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Defining the Sensory Profiles of Raw Almond (*Prunus dulcis*) Varieties and the Contribution of Key Chemical Compounds and Physical Properties

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ABSTRACT: This study describes the sensory composition of commercial sweet almond varieties across two California growing seasons. It also discusses the relationship between sensory attributes and chemical and physical measures. Raw, whole almonds (43 samples each of 13 varieties in 2015 and 40 samples each of 10 varieties in 2016) were evaluated for their sensory profiles using descriptive sensory analysis. The 2016 samples were also analyzed for macro- and micronutrients, amygdalin, volatile composition (using gas chromatography–mass spectrometry), and physical properties, and the results were modeled with the sensory data. Independence, Sonora, and Wood Colony were harder, more fracturable, and crunchy, whereas Fritz and Monterey were more moist and chewy, reflecting their moisture contents. Aldrich and Fritz were higher in marzipan/ benzaldehyde flavor, which is related to amygdalin, benzaldehyde, phenylethyl alcohol, and benzyl alcohol. New insights are provided into sweet-almond composition and the sensorial contribution of headspace volatiles. This assists almond growers and processors in describing and marketing almond varieties.

KEYWORDS: almond, amygdalin, analytical, benzaldehyde, flavor, moisture, sweet, texture, volatile

INTRODUCTION

There are over 30 almond varieties grown internationally.¹ In the United States, almonds are primarily grown in California, which contributes approximately 80% of the global almond supply.² Almond varieties are classified in industry by the appearance of the shell and nut³ or by flavor phenotypes.¹ Flavor phenotypes are characterized by the level of bitterness, which is linked to a naturally occurring compound, amygdalin (vitamin B17).⁴ Bitter almonds contain high levels of amygdalin, whereas only trace levels are found in sweet almonds.^{5,6} Only sweet almonds are grown in California.

Amygdalin breaks down during chewing to release hydrogen cyanide and benzaldehyde. Bitter almonds can be poisonous to humans because of their high levels of hydrogen cyanide. Benzaldehyde, on the other hand, is nontoxic and is responsible for the "pure almond" flavor in synthetic almond extracts, oils, and essences.⁷ Chemical and sensory analyses have linked amygdalin and benzaldehyde to the marzipan flavor in sweet almonds.⁶ Benzaldehyde is also linked to the cherry flavor in sweet cherry cultivars.⁸

There is more to almonds than just marzipan flavor, however. In a study of 20 almond varieties,⁹ an extensive sensory profile was created consisting of 86 attributes (15 appearance, 9 aroma, 36 flavor, 3 basic taste, and 4 chemical-feeling factor descriptors). Another study used a much shorter lexicon consisting of six sensory attributes to differentiate Mission and Nonpareil cultivars from European cultivars.¹⁰

Almond varieties and cultivars have been shown to differ in their volatile profiles,¹¹ nonvolatile metabolites (pyranosides, peptides, amino acids, etc.),¹² and tocopherol and fatty acid profiles.¹³ Contents of tocopherol and other tocopherol homologues were also found to be different among almond oil cultivars,^{14,15} despite both studies also measuring significant variability across 2 growing years. Similarly, large harvest-year effects were found in almond nutrient contents across 3 years,¹⁶ including moisture, fatty acids, fiber, ash, minerals (K and Zn), riboflavin, niacin, β -sitosterol, and stigmasterol; however, authors found similar nutrient profiles among seven almond varieties in the same study.

