ± 0.334 | 24.710 ± 0.190 | 890.813 ± 30.255 | 954.915 ± 12.885 |
| Booth | 1.020 ± 0.108 | 8.502 ± 0.064 | 29.447 ± 2.694 | 849.695 ± 25.991 | 924.003 ± 30.832 |
| Butte | 0.911 ± 0.002 | 6.641 ± 0.090 | 26.653 ± 1.723 | 818.530 ± 79.058 | 885.230 ± 24.002 |
| Capitola | 1.058 ± 0.415 | 7.206 ± 0.098 | 31.220 ± 6.014 | 751.061 ± 75.189 | 888.663 ± 28.858 |
| Carmel | 0.445 ± 0.103 | 8.993 ± 0.155 | 15.311 ± 2.677 | 692.562 ± 81.235 | 909.495 ± 0.602 |
| Durango | 0.944 ± 0.016 | 9.293 ± 1.616 | 23.864 ± 3.950 | 715.618 ± 1.517 | 852.734 ± 80.874 |
| Eddie | 0.824 ± 0.357 | 7.835 ± 0.168 | 27.627 ± 8.391 | 835.807 ± 47.937 | 821.937 ± 37.321 |

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|---|---|---|---|---|---|
| Folsom | 0.679 ± 0.008 | 12.584 ± 2.566 | 22.077 ± 3.643 | 809.935 ± 35.374 | 790.545 ± 81.716 |
| Independence | 0.621 ± 0.189 | 12.877 ± 0.688 | 10.712 ± 0.757 | 600.480 ± 41.305 | 695.279 ± 53.011 |
| Jenette | 0.666 ± 0.039 | 7.141 ± 0.115 | 22.093 ± 4.071 | 772.721 ± 106.653 | 717.311 ± 84.170 |
| Kester (2-19E) | 0.802 ± 0.111 | 9.122 ± 1.771 | 23.982 ± 1.763 | 776.418 ± 65.464 | 764.641 ± 17.236 |
| Mission | 0.575 ± 0.140 | 7.330 ± 1.568 | 19.473 ± 1.712 | 689.559 ± 50.311 | 749.720 ± 3.867 |
| Monterey | 0.462 ± 0.082 | 6.806 ± 0.182 | 12.873 ± 3.617 | 638.769 ± 34.618 | 789.439 ± 60.038 |
| Nonpareil | 0.88 ± 0.017 | 9.168 ± 1.259 | 26.121 ± 1.945 | 821.938 ± 42.344 | 872.093 ± 56.853 |
| Peerless | 0.916 ± 0.334 | 6.362 ± 0.889 | 28.860 ± 5.250 | 827.045 ± 78.710 | 891.674 ± 29.161 |
| Pyrenees | 0.730 ± 0.149 | 6.965 ± 0.056 | 28.967 ± 1.967 | 739.205 ± 29.427 | 845.275 ± 36.458 |
| Self Fruit P13.019 | 0.194 ± 0.083 | 8.060 ± 0.481 | 9.450 ± 1.019 | 802.144 ± 12.691 | 736.739 ± 117.036 |
| Self Fruit P16.013 | 0.521 ± 0.094 | 5.998 ± 0.015 | 22.992 ± 3.854 | 854.954 ± 12.744 | 624.690 ± 41.425 |
| Shasta | 0.652 ± 0.092 | 7.461 ± 0.120 | 26.928 ± 1.660 | 787.734 ± 31.211 | 738.129 ± 201.852 |
| Sonora | 0.786 ± 0.027 | 6.762 ± 0.431 | 24.869 ± 1.286 | 840.686 ± 7.661 | 802.621 ± 110.648 |
| Sterling | 1.418 ± 0.019 | 8.030 ± 0.307 | 33.977 ± 3.049 | 827.39 ± 27.677 | 742.919 ± 26.216 |
| Sweetheart | 0.723 ± 0.049 | 8.582 ± 2.988 | 23.880 ± 2.712 | 747.561 ± 53.793 | 810.324 ± 69.109 |
| UCD-1-16 | 0.572 ± 0.185 | 7.206 ± 0.410 | 21.935 ± 6.145 | 780.181 ± 56.786 | 807.061 ± 73.723 |

| | | | | | |
|---|---|---|---|---|---|
| UCD 1-232 | 0.519 ± 0.017 | 5.614 ± 0.548 | 22.424 ± 0.356 | 776.912 ± 50.946 | 716.938 ± 53.731 |
| UCD 1-271 | 0.981 ± 0.240 | 5.458 ± 0.606 | 30.810 ± 3.312 | 539.834 ± 2.328 | 682.352 ± 4.820 |
| UCD 3-40 | 0.888 ± 0.261 | 6.178 ± 0.468 | 20.633 ± 3.172 | 676.974 ± 25.409 | 658.910 ± 37.972 |
| UCD 7-159 | 0.601 ± 0.019 | 6.278 ± 0.690 | 18.607 ± 3.081 | 568.571 ± 4.385 | 760.303 ± 181.363 |
| UCD 8-27 | 1.182 ± 0.191 | 11.133 ± 1.030 | 25.633 ± 1.450 | 503.293 ± 15.641 | 858.108 ± 43.046 |
| UCD 8-160 | 1.107 ± 0.006 | 4.849 ± 0.111 | 26.397 ± 1.638 | 675.456 ± 15.237 | 875.543 ± 67.703 |
| UCD 8-201 | 2.086 ± 0.598 | 10.283 ± 0.513 | 51.771 ± 7.318 | 923.210 ± 46.556 | 863.183 ± 85.183 |
| UCD 18-20 | 0.682 ± 0.345 | 7.299 ± 0.675 | 20.143 ± 4.577 | 716.961 ± 17.236 | 800.580 ± 3.351 |
| Winters | 0.668 ± 0.168 | 9.049 ± 0.889 | 17.897 ± 3.146 | 787.902 ± 17.975 | 775.866 ± 31.599 |
| Y116-161-99 | 0.640 ± 0.041 | 7.424 ± 0.754 | 22.456 ± 0.995 | 741.692 ± 20.335 | 781.638 ± 39.762 |
| Y117-86-03 | 0.929 ± 0.071 | 7.563 ± 0.011 | 28.256 ± 1.260 | 705.679 ± 9.473 | 819.848 ± 14.275 |
| Y117-91-03 | 0.840 ± 0.046 | 9.548 ± 0.079 | 26.802 ± 2.873 | 699.865 ± 76.057 | 851.297 ± 30.200 |
| Y121-42-99 | 1.266 ± 0.204 | 9.775 ± 1.374 | 29.636 ± 5.794 | 718.697 ± 85.250 | 884.465 ± 16.707 |
| Capella | 0.336 ± 0.046 | 6.085 ± 0.337 | 12.886 ± 2.238 | 597.664 ± 18.675 | 871.223 ± 35.434 |
| Carina | 0.957 ± 0.487 | 8.041 ± 0.785 | 22.292 ± 5.809 | 688.634 ± 18.110 | 822.774 ± 33.083 |
| Maxima | 0.871 ± 0.017 | 5.783 ± 0.606 | 25.487 ± 2.465 | 645.911 ± 0.366 | 838.658 ± 55.546 |

| | | | | | |
|---|---|---|---|---|---|
| Mira | 1.200 ± 0.097 | 8.567 ± 0.699 | 23.500 ± 1.894 | 781.917 ± 42.318 | 873.103 ± 6.832 |
| Rhea | 0.674 ± 0.314 | 9.435 ± 0.016 | 19.756 ± 5.181 | 645.880± 25.200 | 880.522 ± 17.324 |
| Vela | 0.608 ± 0.148 | 6.401 ± 0.065 | 19.921 ± 3.450 | 536.055 ± 6.014 | 870.815 ± 31.051 |
| Constanti | 0.191 ± 0.042 | 7.937 ± 0.554 | 10.810 ± 1.198 | 468.771 ± 42.321 | 795.703 ± 75.173 |
| Marinada | 0.802 ± 0.014 | 7.878 ± 0.244 | 18.586 ± 0.426 | 586.507 ± 44.808 | 780.746 ± 54.020 |
| Tarraco | 0.384 ± 0.120 | 7.816 ± 0.703 | 11.139 ± 1.251 | 592.177 ± 69.487 | 832.404 ± 19.035 |
| Selection 29-148 | 0.303 ± 0.028 | 9.097 ± 0.532 | 11.867 ± 1.175 | 590.607 ± 10.583 | 809.895 ± 50.867 |
| Selection 30-297 | 0.152 ± 0.044 | 6.628 ± 0.013 | 11.091 ± 0.558 | 587.755 ± 48.782 | 771.999 ± 2.726 |
| Guara | 0.437 ± 0.129 | 6.939 ± 0.775 | 18.981 ± 0.598 | 678.198 ± 0.513 | 805.468 ± 50.058 |
| Mardia | 0.471 ± 0.122 | 9.046 ± 0.050 | 16.871 ± 1.363 | 498.308 ± 12.230 | 711.266 ± 183.280 |
| Soleta | 0.358 ± 0.062 | 4.694 ± 0.347 | 18.186 ± 1.676 | 525.483 ± 26.712 | 577.082 ± 6.484 |
| Vialfas | 0.261 ± 0.074 | 5.667 ± 0.505 | 14.986 ± 3.218 | 528.393 ± 3.467 | 628.222 ± 78.807 |
| Antoneta | 0.229 ± 0.049 | 7.836 ± 0.451 | 10.076 ± 0.915 | 589.326 ± 68.161 | 704.673 ± 29.310 |
| Makako | 0.149 ± 0.023 | 5.816 ± 1.096 | 10.970 ± 0.138 | 378.794 ± 6.565 | 662.618 ± 88.784 |
| Marta | 0.346 ± 0.006 | 6.976 ± 0.127 | 13.018 ± 1.188 | 542.876 ± 16.961 | 594.057 ± 8.175 |
| Penta | 0.191 ± 0.014 | 4.884 ± 0.153 | 13.724 ± 2.117 | 456.057 ± 27.054 | 558.285 ± 42.415 |