Growing location or region is also thought to influence the sensory profile of almonds, as it has been shown to influence volatile compounds,¹¹ nonvolatile metabolites,¹² tocopherol content,¹⁵ minerals and ash,¹⁶ and minerals and fatty acids.¹⁷

One of the most popular ways to consume almonds is roasted (baked at high heat). The roasting process increases concentrations of pyrazines, furans, and pyrrols,^{18,19} through nonenzymatic Maillard browning reactions. Roasting also significantly decreases concentrations of benzaldehydes and

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some alcohols.¹⁹ Roasting produces toasted aromas and flavors, and eventually burnt notes in almonds, as well as textural changes.¹⁸ In general, dry roasted almonds are harder and more crisp, crunchy, and fracturable than raw almonds.²⁰ Varela and coauthors investigated perceived crispness of roasted almonds, describing a combination of auditory (acoustic) and mechanical (force to break) cues while chewing.²¹

Almonds are also affected by storage conditions, where reduced quality can result from moisture migration, lipid oxidation, or rancidity development. The oxidative stability of almonds has been investigated using various chemical and sensory techniques for temperature and humidity,^{22–25} type of atmosphere,^{24,26} physical shape,^{23,24} harvest time,²³ packaging,^{22,26} and roast level.^{27,28}

Few studies have investigated consumer liking of almonds, despite this being essential for accurate marketing. Vickers and coauthors reported consumers' preference for almond textures that are high in crispiness, crunchiness, and persistence of crunch.²⁰ In another study, consumers were found to prefer fresher almonds (as opposed to aged, oxidized almonds) at different roast levels.²⁸ However, consumers rejected almond samples stored at high temperatures, in high humidity, and in polypropylene bags (rather than in high barrier bags),²² which are potentially related to low force peak compression (low crunchiness) and low sweetness.

This study aimed to define the sensory profiles of sweet almond varieties and their consistency over multiple growing seasons. A secondary objective was to investigate the contribution of chemical compounds and physical measures to key sensory attributes.

MATERIALS AND METHODS

Almond Samples. Raw, whole almonds (*Prunus dulcis*) from 13 major varieties were harvested from different commercial almond growers in the Central Valley of California over two growing seasons, 2015 and 2016. In 2015, 43 samples, consisting of 13 varieties, were evaluated, and in 2016, 40 samples, consisting of 10 varieties, were evaluated. Ten almond varieties overlapped between the two growing seasons (Table 1).

All samples were raw, unpasteurized, and ungraded. Prior to sensory assessment, samples were sorted to remove insect- and machine-damaged almonds and dusted using 4 in. paint brushes and

Table 1. List of Almond Varieties and Number of Samples in the Study

almond varieties	2015	2016	assessed across two growing seasons
Aldrich	4	4	×
Butte	4	0	
Butte/Padre	3	4	×
Carmel	2	4	×
Fritz	4	4	×
Independence	1	4	×
Mission	4	0	
Monterey	4	4	×
Nonpareil	4	4	×
Padre	1	0	
Price	4	4	×
Sonora	4	4	×
Wood Colony	4	4	×
total number of samples	43	40	

metal colanders. The samples were stored in airtight containers and refrigerated (~4 $^{\circ}C)$ upon receipt and for the duration of the study.

Descriptive Sensory Analysis. Descriptive sensory analysis was conducted by Covance Food Solutions (now Eurofins Scientific) to evaluate the sensory profiles of almond varieties and their consistency. Analyses were conducted in November 2015 (2015 growing season) and January 2017 (2016 growing season) within approximately three months of harvesting. Ten trained descriptive panelists participated in each sensory analysis, with approximately half participating in both analyses. These panelists were highly trained in the use of standardized vocabulary to describe the appearance, flavor, and texture of a wide variety of products.

Panelists participated in three 2 h training sessions each year. They reviewed almond taste, flavor, and texture references (some of which were anchored to line scales), as well as definitions of terms and evaluation procedures (see Table 2).

Panelists were served ~ 60 g of each sample in 85 g opaque soufflé cups with lids, coded with random three-digit numbers. Panelists tasted at least three almonds and averaged their assessments across the sample.

The same lexicon was used to assess almond samples in both years. Panelists rated 10 aroma-attribute, 12 flavor-attribute, and 13 textureattribute intensities on 15 point scales, most anchored from "None" to "Extreme", except for a few attributes, for which other opposite adjectives were used (Table 2). Panelists expectorated all samples.

For data collection, panelists evaluated eight samples in a 2 h testing session, with a 15 min break after four samples. All samples were assessed in duplicate. Data were collected over a period of 10–11 testing sessions for both growing seasons, spanning 3 weeks.