| | | | | | |
|---|---|---|---|---|---|
| Selection D00-360 | 0.341 ± 0.008 | 6.714 ± 0.050 | 15.256 ± 0.210 | 620.254 ± 51.090 | 541.241 ± 18.311 |
| Selection D01-188 | 0.194 ± 0.048 | 6.242 ± 0.385 | 13.046 ± 1.407 | 574.340 ± 6.238 | 625.074 ± 100.247 |
| Selection D06-795 | 0.479 ± 0.040 | 6.212 ± 0.619 | 20.549 ± 2.310 | 565.870 ± 17.400 | 707.809 ± 16.758 |
| Matan | 0.647 ± 0.010 | 8.059 ± 0.277 | 16.387 ± 1.144 | 497.695 ± 79.218 | 872.945 ± 216.779 |
| Total Average | 0.680 ± 0.373 | 7.663 ± 1.803 | 21.272 ± 7.804 | 684.171 ± 132.673 | 713.787 ± 138.331 |

**Tocopherols**

Tocopherols are the main antioxidant present in almonds and include the isomers delta (δ), beta (β), gamma (γ), and alpha (α) tocopherol. The average concentration of each isomer were δ = 0.680 ± 0.373 mg/kg of oil, β = 7.663 ± 1.803 mg/kg of oil, γ = 21.272 ± 7.804 mg/kg of oil, and α = 684.171 ± 132.673 mg/kg of oil. The average values for α-tocopherol and β-tocopherol were within the range found by Kodad et al. (2018) (85 – 840 mg/kg and 0.12 – 80 mg/kg respectively) but were higher for γ-tocopherol and δ-tocopherol (0.14-0.84 mg/kg and 0.02- 0.16 mg/kg respectively). The lowest average concentrations were 0.149 ± 0.023 (Makako), 4.694 ± 0.347 (Soleta), 9.450 ± 1.019 (Self Fruit P13.019), and 378.794 ± 6.565 (Makako) mg/kg of oil for δ, β, γ, and α respectively. The highest average concentrations were 2.086 ± 0.598 (UCD 8-201), 12.877 ± 0.688 (Independence), 51.771 ± 7.318 (UCD 8-201), and 966.914 ± 56.076 (Aldrich) mg/kg of oil for δ, β, γ, and α respectively (**Table 8**). Statistically, significant differences ($p < 0.001$) of all tocopherol isomers were present in the varieties. UCD 8-201 showed a significantly higher γ tocopherol concentration than other varieties. The average total tocopherol content was 713.787 ± 138.331 mg/kg of oil. The highest total tocopherol concentration was in Aldrich at 1005.017 ± 57.970 mg/kg of oil while the lowest concentration was 541.241 ± 18.311 mg/kg of oil in Selection D00-360. As the main antioxidant, almonds with higher levels of tocopherols (e.g .Aldrich, Bennet, Booth) may have longer shelf life potential than varieties with inherently lower levels of total tocopherols (e.g. Selection D00-360, Mardia). Additionally, almonds with higher levels of saturated fatty acids in conjunction with lower levels of total tocopherols may indicate varieties that are more susceptible to lipid oxidation and shorter shelf life.

**Benzaldehyde and Volatiles**

A total amount of fifty-three volatile compounds identified in ground raw almonds. Three of the compound identities were confirmed with authentic standards, while the identities of the other compounds were made by comparing the MS spectra to the NIST 17 library. All volatiles were quantified using an external calibration curve. The integration limit was set at a signal-to-noise ratio of 7. The calibration curves were assigned to the volatile compounds based on similar volatility and expected headspace activity of the compound. Aldehydes, alkanes, benzenes, and furans were quantified utilizing the benzaldehyde-$d_6$ standard curve. Ketones were quantified with the 2-nonanone-1,1,1,3,3-$d_5$ standard curve, and alcohols and acids with the n-hexyl-$d_{13}$ alcohol standard curve. The values observed were low when compared with other studies of almond volatiles (Luo et al. 2018; Mexis et al. 2009; Xiao et al.(2014). This could be due to the prolonged storage within the cold room after harvesting. Volatile compounds positively associated with almond flavor are benzaldehyde, phenylethyl alcohol, and benzyl alcohol (King et al. 2019). Benzaldehyde was found at an average concentration of 0.053 ± 0.218 µg/kg of almonds, with the highest concentration found in Pyrenees at 1.593 ± 0.014 µg/kg of almonds. Phenylethyl alcohol and benzyl alcohol concentrations were low with average concentrations of 0.008 ± 0.052 and 0.004 ± 0.040 µg/kg of almonds respectively (**Table 9**). Hexanal, a product of the oxidation of unsaturated fatty acids, is negatively associated with almond flavor and is a marker for increased rancidity (King et al. 2019). Hexanal levels ranted in the varieties with an average concentration of 1.727 ± 4.399 µg/kg of almonds. The highest levels were present in the Nonpareil almonds (18.676 ± 14. 984 µg/kg), which indicate that these almonds were more oxidized than some of the other samples, although levels were well below the levels in which rancidity is detected in roasted almonds (2,380 ± 40 µg/kg) (Franklin et al. 2017).

**Table 9.** Average concentrations of volatiles found in raw ground almonds (µg/kg of almonds). Concentrations marked 0 states it was under the limit of quantification.