The samples were served in a monadic—sequential manner (i.e., one at a time, one after the other). As much as possible, the serving order of the samples was balanced, with products seen approximately an equal number of times in each possible position order.

Ambient Alhambra drinking water and unsalted crackers were provided as palate cleansers between samples. Data were collected using the sensory software Sensory Information Management System (SIMS, 2016, Version 6.0).

Analytical Measures. Almond samples in 2016 were analyzed for 72 chemical compounds and physical measures in duplicate, including 19 macro- and micronutrients, moisture content, amygdalin, and 51 volatile compounds (Table 3), using headspace solid-phase microextraction (HS-SPME)–gas chromatography–mass spectrometry (GC/MS). Amygdalin and all volatile compounds were analyzed by the Mitchell Lab, Food Science & Technology Department, University of California, Davis. The macro- and micronutrients and physical measures were analyzed by Covance Laboratories (Madison, WI), all within approximately 12 months of harvesting. Because of resource constraints, the analytical compositions of the 2015 almond samples were not analyzed.

Chemicals and Reagents. Amygdalin (>99%), benzaldehyde (>99%), benzaldehyde-d₆ (98 atom % D), naphthalene (>99%), 3methyl-1-butanol (>98%), 1-pentanol (>99%), 1-heptanol (>99%), 1hexanol (>99%), 1-octanol (>99%), and phenylethyl alcohol (>99%) were purchased from Sigma-Aldrich (St. Louis, MO). Authentic standards hexanal (>99%), nonanal (95%), 2-methyl-1-propanol (>99%), 3-(methylthio)-1-propanol (>98%), and 2-ethyl-1-hexanol (>99%) were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI). 1-Butanol (99%) and benzyl alcohol (>95%) standards were obtained from Acros Organics (Thermo Fisher Scientific Inc., Waltham, MA). Stable-isotope standards n-butyl-do alcohol and *n*-hexyl- d_{13} alcohol (99.5 atom % D) were purchased from C/D/N Isotopes Inc. (Pointe-Claire, QC, Canada). The internal standard luteolin was purchased from Indofine Chemical Company (Hilaborough, NJ). HPLC-grade acetic acid, acetonitrile, and methanol along with ACS-grade sodium chloride were obtained from Fisher Scientific (Pittsburgh, PA).

HS-SPME GC/MS Volatile Analysis. One gram of sieved almond was weighed into a 10 mL glass headspace vial (Agilent Technologies, Santa Clara, CA). One microliter of internal standard (200 μ g mL⁻¹ *n*-hexyl-d₁₃ alcohol in methanol) was added to the almond sample,

Table 2. List of Sensory Attributes, References, and Definitions Used in Descriptive Analyses of Raw Almonds in 2015 and 2016