| Varietal Name | Aldrich | Bennett | Booth | Butte | Capitola | Carmel | Durango | Eddie | Folsom |
|---|---|---|---|---|---|---|---|---|---|
| Heptane, 2,2,4,6,6-pentamethyl- | 0.809 ± 0.196 | 0.308 ± 0.436 | 2.772 ± 0.086 | 1.883 ± 0.272 | 0.233 ± 0.330 | 2.733 ± 0.268 | 1.201 ± 0.251 | 3.215 ± 0.022 | 3.043 ± 0.450 |
| Toluene | 2.424 ± 0.238 | 1.423 ± 0.346 | 1.717 ± 0.035 | 1.598 ± 0.268 | 1.064 ± 0.589 | 1.012 ± 0.363 | 0.583 ± 0.014 | 0.761 ± 0.480 | 0.289 ± 0.223 |
| Hexanal | 3.594 ± 0.203 | 0.811 ± 0.692 | 0.704 ± 0.626 | 0.308 ± 0.248 | 0 | 0.232 ± 0.047 | 0.887 ± 0.558 | 0.377 ± 0.024 | 0.214 ± 0.006 |
| Ethyl Acetate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2-Heptenal, (E)- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Nonanal | 2.099 ± 0.102 | 0.483 ± 0.477 | 0.320.185 | 0 | 0.291 ± 0.072 | 0 | 2.663 ± 1.184 | 0.764 ± 0.356 | 0.309 ± 0.293 |
| Benzaldehyde | 0.133 ± 0.066 | 0 | 0 | 0 | 0 | 0.016 ± 0.022 | 0.197 ± 0.092 | 0 | 0 |
| Benzene | 2.773 ± 0.077 | 2.305 ± 0.145 | 2.195 ± 0.062 | 1.423 ± 0.746 | 1.435 ± 0.148 | 1.109 ± 0.183 | 0.698 ± 0.362 | 0.956 ± 0.341 | 0.582 ± 0.022 |
| Furan, 2-pentyl- | 0.026 ± 0.036 | 0 | 0.008 ± 0.011 | 0 | 0.018 ± 0.026 | 0 | 0.311 ± 0.067 | 0.175 ± 0.158 | 0.253 ± 0.044 |
| Formamide, N,N-dimethyl- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Butyrolactone | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.326 ± 0.223 | 0 |
| Acetone | 0.861 ± 0.000 | 0.769 ± 0.199 | 1.849 ± 0.001 | 0.779 ± 0.031 | 0.701 ± 0.106 | 1.609 ± 0.147 | 1.141 ± 0.051 | 1.473 ± 0.165 | 2.447 ± 0.036 |
| 2-Butanone | 0.038 ± 0.003 | 0 | 0 | 0 | 0 | 0 | 0.116 ± 0.023 | 0.166 ± 0.005 | 0.259 ± 0.056 |
| 2-Heptanone | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2(3H)-Furanone, dihydro-5-methyl- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.014 ± 0.019 | 0 |
| 2H-Pyran-2-one, tetrahydro- | 0 | 0 | 0 | 0.048 ± 0.016 | 0 | 0 | 0 | 0.019 ± 0.027 | 0 |
| 2(3H)-Furanone, 5-ethyldihydro- | 0.710 ± 0.139 | 0.376 ± 0.017 | 0.384 ± 0.109 | 0.223 ± 0.008 | 0.332 ± 0.040 | 0.238 ± 0.004 | 0.425 ± 0.034 | 0.860 ± 0.090 | 0.669 ± 0.009 |
| 2(3H)-Furanone, dihydro-5-propyl- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Methyl Alcohol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.046 ± 0.065 | 0 |
| Isopropyl Alcohol | 2.581 ± 0.283 | 3.768 ± 0.093 | 4.690 ± 0.227 | 2.965 ± 0.738 | 2.897 ± 0.280 | 3.943 ± 0.239 | 2.229 ± 0.316 | 4.865 ± 1.819 | 5.287 ± 0.321 |
| Ethanol | 6.521 ± 0.147 | 6.198 ± 0.496 | 3.044 ± 0.611 | 4.283 ± 0.501 | 2.780 ± 0.244 | 2.122 ± 0.638 | 4.445 ± 0.099 | 17.648 ± 6.272 | 9.212 ± 0.247 |
| 2-Butanol | 1.072 ± 0.031 | 1.396 ± 0.430 | 1.083 ± 0.146 | 2.216 ± 1.286 | 1.142 ± 0.106 | 0.747 ± 0.084 | 0.707 ± 0.269 | 1.831 ± 0.859 | 1.004 ± 0.304 |
| 1-Propanol | 0.363 ± 0.289 | 0.232 ± 0.206 | 5.914 ± 2.440 | 3.418 ± 1.112 | 0.472 ± 0.010 | 4.182 ± 0.226 | 0.962 ± 0.135 | 4.013 ± 2.125 | 5.128 ± 0.105 |
| 1-Propanol, 2-methyl- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.192 ± 0.272 | 0.016 ± 0.023 |
| 3-Pentanol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Pentanol | 0 | 0.282 ± 0.051 | 0.692 ± 0.375 | 0.542 ± 0.619 | 0.667 ± 0.251 | 0 | 0 | 0.850 ± 0.558 | 0.136 ± 0.087 |
| 1-Butanol, 3-methyl- | 1.111 ± 0.076 | 2.246 ± 0.537 | 2.200 ± 0.006 | 1.718 ± 0.246 | 0.952 ± 0.066 | 0 | 1.494 ± 0.230 | 4.029 ± 1.269 | 4.318 ± 0.249 |
| 1-Pentanol | 9.912 ± 0.462 | 6.782 ± 0.363 | 10.390 ± 0.600 | 4.665 ± 0.398 | 8.351 ± 0.320 | 6.135 ± 0.126 | 10.170 ± 0.322 | 13.572 ± 2.356 | 12.516 ± 0.254 |
| 2-Heptanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.040 ± 0.056 | 0 |
| 1-Hexanol | 63.071 ± 3.306 | 49.067 ± 2.499 | 58.867 ± 2.926 | 33.017 ± 1.527 | 55.279 ± 1.182 | 38.141 ± 0.325 | 66.572 ± 2.011 | 87.392 ± 12.397 | 78.840 ± 0.590 |
| Acetic acid | 2.331 ± 0.376 | 2.725 ± 0.282 | 4.638 ± 0.123 | 0 | 1.145 ± 0.169 | 0 | 1.866 ± 0.038 | 3.372 ± 0.995 | 1.540 ± 0.047 |
| 1-Octen-3-ol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1-Heptanol | 0.249 ± 0.037 | 0 | 0 | 0 | 0 | 0 | 0.344 ± 0.180 | 0.704 ± 0.128 | 0.293 ± 0.128 |
| 1-Octanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2,3-Butanediol | 0 | 0.469 ± 0.055 | 1.481 ± 0.986 | 1.075 ± 0.357 | 0.260 ± 0.251 | 0.783 ± 0.103 | 0.480 ± 0.225 | 4.154 ± 1.006 | 1.021 ± 0.267 |
| 1-Nonanol | 0.275 ± 0.009 | 0.280 ± 0.042 | 0.213 ± 0.128 | 0.295 ± 0.100 | 0.768 ± 0.259 | 1.094 ± 0.074 | 2.387 ± 0.411 | 2.112 ± 0.713 | 0.976 ± 0.092 |
| Pentanoic acid | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Hexanoic acid | 5.075 ± 3.120 | 1.520 ± 1.358 | 3.374 ± 0.027 | 0.076 ± 0.108 | 2.422 ± 1.120 | 1.089 ± 0.042 | 2.833 ± 1.548 | 7.311 ± 0.234 | 5.591 ± 0.354 |
| Benzyl alcohol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Phenylethyl Alcohol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Nonanoic acid | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

| Independence | Jenette | Kester (2-19E) | Mission | Monterey | Nonpareil | Peerless | Pyreness | Self Fruit P13.019 | Self Fruit P16.013 | Shasta |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.041 ± 0.058 | 1.292 ± 0.121 | 3.794 ± 0.189 | 1.664 ± 0.058 | 1.974 ± 0.367 | 2.898 ± 0.559 | 2.260.176 | 0.209 ± 0.296 | 0.431 ± 0.019 | 0.673 ± 0.103 | 0 |
| 0.524 ± 0.471 | 0.475 ± 0.212 | 0.151 ± 0.041 | 0.718 ± 0.009 | 0.435 ± 0.237 | 0.419 ± 0.329 | 0.906 ± 0.235 | 0.333 ± 0.161 | 0.565 ± 0.150 | 0.259 ± 0.281 | 0.547 ± 0.188 |
| 0.060.085 | 0 | 0.137 ± 0.194 | 0.259 ± 0.366 | 0.604 ± 0.013 | 18.676 ± 14.984 | 2.423 ± 0.386 | 9.230 ± 1.779 | 0.543 ± 0.286 | 0.264 ± 0.071 | 0.339 ± 0.125 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0.392 ± 0.307 | 0.534 ± 0.243 | 0.462 ± 0.606 | 0.163 ± 0.231 | 5.037 ± 0.927 | 1.005 ± 0.200 | 4.771 ± 2.394 | 1.123 ± 0.765 | 0.795 ± 0.069 | 0.063 ± 0.089 |
| 0 | 0 | 0 | 0 | 0 | 0.080.016 | 0.215 ± 0.009 | 1.593 ± 0.014 | 0.480.009 | 0.172 ± 0.013 | 0 |
| 0.887 ± 0.214 | 0.721 ± 0.070 | 0.726 ± 0.140 | 0.847 ± 0.033 | 0.676 ± 0.027 | 0 | 0.033 ± 0.047 | 0.164 ± 0.022 | 0.325 ± 0.280 | 0.091 ± 0.128 | 0.200.060 |
| 0.093 ± 0.132 | 0 | 0.214 ± 0.084 | 0 | 0.044 ± 0.063 | 0.179 ± 0.110 | 0.370.088 | 0 | 0.113 ± 0.049 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0.017 ± 0.024 | 0 | 0 | 0 | 0.514 ± 0.481 | 0 | 0 | 0 | 0 | 0.038 ± 0.054 |
| 1.470 ± 0.090 | 1.014 ± 0.008 | 2.723 ± 0.034 | 1.083 ± 0.029 | 0.686 ± 0.023 | 1.919 ± 0.198 | 1.582 ± 0.007 | 3.603 ± 0.208 | 0.872 ± 0.217 | 1.313 ± 0.139 | 7.264 ± 0.959 |
| 0.087 ± 0.040 | 0 | 0.404 ± 0.013 | 0 | 0 | 0 | 0 | 0.436 ± 0.029 | 0 | 0.004 ± 0.006 | 0.292 ± 0.089 |
| 0.522 ± 0.008 | 0 | 0 | 0 | 0 | 0.821 ± 0.019 | 0.776 ± 0.025 | 1.206 ± 0.045 | 0 | 0 | 0 |
| 0.059 ± 0.012 | 0 | 0 | 0 | 0 | 0.043 ± 0.036 | 0 | 0.112 ± 0.034 | 0 | 0 | 0 |
| 0.067 ± 0.095 | 0 | 0 | 0 | 0 | 0.132 ± 0.048 | 0.066 ± 0.001 | 0.276 ± 0.027 | 0 | 0 | 0 |
| 0.454 ± 0.061 | 0.263 ± 0.083 | 0.452 ± 0.084 | 0.235 ± 0.093 | 0.726 ± 0.069 | 1.113 ± 0.084 | 0.317 ± 0.002 | 0.547 ± 0.011 | 0.344 ± 0.036 | 0.259 ± 0.042 | 0.152 ± 0.024 |
| 0 | 0.022 ± 0.031 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.592 ± 0.010 | 0.051 ± 0.073 | 0 | 0.258 ± 0.074 |
| 6.223 ± 0.374 | 4.961 ± 0.606 | 4.228 ± 0.751 | 1.828 ± 0.148 | 1.096 ± 0.227 | 6.500 ± 0.902 | 6.142 ± 0.099 | 8.106 ± 2.053 | 2.669 ± 0.816 | 3.615 ± 0.500 | 29.154 ± 1.599 |
| 13.931 ± 0.909 | 11.281 ± 0.992 | 2.820 ± 0.276 | 5.602 ± 0.964 | 2.767 ± 0.269 | 14.985 ± 3.289 | 5.524 ± 0.400 | 6.132 ± 1.256 | 12.200 ± 0.228 | 5.726 ± 0.471 | 55.128 ± 16.773 |
| 1.346 ± 0.099 | 1.477 ± 0.015 | 1.069 ± 0.067 | 0.632 ± 0.230 | 0.732 ± 0.269 | 1.464 ± 0.589 | 1.915 ± 0.947 | 2.309 ± 0.542 | 2.099 ± 0.343 | 1.126 ± 0.091 | 3.420 ± 0.251 |
| 0.580 ± 0.122 | 1.855 ± 0.209 | 4.040 ± 0.246 | 0.043 ± 0.061 | 0.655 ± 0.260 | 5.495 ± 2.484 | 2.283 ± 0.133 | 2.041 ± 0.011 | 0.895 ± 0.027 | 0.926 ± 0.174 | 0.927 ± 0.508 |
| 0.615 ± 0.035 | 0 | 0 | 0 | 0 | 2.925 ± 4.136 | 0.287 ± 0.009 | 0.680 ± 0.015 | 0.821 ± 0.182 | 0 | 0.999 ± 0.113 |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.730 ± 2.478 | 0 | 0 | 13.136 ± 0.755 |
| 0.846 ± 0.075 | 0.728 ± 0.010 | 0.410 ± 0.172 | 0 | 0 | 1.624 ± 1.599 | 0.925 ± 0.130 | 2.59 ± 0.990 | 0 | 0 | 0.211 ± 0.009 |
| 6.410 ± 0.312 | 3.234 ± 0.120 | 1.767 ± 0.293 | 1.389 ± 0.124 | 0.663 ± 0.316 | 4.196 ± 1.461 | 3.475 ± 0.330 | 3.178 ± 0.186 | 3.552 ± 0.586 | 0.302 ± 0.121 | 6.098 ± 0.162 |
| 5.733 ± 0.179 | 9.056 ± 0.048 | 7.917 ± 0.630 | 7.327 ± 3.748 | 11.94 ± 3.013 | 16.414 ± 0.962 | 5.080 ± 0.538 | 4.887 ± 0.094 | 8.944 ± 0.025 | 8.014 ± 0.035 | 2.378 ± 0.393 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 42.218 ± 0.904 | 64.790 ± 8.686 | 56.289 ± 8.819 | 48.295 ± 17.559 | 68.919 ± 18.243 | 86.311 ± 4.444 | 39.682 ± 2.212 | 26.945 ± 1.214 | 62.999 ± 0.406 | 46.524 ± 1.822 | 22.215 ± 0.567 |
| 0.025 ± 0.035 | 1.584 ± 0.256 | 1.047 ± 0.284 | 0 | 0 | 5.163 ± 2.078 | 0 | 0.190 ± 0.268 | 0.206 ± 0.028 | 0 | 1.099 ± 0.274 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0.032 ± 0.046 | 0.160 ± 0.221 | 0.246 ± 0.348 | 0.745 ± 1.054 | 1.334 ± 0.121 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0.019 ± 0.028 | 0 | 0 | 0 | 0 | 0 | 0 |
| 7.100 ± 0.153 | 1.156 ± 0.777 | 0 | 0.577 ± 0.602 | 1.155 ± 0.055 | 5.262 ± 5.197 | 1.425 ± 0.059 | 1.902 ± 0.322 | 4.245 ± 1.089 | 0 | 11.491 ± 0.827 |
| 1.295 ± 0.308 | 1.204 ± 0.716 | 1.359 ± 0.312 | 1.900 ± 0.194 | 2.362 ± 0.040 | 0.261 ± 0.203 | 0.943 ± 0.299 | 0 | 2.782 ± 0.281 | 1.409 ± 0.354 | 0.617 ± 0.023 |
| 0 | 0 | 0 | 0 | 0 | 0.548 ± 0.014 | 0 | 0 | 0 | 0 | 0 |
| 0.590 ± 0.060 | 3.087 ± 0.494 | 5.026 ± 0.726 | 2.714 ± 1.493 | 2.561 ± 0.503 | 8.971 ± 1.929 | 1.589 ± 0.731 | 0.026 ± 0.036 | 3.878 ± 0.505 | 4.049 ± 0.160 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0.431 ± 0.609 | 0.241 ± 0.278 | 0.126 ± 0.178 | 0 | 0.056 ± 0.079 | 0.140 ± 0.198 |