					aroma–flavor
sensory attribute	:	scale	refe	rence	definition
total aroma–flavor ir	ntensity				total intensity of all the aromas and odors or tastes and flavors in the sample
sweet aromatic (nonfruity)	,	3.5	0.75 g of Spio Vanilla in 2 2% milk	ce Island 00 mL of	total aroma-flavor intensity associated with any nonfruity, sweet aroma (reminiscent of products with a sweet taste such as vanilla, caramel, dark chocolate, honey, brown sugar, maple syrup, and butterscotch)
marzipan/benzaldehy	7de	NR ^a	0.75 g of Spie Almond Ex 200 mL of	ce Island tract in 2% milk	aroma–flavor intensity associated with marzipan or benzaldehyde, reminiscent of maraschino cherries or almond extract
fruity/sour		NR 50	1 dried aprico kefir	ot	aroma-flavor intensity associated with fruit, such as dried apricots, and fermented fruit, such as sour aromatics
hav		NR	alfalfa hav		aroma-flavor intensity associated with hay or dried grass
unrine/heany		30 (flavor)	green banana		aroma-flavor intensity associated with unrine immature green or vegetal (like green hears)
		4.0 (aroma)	fresh green be overnight ir	eans soaked 1 water	or other nuts, such as peanuts and walnuts
		NR	walnut nut ar	nd brazil nut	
musty/earthy		NR	raw mushroo	ms	aroma-flavor intensity associated with musty, stale, dank, wet cellar, dirt, and earthy, such as
		NR	humic acid		potato skins and musinoonis
		NR	dirty potato s	kins	
woody		NR	fresh wood p	lank	aroma-flavor intensity associated with wood, sawdust, pencil shavings, or cut lumber
total off aroma—flavo	or				total aroma-flavor intensity associated with off-notes, including rancid, solvent, cardboard, rubber, medicinal, etc.
rubber/medicinal		NR	rubber stoppe warm water	er soaked in	aroma—flavor intensity associated with rubber, leather, medicinal, phenolic, Band-Aid, petroleum or metallic
awaat		2.0	2.0 g of sucre	aa in 250 ml	and of the basis testes, common to suggest
sweet		5.0	of drinking	water	one of the basic tastes, common to sucrose.
		5.0	of drinking	water	
bitter		2.0	0.025% caffei	ne	one of the basic tastes, characteristic of caffeine or quinine
					texture (initial)
sensory attribute	scale	refere	nce		definition
hardness (force to	5.0	Nabisco Chine	Abov cookie	force required	to chew through the sample using the malars from soft (low numbers) to hard (high numbers)
break)	7.0	Nabisco Wheat	Thin cracker	ioree requiree	to chew through the sample using the molars, nom sole (low humbers) to hard (ligh humbers)
	9.0 8.0	Nabisco Orao	T IIII Clacker		
	10.0	Old London M	elba toast		
	11.0	Nabisco Gingor	Span		
fracturability	4.0	Nabisco Rogula	r Chins Abov	force with wh	ich the sample breeks, includes brittleness ^b
nacturability	5.0	Nabisco graham	cracker	loree with wi	the sample breaks, includes bittleness
	7.5	Nabisco Oreo	relacker		
	10.0	Old London M	elba toast		
	11.0	Nabisco Ginger	Snan		
crunchy	15	Cheetos Puff	Shap	amount of lo	w nitched noise a heavier, harder product makes during the chewing process
cruncity	2.0	General Mills (orn Chex	amount of 10	wprened hoise a heavier, narder product makes during the encoding process
	4.0	Nabisco Regula	r Chips Aboy		
	5.0	Nabisco Oreo	r emps ruiey		
	7.0	General Mills W	Vheat Chex		
denseness	5.0	Pringles potato	chip	compactness	of the cross-section from airy (low numbers) to dense (high numbers)
denseness	11.0	Keebler Pecan S	Sandie cookie	compactness	
	12.0	Nabisco Fig Ne	wton		
roughness	6.0	Pringles potato	chip	degree to whi	ch the surface of the sample is rough (low numbers), as opposed to smooth (high numbers).
	9.0	Nabisco Wheat	Thin cracker	including ja	gged pieces and edges and rough skin
	14.0	Nature Valley g	ranola bar	te	xture (chewdown)
sensory attribute	scale	referen	ce		definition
chewiness	6.0	Snickers bar		total amount o swallowing	f "work" or force required to chew the sample once the bolus has broken down prior to
cohesiveness of	1.5	Bush garbanzo b	eans	degree to which	h the sample sticks to itself or forms a tight bolus as it is being chewed
mass	5.0	Pringles potato c	hip	8	1 0 0
	6.5	Puffed Cheetos	ĩ		
	7.5	Nabisco graham	cracker		
moistness of mass	1.0	Nature Valley gr	anola bar	degree to whic	h the sample mass is moist (low numbers) or dry (high numbers)
	4.0	Nabisco Regular	Chips Ahoy	0	· · · · · · · · · · · · · · · · · · ·
	()	Snickers	- /		
	6.0	omenens			