| Sonora | Sterling | Sweetheart | UCD-1-16 | UCD 1-232 | UCD 1-271 | UCD 3-40 | UCD 7-159 | UCD 8-27 | UCD 8-160 | UCD 8-201 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1.205 ± 0.333 | 1.537 ± 0.107 | 1.864 ± 0.076 | 0.859 ± 0.029 | 3.540 ± 1.362 | 1.776 ± 0.085 | 1.449 ± 0.023 | 1.415 ± 0.207 | 4.002 ± 0.277 | 1.784 ± 0.459 | 1.213 ± 0.178 |
| 0.080.094 | 0 | 0.382 ± 0.305 | 0.136 ± 0.022 | 0.147 ± 0.051 | 1.709 ± 0.002 | 1.415 ± 0.169 | 0.765 ± 0.096 | 0.969 ± 0.052 | 0.019 ± 0.027 | 0.078 ± 0.111 |
| 0.417 ± 0.277 | 0.821 ± 0.359 | 0.042 ± 0.060 | 0.045 ± 0.063 | 5.707 ± 7.158 | 1.190.017 | 0.616 ± 0.228 | 0 | 0.619 ± 0.180 | 0.738 ± 0.354 | 1.200 ± 1.272 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 1.260 ± 1.782 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.114 ± 0.161 | 1.160.643 | 1.311 ± 0.386 | 1.119 ± 0.759 | 2.036 ± 0.532 | 1.429 ± 0.023 | 0.625 ± 0.411 | 0.370.066 | 0.325 ± 0.449 | 0.834 ± 0.609 | 0.868 ± 0.866 |
| 0 | 0 | 0 | 0 | 0.183 ± 0.259 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0.191 ± 0.050 | 0 | 0 | 0 | 0 | 0 | 0.006 ± 0.009 | 0 | 0 |
| 0.026 ± 0.037 | 0.501 ± 0.199 | 0.373 ± 0.329 | 0.019 ± 0.027 | 2.341 ± 2.611 | 1.005 ± 0.104 | 0.023 ± 0.032 | 0 | 0.109 ± 0.154 | 0.216 ± 0.158 | 0.385 ± 0.011 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.046 ± 0.011 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.094 ± 0.040 | 0 |
| 1.493 ± 0.117 | 1.026 ± 0.081 | 0.719 ± 0.102 | 0.739 ± 0.024 | 2.255 ± 0.285 | 1.228 ± 0.048 | 1.981 ± 0.019 | 1.877 ± 0.303 | 2.522 ± 0.250 | 2.071 ± 0.096 | 1.800 ± 0.059 |
| 0 | 0 | 0 | 0 | 0 | 0.040 ± 0.056 | 0.229 ± 0.047 | 0.113 ± 0.033 | 0.244 ± 0.093 | 0.285 ± 0.042 | 0 |
| 0.272 ± 0.069 | 0 | 0 | 0 | 1.461 ± 2.066 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.459 ± 0.002 | 0 | 0 | 0 | 0.054 ± 0.076 | 0 | 0 | 0 | 0.009 ± 0.013 | 0 | 0 |
| 0.692 ± 0.036 | 0 | 0 | 0.022 ± 0.032 | 0.107 ± 0.129 | 0 | 0 | 0 | 0.030 ± 0.043 | 0.077 ± 0.060 | 0 |
| 0.599 ± 0.015 | 0.646 ± 0.046 | 0.640 ± 0.011 | 0.324 ± 0.095 | 1.326 ± 0.970 | 0.459 ± 0.002 | 0.333 ± 0.054 | 0.367 ± 0.025 | 0.543 ± 0.048 | 0.678 ± 0.019 | 0.793 ± 0.114 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.370 ± 0.052 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 7.041 ± 0.055 | 6.421 ± 0.700 | 5.739 ± 0.823 | 3.855 ± 0.546 | 8.088 ± 1.899 | 6.252 ± 0.716 | 5.503 ± 0.185 | 5.941 ± 0.518 | 7.569 ± 0.692 | 6.096 ± 0.292 | 5.106 ± 0.686 |
| 7.956 ± 0.103 | 5.617 ± 1.293 | 6.857 ± 0.786 | 3.353 ± 1.085 | 5.974 ± 0.939 | 10.708 ± 0.188 | 4.355 ± 2.031 | 12.107 ± 2.284 | 6.347 ± 1.018 | 7.615 ± 0.378 | 5.597 ± 0.211 |
| 1.854 ± 0.206 | 1.187 ± 0.227 | 1.569 ± 0.276 | 1.253 ± 0.296 | 1.138 ± 0.626 | 1.284 ± 0.021 | 1.050 ± 0.086 | 1.777 ± 0.172 | 1.367 ± 0.544 | 0.915 ± 0.278 | 1.225 ± 0.132 |
| 3.673 ± 0.900 | 1.590 ± 0.134 | 1.780 ± 0.138 | 0.211 ± 0.032 | 1.434 ± 0.227 | 0.138 ± 0.025 | 1.686 ± 0.190 | 3.312 ± 0.069 | 2.651 ± 0.316 | 2.335 ± 0.158 | 3.511 ± 0.646 |
| 0.529 ± 0.109 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 2.784 ± 0.974 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.995 ± 0.282 | 0.572 ± 0.163 | 0.714 ± 0.091 | 0.456 ± 0.111 | 0.920 ± 0.116 | 0 | 0 | 0.307 ± 0.113 | 0.393 ± 0.098 | 0.186 ± 0.236 | 0.191 ± 0.096 |
| 3.942 ± 0.304 | 1.803 ± 0.007 | 2.179 ± 0.621 | 1.715 ± 0.249 | 2.098 ± 0.869 | 0.578 ± 0.089 | 0.273 ± 0.091 | 2.265 ± 0.225 | 1.314 ± 0.291 | 2.288 ± 0.135 | 2.691 ± 0.416 |
| 7.033 ± 0.508 | 16.908 ± 0.473 | 19.782 ± 0.246 | 8.506 ± 0.688 | 30.254 ± 24.023 | 10.988 ± 0.470 | 8.987 ± 0.365 | 8.542 ± 0.606 | 11.271 ± 0.897 | 10.770 ± 0.201 | 15.887 ± 3.060 |
| 0 | 0 | 0 | 0 | 1.197 ± 1.692 | 0 | 0 | 0 | 0 | 0 | 0 |
| 46.223 ± 0.479 | 106.931 ± 4.632 | 99.431 ± 3.269 | 62.909 ± 4.423 | 237.421 ± 213.089 | 80.385 ± 3.910 | 49.053 ± 2.108 | 52.046 ± 3.828 | 70.409 ± 7.967 | 63.588 ± 4.764 | 97.853 ± 29.955 |
| 0 | 1.242 ± 0.256 | 1.309 ± 0.216 | 1.209 ± 0.116 | 3.727 ± 0.687 | 0 | 0.981 ± 0.433 | 1.861 ± 1.252 | 2.748 ± 1.258 | 1.280 ± 0.077 | 2.345 ± 0.383 |
| 0 | 0 | 0 | 0 | 1.012 ± 1.431 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 1.012 ± 0.063 | 0.834 ± 0.003 | 0 | 5.160 ± 6.925 | 0.083 ± 0.052 | 0 | 0 | 0.575 ± 0.144 | 0.435 ± 0.173 | 0.753 ± 0.610 |
| 0 | 0 | 0 | 0 | 1.796 ± 2.539 | 0 | 0 | 0 | 0 | 0 | 0.200 ± 0.284 |
| 4.599 ± 0.034 | 28.678 ± 38.638 | 1.481 ± 1.332 | 0.870 ± 0.252 | 1.141 ± 0.113 | 0 | 1.296 ± 0.534 | 1.487 ± 0.783 | 3.246 ± 1.352 | 3.199 ± 0.561 | 0.525 ± 0.395 |
| 1.475 ± 0.766 | 1.650 ± 0.359 | 1.398 ± 0.128 | 1.559 ± 0.181 | 3.026 ± 2.238 | 0.601 ± 0.287 | 0.027 ± 0.107 | 0.069 ± 0.002 | 0.558 ± 0.121 | 0.668 ± 0.412 | 0.380 ± 0.126 |
| 0 | 0.003 ± 0.004 | 0 | 0 | 0.983 ± 1.390 | 0 | 0 | 0 | 0 | 0 | 0.235 ± 0.142 |
| 0.795 ± 0.303 | 8.989 ± 0.392 | 7.579 ± 0.907 | 4.511 ± 0.301 | 11.333 ± 2.643 | 7.100 ± 0.173 | 5.231 ± 0.998 | 3.343 ± 0.116 | 5.832 ± 0.046 | 8.363 ± 0.131 | 13.776 ± 1.266 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0.036 ± 0.051 | 0.113 ± 0.160 | 0 | 0 | 0.079 ± 0.111 | 0.013 ± 0.018 | 0 | 0.719 ± 0.280 |

| UCD 18-20 | Winters | Y116-161-99 | Y117-86-03 | Y117-91-03 | Y121-42-99 | Capella | Carina | Maxima | Mira |
|---|---|---|---|---|---|---|---|---|---|
| 1.761 ± 0.283 | 3.868 ± 0.649 | 0.740.128 | 0.907 ± 0.052 | 1.020.193 | 1.994 ± 0.308 | 0.703 ± 0.057 | 0.431 ± 0.128 | 0 | 1.143 ± 0.157 |
| 0.118 ± 0.167 | 0.118 ± 0.167 | 0 | 0.463 ± 0.145 | 0.091 ± 0.027 | 0.114 ± 0.072 | 0 | 0.012 ± 0.018 | 0 | 0 |
| 0 | 11.389 ± 16.041 | 0 | 0 | 0 | 0.252 ± 0.035 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0.011 ± 0.016 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.062 ± 0.069 | 1.820 ± 1.780 | 0.199 ± 0.258 | 0 | 0.128 ± 0.181 | 0.474 ± 0.013 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0.005 ± 0.006 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0.078 ± 0.110 | 0 | 0.057 ± 0.080 | 0.073 ± 0.103 | 0.330.095 | 0.491 ± 0.061 | 0.198 ± 0.104 | 0.319 ± 0.099 | 0.483 ± 0.141 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0.226 ± 0.319 | 0 | 0 | 1.808 ± 0.042 | 2.767 ± 0.251 | 0.029 ± 0.041 | 2.739 ± 0.288 |
| 0.780 ± 0.179 | 2.905 ± 0.513 | 0.920 ± 0.044 | 1.131 ± 0.423 | 1.018 ± 0.167 | 1.905 ± 0.405 | 5.58 ± 1.102 | 2.433 ± 0.556 | 0.774 ± 0.081 | 3.242 ± 0.925 |
| 0 | 0 | 0 | 0 | 0 | 0.276 ± 0.058 | 0.238 ± 0.101 | 0.162 ± 0.146 | 0 | 0.105 ± 0.067 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0.490 ± 0.118 | 0 | 0 | 0.591 ± 0.069 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.056 ± 0.038 | 0.093 ± 0.095 | 0.355 ± 0.058 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.085 ± 0.120 | 0 | 0.137 ± 0.078 |
| 0.073 ± 0.017 | 1.194 ± 0.688 | 0.287 ± 0.023 | 0.682 ± 0.076 | 0.728 ± 0.106 | 0.559 ± 0.085 | 0.327 ± 0.083 | 0.325 ± 0.016 | 0.407 ± 0.114 | 0.632 ± 0.108 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.077 ± 0.108 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3.320 ± 0.269 | 7.035 ± 1.519 | 3.456 ± 0.821 | 9.936 ± 1.370 | 5.146 ± 0.513 | 3.910 ± 1.141 | 17.321 ± 2.677 | 15.724 ± 0.211 | 6.082 ± 0.213 | 12.777 ± 2.232 |
| 2.983 ± 1.244 | 3.220 ± 0.004 | 15.993 ± 0.139 | 25.964 ± 5.526 | 4.909 ± 2.316 | 4.722 ± 2.732 | 58.714 ± 5.634 | 51.693 ± 5.771 | 8.737 ± 0.548 | 48.426 ± 18.922 |
| 0.944 ± 0.046 | 0.947 ± 0.573 | 1.122 ± 0.061 | 2.049 ± 0.161 | 1.303 ± 0.213 | 1.010 ± 0.267 | 1.060 ± 0.167 | 2.750 ± 0.236 | 1.315 ± 0.566 | 1.383 ± 0.155 |
| 2.244 ± 0.092 | 3.672 ± 1.944 | 2.986 ± 0.494 | 3.586 ± 0.098 | 4.962 ± 0.128 | 6.582 ± 0.721 | 1.895 ± 0.660 | 4.233 ± 0.027 | 1.808 ± 0.135 | 2.842 ± 0.894 |
| 0 | 0 | 0 | 0.587 ± 0.620 | 0 | 0 | 1.005 ± 0.457 | 3.264 ± 0.786 | 0.757 ± 0.466 | 1.669 ± 0.523 |
| 0 | 0.055 ± 0.078 | 0 | 0.784 ± 0.128 | 0 | 0 | 0 | 0.842 ± 1.037 | 1.177 ± 1.664 | 0 |
| 0 | 0.137 ± 0.193 | 0 | 0.374 ± 0.172 | 0.238 ± 0.051 | 0 | 0.274 ± 0.388 | 2.455 ± 0.164 | 0.911 ± 0.706 | 0.892 ± 0.063 |
| 0.564 ± 0.064 | 1.142 ± 0.080 | 0.941 ± 0.254 | 6.472 ± 3.386 | 2.568 ± 0.555 | 2.074 ± 0.568 | 10.564 ± 3.845 | 21.707 ± 0.903 | 4.292 ± 2.025 | 14.165 ± 1.314 |
| 6.012 ± 0.072 | 20.987 ± 10.517 | 10.110 ± 0.436 | 15.713 ± 0.668 | 17.786 ± 2.680 | 13.041 ± 1.209 | 5.355 ± 0.519 | 4.921 ± 0.025 | 6.585 ± 2.791 | 9.430 ± 2.204 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 45.042 ± 0.177 | 141.211 ± 94.337 | 55.334 ± 2.265 | 94.009 ± 6.534 | 110.527 ± 28.058 | 75.520 ± 9.508 | 33.616 ± 1.137 | 25.230 ± 0.592 | 39.160 ± 13.371 | 56.250 ± 11.119 |
| 1.932 ± 0.091 | 4.030 ± 1.216 | 0.556 ± 0.005 | 4.742 ± 2.312 | 0.853 ± 0.117 | 0.863 ± 0.002 | 4.455 ± 3.119 | 7.904 ± 0.770 | 0.252 ± 0.356 | 2.504 ± 0.776 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 2.771 ± 3.410 | 0 | 0.603 ± 0.223 | 0.954 ± 0.730 | 0.488 ± 0.133 | 0 | 0 | 0 | 0 |
| 0 | 1.636 ± 2.313 | 0 | 0 | 0.138 ± 0.195 | 0 | 0 | 0 | 0 | 0 |
| 0.816 ± 0.611 | 2.506 ± 1.269 | 0 | 7.867 ± 5.484 | 0.876 ± 0.448 | 0.076 ± 0.108 | 6.714 ± 0.695 | 33.165 ± 11.466 | 4.103 ± 2.076 | 19.804 ± 10.544 |
| 0.452 ± 0.184 | 0.482 ± 0.117 | 0 | 0.298 ± 0.065 | 0.234 ± 0.243 | 0.384 ± 0.340 | 0.138 ± 0.195 | 0.575 ± 0.206 | 0 | 0.116 ± 0.165 |
| 0 | 0.984 ± 1.187 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3.318 ± 0.070 | 22.784 ± 14.565 | 4.946 ± 0.108 | 8.759 ± 1.184 | 10.256 ± 0.584 | 7.405 ± 1.540 | 0.662 ± 0.412 | 0 | 0 | 0.081 ± 0.115 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0.338 ± 0.478 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