Table 2. continued

			texture (chewdown)
sensory attribute	scale	reference	definition
mealy mouthcoating	7.5 a	lmond flour	amount of mealiness, graininess, or particulates coating the mouth, perceived particularly in the back of the throat after swallowing
awareness of skins			awareness of skins in the sample during chewdown, including toughness and skin flakes
			texture (expectorate and residual)
sensory attribute	scale	reference	definition
sensory attribute residual toothpacking	scale g 7.5	reference Nabisco graham cracker	definition amount of residual sample that has become impacted into the molars on chew down and has remained there post swallowing.
sensory attribute residual toothpacking amount of residual particulate	scale g 7.5 6.0	reference Nabisco graham cracker corn grits or meal	definition amount of residual sample that has become impacted into the molars on chew down and has remained there post swallowing. amount of particulates left in the mouth after swallowing

"Not rated or anchored to the line scale. Used as a character reference only. ^bGenerally, an increase in auditory signals results from higher fracturability.

followed by 700 μ L of saturated sodium chloride solution. The headspace vial was capped with a 3 mm PTFE-lined silicone septa (Supelco Company, Bellefonte, PA) and vortexed for 1 min to form a pastelike mixture. Each sample was incubated at room temperature for at least 15 h prior to extraction to achieve headspace equilibration with the least standard deviation of headspace compounds. Sample extraction and gas chromatography were accomplished using a Gerstel MultiPurpose Sampler (GERSTEL, Mülheim an der Ruhr, Germany) coupled with an Agilent 7890A GC-7000 GC/MS Triple Quad MS (Agilent Technologies, Santa Clara, CA). The samples were agitated at 700 rpm and incubated at 45 °C for 10 min prior to headspace extraction. Samples were next extracted using 1 cm of 30/50 μm StableFlex DVB/CAR/PDMS fiber (Supelco Company) at a depth of 22 mm for 40 min at 250 rpm. The fiber was desorbed at a splitless injection at 250 °C for 0.9 min; this was followed by opening of the purge valve at 50 mL/min for a total of a 30 min injection time. Helium was used as the carrier gas at a constant flow rate of 1 mL/ min. Volatiles were separated on a DB-Wax column (30 m \times 0.25 mm, 0.25 μ m, Agilent Technologies). The oven-temperature gradient was set at 40 °C for 4 min; this was followed by a ramp of 5 °C min⁻¹ to 240 °C, which was held for 3 min. The transfer line was kept at 250 °C, and the detector was set at EI with a source temperature of 230 °C and a quadrupole temperature of 150 °C. Total-ion chromatograms were collected by scanning from m/z 30 to 350 with a solvent delay at 2.5 min under full-scan mode. Identification of volatile compounds was made by calculating the retention indices and by comparison with reference values. Authentic standards were used for confirmation when available. Relative quantification was performed on all compounds using n-hexyl- d_{13} as an internal standard. Calibration curves were established in devolatilized almonds using benzaldehyde- d_{6} , *n*-butyl- d_{9} alcohol, or naphthalene. The responses were normalized to *n*-hexyl- d_{13} , and the relative responses were used to make the standard curves. The benzaldehyde- d_6 , *n*-butyl- d_9 alcohol, and naphthalene standard curves were used to perform relative quantification of the aldehydes, alcohols, and hydrocarbons, respectively.

Amygdalin Analysis. The extraction and analysis methods were previously reported.⁵ Briefly, 50 mg of sieved almond sample was extracted in 1 mL of methanol containing 0.1% acetic acid and shaken overnight at 250 rpm. The mixture was centrifuged at 3200g for 15 min, and the supernatant was collected and evaporated to dryness under a nitrogen stream at room temperature. The sample was then reconstituted in 1 mL of 0.1% acetic acid in water followed by a cleanup step using a HyperSep C18 3 mL SPE column (Thermo Scientific, Pittsburgh, PA). Amygdalin was eluted with 4 mL of methanol–water (40:60, v/v) and filtered through a 0.2 μ m nylon filter (EMD Millipore, Billerica, MA) prior to MS/MS analysis. The internal reference standard luteolin was added to the sample after filtration at a concentration of 20 μ g mL⁻¹. Amygdalin analysis was performed on an Agilent 1290 UHPLC system interfaced to a 6460 triple quadrupole mass spectrometer (UHPLC-MS/MS) with an electrospray-ionization source (ESI) via Jet Stream Technology (Agilent Technologies, Santa Clara, CA). Chromatography was performed on a Zorbax Eclipse Plus C18 column (2.1 × 100 mm, 1.8 μ m, Agilent Technologies).