| Rhea | Vela | Constanti | Marinada | Tarraco | Selection 29-148 | Selection 30-297 | Guara | Mardia | Soleta |
|---|---|---|---|---|---|---|---|---|---|
| 0.281 ± 0.257 | 0.295 ± 0.417 | 1.219 ± 0.522 | 1.073 ± 0.247 | 0 | 0.721 ± 0.190 | 0 | 0.188 ± 0.147 | 0.535 ± 0.309 | 0.692 ± 0.239 |
| 0.012 ± 0.017 | 0 | 0.499 ± 0.287 | 0.796 ± 0.149 | 0.048 ± 0.054 | 1.702 ± 0.136 | 0.510.290 | 0.456 ± 0.644 | 0.066 ± 0.094 | 0.078 ± 0.069 |
| 0 | 0 | 0.508 ± 0.073 | 0 | 0.048 ± 0.068 | 0.076 ± 0.107 | 16.215 ± 12.767 | 7.072 ± 2.211 | 0.315 ± 0.130 | 1.097 ± 0.283 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 6.718 ± 4.427 | 2.813 ± 0.632 | 0.123 ± 0.046 | 0.667 ± 0.463 |
| 0 | 0 | 0 | 0.007 ± 0.010 | 0.069 ± 0.097 | 0 | 0 | 0.051 ± 0.072 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0.093 ± 0.132 | 0 | 0.564 ± 0.072 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 2.624 ± 0.458 | 1.082 ± 0.708 | 1.590.936 | 0.126 ± 0.016 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1.536 ± 0.071 | 1.095 ± 0.053 | 2.337 ± 0.116 | 1.478 ± 0.212 | 1.586 ± 0.143 | 1.738 ± 0.189 | 1.661 ± 0.147 | 1.846 ± 0.246 | 1.490 ± 0.237 | 0.903 ± 0.133 |
| 0 | 0 | 0.296 ± 0.031 | 0.195 ± 0.073 | 0.567 ± 0.084 | 0.120 ± 0.053 | 0.726 ± 0.074 | 0.277 ± 0.034 | 0.329 ± 0.079 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0.616 ± 0.126 | 0 | 0 | 0 | 0 |
| 0.118 ± 0.045 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0.031 ± 0.037 | 0 | 0 | 0 | 0 |
| 0.391 ± 0.017 | 0.109 ± 0.017 | 0.007 ± 0.025 | 0 | 0 | 0.040 ± 0.039 | 0.009 ± 0.013 | 0.070 ± 0.022 | 0.015 ± 0.021 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5.766 ± 0.374 | 7.205 ± 0.030 | 2.268 ± 0.026 | 1.725 ± 0.172 | 1.819 ± 0.464 | 3.768 ± 0.228 | 2.360 ± 0.255 | 4.355 ± 0.019 | 2.562 ± 0.194 | 1.223 ± 0.154 |
| 10.382 ± 0.217 | 5.870 ± 1.320 | 6.432 ± 0.227 | 2.651 ± 0.025 | 2.890 ± 0.164 | 3.663 ± 0.033 | 8.139 ± 1.246 | 4.041 ± 0.812 | 4.295 ± 0.739 | 16.482 ± 1.846 |
| 1.231 ± 0.266 | 0.975 ± 0.090 | 0.607 ± 0.033 | 0.330 ± 0.116 | 1.888 ± 0.132 | 0.672 ± 0.207 | 3.627 ± 0.343 | 1.022 ± 0.056 | 1.003 ± 0.088 | 0.066 ± 0.093 |
| 1.866 ± 0.125 | 1.652 ± 0.027 | 2.718 ± 0.026 | 0.492 ± 0.012 | 0.651 ± 0.131 | 1.829 ± 0.023 | 4.032 ± 0.811 | 2.388 ± 0.550 | 1.813 ± 0.835 | 2.507 ± 0.177 |
| 0 | 0 | 0.291 ± 0.039 | 0.834 ± 0.125 | 0.390 ± 0.023 | 0.043 ± 0.006 | 0.455 ± 0.085 | 0.078 ± 0.031 | 1.128 ± 0.474 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0.329 ± 0.274 | 0 | 0 | 0 | 0 | 0.308 ± 0.436 | 0 | 0 | 0 |
| 2.438 ± 0.125 | 0.592 ± 0.447 | 4.039 ± 0.167 | 4.480 ± 0.336 | 1.644 ± 0.178 | 2.168 ± 0.101 | 5.295 ± 0.981 | 1.498 ± 0.007 | 3.488 ± 0.445 | 0.440 ± 0.336 |
| 5.534 ± 0.425 | 2.826 ± 0.311 | 2.118 ± 0.253 | 0.922 ± 0.092 | 1.834 ± 1.099 | 2.488 ± 0.364 | 1.756 ± 0.340 | 2.808 ± 0.144 | 1.751 ± 0.411 | 1.841 ± 0.061 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 34.465 ± 4.178 | 20.430 ± 0.336 | 15.093 ± 0.170 | 12.095 ± 0.891 | 16.573 ± 6.600 | 15.426 ± 1.475 | 17.346 ± 4.642 | 14.140 ± 1.052 | 17.718 ± 2.011 | 17.319 ± 1.942 |
| 0.062 ± 0.048 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.020 ± 0.028 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2.230 ± 0.357 | 1.596 ± 0.005 | 2.540 ± 1.545 | 1.124 ± 0.613 | 0.274 ± 0.117 | 1.189 ± 0.254 | 2.566 ± 0.275 | 2.014 ± 0.690 | 3.183 ± 0.243 | 0.148 ± 0.210 |
| 0.146 ± 0.206 | 0 | 0.597 ± 0.352 | 0.555 ± 0.241 | 0.401 ± 0.050 | 0.074 ± 0.085 | 0.038 ± 0.013 | 0 | 1.958 ± 0.584 | 1.046 ± 0.855 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0.660 ± 0.714 | 0.055 ± 0.077 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0.873 ± 1.234 | 0 | 0 | 0 |

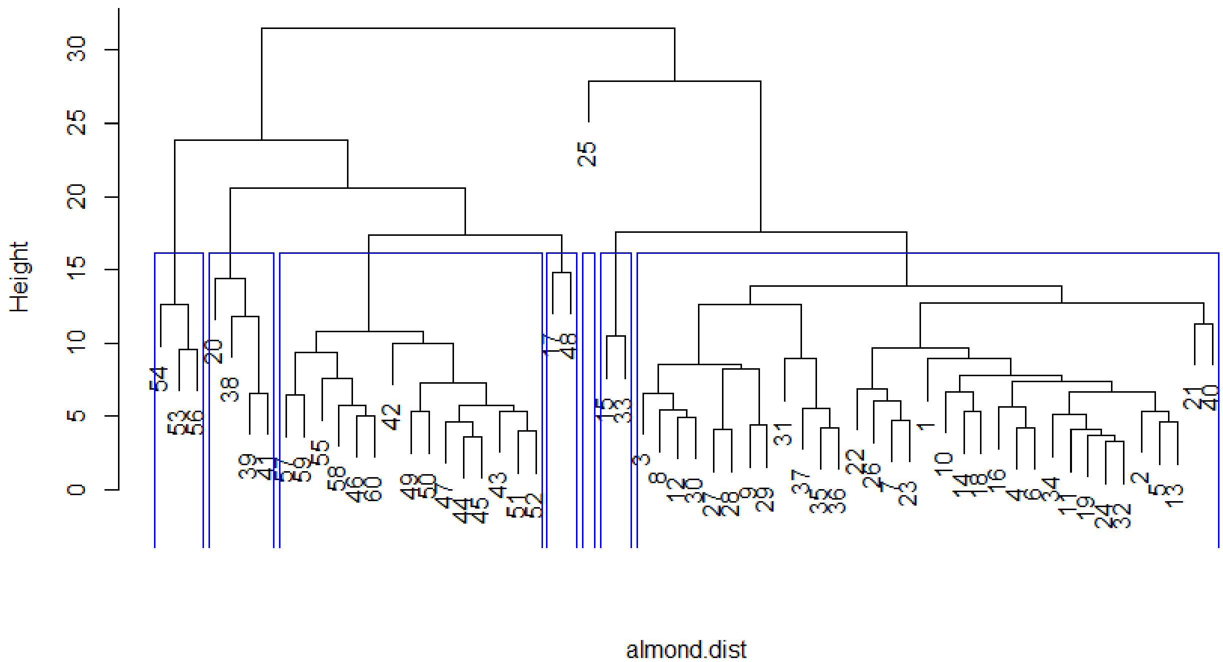
| Vialfas | Antoneta | Makako | Marta | Penta | Selection D00-360 | Selection D01-188 | Selection D06-795 | Matan | Total Average |
|---|---|---|---|---|---|---|---|---|---|
| 0.325 ± 0.385 | 0.813 ± 0.009 | 0.292 ± 0.385 | 0.571 ± 0.259 | 0.132 ± 0.064 | 0 | 0 | 0.108 ± 0.153 | 0 | 1.198 ± 1.118 |
| 1.129 ± 0.949 | 4.847 ± 0.308 | 3.759 ± 0.982 | 1.902 ± 0.229 | 2.195 ± 0.751 | 0.340.305 | 0 | 0 | 1.487 ± 0.206 | 0.711 ± 0.941 |
| 0.168 ± 0.205 | 3.062 ± 1.107 | 1.088 ± 0.050 | 1.597 ± 0.047 | 1.881 ± 0.202 | 3.036 ± 0.977 | 3.059 ± 0.310 | 1.427 ± 0.344 | 0.250.238 | 1.727 ± 4.399 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 ± 0.002 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.021 ± 0.230 |
| 0.394 ± 0.557 | 2.774 ± 1.418 | 1.410.125 | 0.515 ± 0.193 | 1.485 ± 0.139 | 2.362 ± 0.586 | 1.389 ± 0.125 | 0.736 ± 0.282 | 0.176 ± 0.095 | 0.928 ± 1.433 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.053 ± 0.218 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.306 ± 0.622 |
| 0 | 0.103 ± 0.109 | 0 | 0 | 0 | 0 | 0 | 0.386 ± 0.302 | 0 | 0.166 ± 0.425 |
| 0.082 ± 0.006 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.092 ± 0.428 |
| 0 | 3.558 ± 0.077 | 1.239 ± 0.020 | 0.092 ± 0.082 | 1.184 ± 0.647 | 1.472 ± 0.171 | 0 | 1.276 ± 0.191 | 0 | 0.290 ± 0.753 |
| 1.277 ± 0.160 | 1.311 ± 0.139 | 1.358 ± 0.173 | 1.983 ± 0.143 | 0.892 ± 0.058 | 1.192 ± 0.148 | 1.314 ± 0.022 | 2.570 ± 0.560 | 2.109 ± 0.422 | 1.721 ± 1.130 |
| 0.190 ± 0.019 | 0 | 0.365 ± 0.043 | 0.434 ± 0.079 | 0.047 ± 0.018 | 0.190 ± 0.031 | 0.559 ± 0.046 | 0.327 ± 0.028 | 0.278 ± 0.025 | 0.140 ± 0.178 |
| 0 | 2.272 ± 0.519 | 0.238 ± 0.065 | 0.714 ± 0.021 | 0.570 ± 0.024 | 0.292 ± 0.072 | 1.458 ± 0.375 | 0.264 ± 0.025 | 0 | 0.209 ± 0.489 |
| 0 | 0.418 ± 0.006 | 0.077 ± 0.048 | 0 | 0.325 ± 0.072 | 0 | 0.110 ± 0.055 | 0 | 0.058 ± 0.026 | 0.039 ± 0.101 |
| 0 | 0 | 0.096 ± 0.034 | 0 | 0 | 0.878 ± 0.116 | 0 | 0.174 ± 0.076 | 0 | 0.049 ± 0.150 |
| 0 | 0.840 ± 0.184 | 0.371 ± 0.034 | 0.273 ± 0.025 | 0.831 ± 0.151 | 0.431 ± 0.055 | 0.379 ± 0.109 | 0.207 ± 0.001 | 0.176 ± 0.041 | 0.419 ± 0.324 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.002 ± 0.014 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.022 ± 0.095 |
| 1.306 ± 0.411 | 5.348 ± 0.787 | 2.769 ± 0.306 | 4.747 ± 0.097 | 2.404 ± 0.234 | 2.945 ± 0.579 | 3.718 ± 0.456 | 2.458 ± 0.988 | 4.054 ± 1.321 | 5.381 ± 4.421 |
| 4.916 ± 0.267 | 3.364 ± 0.400 | 4.465 ± 0.162 | 1.433 ± 0.121 | 3.133 ± 0.103 | 13.143 ± 0.510 | 9.439 ± 0.355 | 6.512 ± 0.749 | 34.307 ± 8.310 | 10.663 ± 13.167 |
| 0.132 ± 0.084 | 1.986 ± 0.343 | 2.242 ± 0.109 | 2.845 ± 0.051 | 1.562 ± 0.097 | 1.988 ± 0.111 | 2.090 ± 0.230 | 0.766 ± 0.026 | 1.262 ± 0.710 | 1.393 ± 0.741 |
| 0.872 ± 0.627 | 1.082 ± 0.167 | 1.974 ± 0.465 | 2.248 ± 0.374 | 0.903 ± 0.225 | 1.634 ± 0.155 | 0.400 ± 0.224 | 3.270 ± 0.178 | 2.035 ± 0.288 | 2.265 ± 1.621 |
| 0.180 ± 0.254 | 8.092 ± 2.302 | 7.769 ± 0.445 | 2.405 ± 0.076 | 3.043 ± 0.228 | 2.481 ± 0.396 | 0.541 ± 0.286 | 1.903 ± 0.307 | 0.173 ± 0.129 | 0.736 ± 1.642 |
| 0 | 0 | 0 | 1.031 ± 0.393 | 0.046 ± 0.064 | 0.743 ± 0.066 | 0 | 0 | 0 | 0.389 ± 1.782 |
| 0 | 2.037 ± 0.013 | 2.163 ± 0.633 | 3.192 ± 0.226 | 2.946 ± 0.126 | 0.503 ± 0.076 | 0.123 ± 0.033 | 0 | 0.465 ± 0.407 | 0.543 ± 0.807 |
| 2.713 ± 0.345 | 16.520 ± 4.848 | 47.494 ± 3.649 | 16.712 ± 1.712 | 20.029 ± 1.471 | 19.067 ± 2.661 | 7.009 ± 1.677 | 13.576 ± 0.959 | 3.745 ± 0.133 | 5.182 ± 7.629 |
| 2.147 ± 0.043 | 7.746 ± 1.701 | 4.491 ± 1.275 | 3.547 ± 0.800 | 7.805 ± 1.300 | 5.298 ± 0.223 | 4.975 ± 0.702 | 2.956 ± 0.552 | 1.890 ± 0.804 | 8.230 ± 6.166 |
| 0 | 0.412 ± 0.362 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.027 ± 0.227 |
| 21.354 ± 2.887 | 28.999 ± 4.793 | 23.149 ± 1.975 | 18.960 ± 3.082 | 43.530 ± 10.282 | 27.397 ± 3.674 | 16.987 ± 1.244 | 11.709 ± 2.944 | 11.625 ± 2.252 | 52.032 ± 43.781 |
| 0 | 6.597 ± 0.657 | 9.806 ± 2.580 | 0.249 ± 0.240 | 11.107 ± 3.883 | 2.001 ± 0.148 | 0 | 4.025 ± 0.033 | 0 | 1.760 ± 2.520 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.017 ± 0.185 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.297 ± 1.065 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.063 ± 0.443 |
| 2.236 ± 0.144 | 26.095 ± 1.838 | 16.418 ± 2.049 | 6.309 ± 0.756 | 7.703 ± 1.990 | 7.825 ± 1.375 | 3.170 ± 0.243 | 9.713 ± 0.529 | 2.899 ± 0.586 | 4.429 ± 7.949 |
| 2.395 ± 1.319 | 0 | 0.272 ± 0.052 | 0.138 ± 0.074 | 0.962 ± 0.402 | 0 | 0 | 0 | 0 | 0.753 ± 0.854 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.046 ± 0.254 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.293 ± 4.566 |
| 0 | 0 | 0.221 ± 0.313 | 0 | 0 | 0 | 0 | 0 | 0 | 0.004 ± 0.040 |
| 0 | 0.190 ± 0.269 | 0.092 ± 0.061 | 0 | 0.210 ± 0.279 | 0 | 0 | 0 | 0 | 0.008 ± 0.052 |
| 0 | 0.330 ± 0.467 | 0.059 ± 0.083 | 0 | 0 | 0 | 0.265 ± 0.210 | 0 | 0 | 0.064 ± 0.223 |

**Cluster Analysis**

The sixty varieties were organized into seven distinct clusters based on how relative the average values for each characterization were to each other (**Figure 7**). The higher height shows greater difference among the clusters. The variety numbers correlate with the numbering associated with each variety in **Table 5**.