Macro- and Micronutrients and Physical Properties. All elements (metals), ash, calories, carbohydrates, fats, fatty acids, fiber, moisture, protein, and tocopherol were analyzed by an accredited commercial laboratory (Covance Laboratories Inc., Madison, WI). Elements were analyzed using ICP emission spectrometry (AOAC 985.01), ash was analyzed using gravimetry (AOAC 923.03), fat was analyzed using Soxhlet (AOAC 960.39), fatty acids were analyzed using gas chromatography (AOAC 996.06), soluble fiber and insoluble fiber were analyzed using gravimetry and enzymatic digestion (AOAC 991.43), moisture was analyzed using gravimetry and a vacuum oven (AOAC 925.09), and protein was analyzed using the Dumas method (AOAC 968.06). Calories,²⁹ carbohydrates,³⁰ and tocopherol³¹ were analyzed using previously described methods.

Data Analysis. All analytical data were analyzed using one-way analysis of variance (ANOVA) with sample main effect. The descriptive-analysis results from both years were analyzed separately, as there was no repeat sample or way to account for panel drift or context effects. The varietal trends between the two years were compared.

Sensory-intensity ratings on the line scales were converted to numbers ranging from 0 to 15 by SIMS. Mean intensities were then calculated for each sensory attribute. Analysis of variance (ANOVA) and Fisher's LSD were used to determine significant differences among the samples and varieties for each sensory attribute using a mixed-effects model. ANOVAs of the sensory data were performed across all samples and across the averaged varietal mean scores within each growing season.

Principal-component analysis (PCA), using correlation matrices, was applied to the mean sensory scores of attributes that showed significant sample differences at 95% levels of confidence to create biplots with all samples. The same process was applied to the variety-level data. The dimensions of the biplots defined the perceptual space for raw almond sensory profiles. All statistical analyses were conducted using SAS (2017, Version 9.4).

The relationships between the 2016 analytical and sensory data were analyzed using Pearson's correlation coefficients, but checks were first made to ensure that the assumption of linearity was appropriate. This was done both visually using scatterplots and by applying regression models for each pair of analytical and sensory measures, fitting both the linear and quadratic terms. There was little evidence of a curvilinear relationship between the two data sources. The analytical data were also correlated with the sensory PCA biplots to provide a visual representation of the relationship between the two data sources.

Finally, partial-least-squares (PLS) regression was applied to sensory attributes that demonstrated a strong linear relationship with the standardized analytical measures, retaining only those terms Table 3. List of the Volatile Compounds in the 2016 Raw Almond Samples with Their Referenced and Calculated Retention Indices (RI) Measured Using HS-SPME GC/MS