Within the seven separate clusters, UCD 1-232 (25) stood out in its own cluster. It also branches off at a relatively high height, meaning it is greatly different from the other varieties. UCD 1-232 is unique among the almond genotypes tested in that it possesses the self-compatibility trait derived from peach and is also unique in that it still possesses a large proportion (> 0.05%) of peach genes. It's genetic uniqueness within the global almond breeding germplasm was recently cited by Pérez de los Cobos et al. (2021). UCD 8-160 (30) is a backcross of UCD 1-232 to Nonpareil almond and so would be expected to have only about 2% peach genes. Even this small proportion of exotic genes, however, results in its distinct separation within the clusters. Other clusters consisted of multiple varieties. There were smaller clusters that were more closely associated with each other than with other varieties. The first cluster from the left consists of Makako (54), Antoneta (53), and Penta (56). The varieties in this cluster were all developed by the CEBAS-CSIC breeding program in Murcia, Spain. The next cluster contains Shasta (20), Capella (28), Carina (39), and Mira (41) which all had the Italian variety Tuono as a parent and the California variety Nonpareil as a grandparent. Nonpareil (15) was similar to Winters (33), as well as Pyrenees (17) and Selection 30-297 (48), all of which have nonpareil as a parent or grandparent. There were two clusters made up of large number of varieties, meaning they are relatively similar, and the previously mentioned clusters were more unique varieties.

**Figure 7.** Cluster dendrogram of the varieties based on the attributes measured.




Similarities within the clusters could often be traced back to breeding origin. Capella (38) to Vela (43) were recent varieties developed by the Australian breeding program at Adelaide, Australia and so has similar parentage. In the same way, Constanti (44) to Selection D06-795 (59) were developed by different breeding Spanish programs; Constanti (44) to Selection 30-297 (48) were from the Spanish Institute of Agrifood Research and Technology (IRTA) breeding program, Guara (49) to Vialfas (52) were from the Aragon Agrifood Research and Technology Center (CITA) breeding program in central Spain, and Antoneta (53) to Selection D06-795 (59) were from the Centro de Edafologia Biologia Aplicada del Segura Consejo Superior De Investigaciones Cientificas (CEBAS-CSIC) breeding program in southern Spain. All of these breeding programs are related in their common use of the Italian variety Tuono as a source for self-compatibility (Pérez de los Cobos et al. 2021). However, the programs differ in that each will be crossing the Tuono self-compatibility source to a different, regionally adapted germplasm. The genetic similarities within this locally adapted germplasm as well as the breeding germplasm differences among the different breeding programs are reflected in the patterns of clustering.

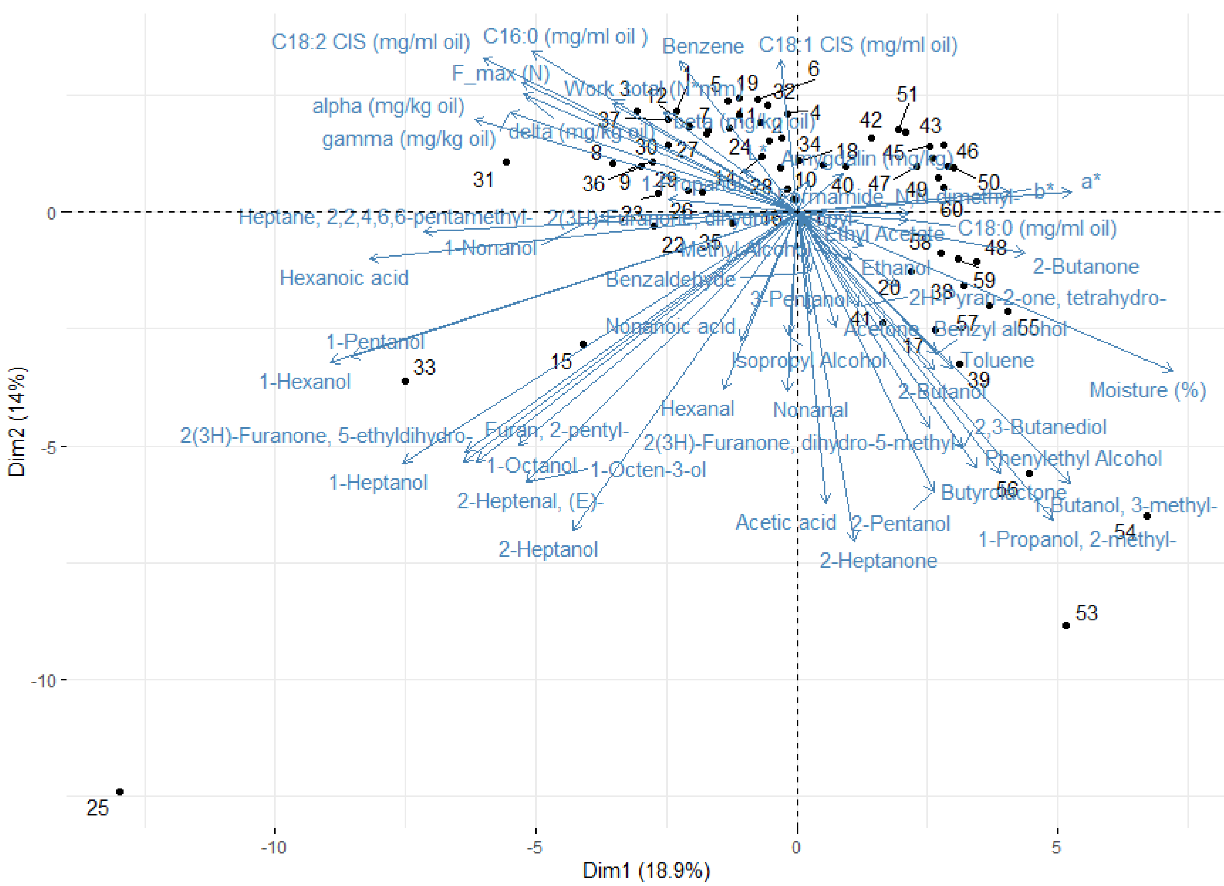
### Principle Component Analysis

PCA was applied to the average values for each variety on each of the characterization measured (**Figure 8**). The PCA plot provides a visual representation of the relationship between the varieties and characterizations, as well as how the attributes interact with each other. The variety numbers labeled on the dots correlate with the numbering associated with each variety in **Table 5**.

Analytical measurement data were displayed as vectors alongside the dots representing the different varieties. Although a PCA biplot provides multiple dimensions to analyze the data, dimension1 and 2 were chosen to represent the most compounds and characteristics. The layout of the vectors represents how associated the attributes are to each other, as well as to the varieties. Positive correlations are apparent when the vectors are in close proximity, while further distance indicates that they are negatively associated. A perpendicular vector indicates there is no correlation. For example, the vectors for maximum force (N) and work (N*mm) were almost $180^o$ separated from moisture (%). This means that those factors were negatively associated with each other, which is plausible since higher moisture content would lead to a less fracturable kernel. Tocopherol isomers (α, β, γ, δ) were also distant from some volatile compounds, many that are products from lipid oxidation such as aldehydes, ketones, and alcohols, and are not desirable over certain concentration limits (Beltrán Sanahuja et al. 2011). This was due to the high antioxidant properties of tocopherol isomers that help elongate shelf life and slow down the formation of undesirable compounds. Aldrich (1) having the highest concentration of total tocopherol was seen far from the hexanal vector.

It was also evident on the PCA biplot that UCD 1-232 (25) was very distinct from other varieties due to its unique genetic composition, which was also seen in the cluster dendrogram. Since this variety was distant from any vectors, it is hard to correlate its uniqueness to a specific characteristic. The clustering of the varieties seen in the cluster dendrogram on the PCA biplot was also evident on the biplot. Nonpareil (15) and Winters (33) were relatively close proximity with one another, as well as with Makako (54), Antoneta (53), and Penta (56), which were separated into their own cluster in the cluster dendrogram. This difference was driven by the volatiles present, mainly alcohol compounds. Pyrenees (17) which had the highest concentration of benzaldehyde was in close proximity to the vector for benzaldehyde, signifying that this variety is closely associated with that attribute.

**Figure 8.** PCA biplot of all the attributes conducted on the sixty raw almond varieties.



## 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 healthy serum lipids, decreased cardiovascular risk, improved vascular health and weight management. Sustainability in almond production includes improved use of water through new technologies, zero-waste generation, valorizing coproducts, and reducing 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 coproducts is still needed for identifying new uses and optimizing and valorizing existing materials.

Aldrich contained the highest amount of tocopherol, which would make this variety a good candidate for a longer shelf-stable almond product. Out of the varieties measured, UCD 1-232 was significantly different from all the other varieties when clustering was applied. Further studies on this variety could provide insight on how the peach genes contribute to its uniqueness and separation from the other varieties. Analyzing the varieties using cluster analysis confirmed that the genetic makeup contributes to the similarities seen within the clusters. The source of the differences seen is due to the breeding program, which is impacted by location and the genetic makeup of the breeding parent or grandparent. Although important compounds were quantitatively measured, further sensory tests need to be performed in order to attest for likeability of the varieties by consumers.

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