volatile compound	measured KI ^a	literature KI ^a (NIST)
butanal ^b	872	867
ethyl acetate ^b	883	884-910
2-butanone ^b	895	881-926
2-methyl-butanal ^b	905	897-914
3-methyl-butanal ^b	909	884-939
isopropyl alcohol ^b	925	884-935
ethanol ^b	931	932-955
pentanal ^b	970	950-984
acetonitrile ^b	999	1003-1026
2-butanol ^b	1032	998-1032
toluene ^b	1037	1037-1042
1-propanol ^b	1048	1002-1045
3-penten-2-ol ^b	1049	1150-1181
hexanal ^c	1088	1066-1083
2-methyl-1-propanol ^c	1114	1083-1108
3-pentanol ^b	1126	1087-1124
2-pentanol ^b	1138	1112-1138
1-butanol ^c	1160	1113-1175
2-methyl-3-pentanol ^b	1171	1121-1167
1-penten-3-ol ^b	1174	1157-1165
3-methyl-2-butenal ^b	1203	1202-1222
3-hexanol ^b	1210	1204-1211
3-methyl-1-butanol ^c	1220	1185-1237
3-methyl-3-buten-1-ol ^b	1259	1236-1250
1-pentanol ^c	1261	1241-1260
acetoin ^b	1287	1255-1285
cyclopentanol ^b	1310	1278-1323
prenol ^b	1328	1318-1325
3-methyl-1-pentanol ^b	1336	1323-1334
1-hexanol ^c	1360	1316-1359
nonanal ^c	1393	1390-1411
2-butoxy-ethanol ^b	1407	1389-1447
acetic acid ^b	1456	1402-1452
1-heptanol ^c	1461	1439-1460
furfural ^b	1463	1439-1480
<i>cis</i> -linaloloxide ^b	1475	1433-1496
2-ethyl-1-hexanol ^c	1495	1470-1496
benzaldehyde ^c	1519	1488-1520
2-(methylthio)-ethanol ^b	1533	1516-1537
[<i>R</i> -(<i>R</i> *, <i>R</i> *)]-2,3-butanediol ^b	1547	1544-1573
1-octanol ^c	1564	1546-1573
2,3-butanediol ^b	1584	1544-1573
dihydro-3-methyl- 2(3H)-furanone ^b	1588	1557-1625
1,2-ethanediol ^b	1631	1621-1635
benzeneacetaldehyde ^b	1641	1618-1659
2-furanmethanol ^b	1688	1661-1690
5-ethyldihydro-2(3 H)-furanone ^b	1701	1669-1745
3-(methylthio)-1-propanol ^c	1722	1715-1744
2-methoxy-phenol ^b	1861	1846-1875
benzyl alcohol ^c	1878	1861-1886
phenylethyl alcohol ^c	1913	1904-1923

"Kovat's retention index based on a 30 m DB-Wax column. The literature value was taken from NIST Standard Database Number 69. ^bCompound tentatively identified by the MS fragmentation pattern and having a calculated KI similar to the literature value. ^cCompound identity confirmed with the authentic standard. that had variable-importance-in-the-projection $\left(\text{VIP}\right)$ scores of 0.8 or above.

RESULTS AND DISCUSSION

Sensory Profiles of Raw Almond Varieties. The sensory descriptive analysis of the two growing seasons were analyzed separately, and the results were compared. ANOVA was performed both at the sample level as well as at the variety level in both years. Significant differences were observed in the sensory profiles of the almond samples and varieties across the two growing seasons.

Nineteen attributes were significantly different across the two growing seasons at both the sample and variety levels: total aroma intensity, hay aroma, fruity/sour aroma, rubber/ medicinal aroma, total flavor intensity, sweet taste, sweet aromatic flavor, marzipan/benzaldehyde flavor, woody flavor, hardness, fracturability, crunchy, roughness, chewiness, cohesiveness of mass, moistness of mass, mealy mouthcoating, amount of residual particulate, and astringent. In both years, musty/earthy flavor was significant only among the varieties, indicating that it is being driven by varietal differences and not by variation within samples.

Only three attributes were similar (not significantly different) among the samples and varieties in both years: marzipan/benzaldehyde aroma, total off flavor, and rubber/ medicinal flavor. This indicates that these attributes are not important in differentiating any of the samples or varieties in this sample set.

In 2015, unripe/beany aroma, woody aroma, hay flavor, and awareness of skins were also significantly different at the sample and variety levels, whereas in 2016, bitter taste and fruity/sour flavor were uniquely significant at both the sample and variety levels.

The PCAs of the statistically significant sensory attributes in each growing season were similar for both the individual samples (43 or 40 samples) and the averaged varietal data (13 or 10 varieties) within each growing season. The results thus focus on the PCA of individual samples, as this biplot is used to overlay the analytical measures for the 2016 data. Lines connect samples for each variety to provide an indication of sensory variability in the first two dimensions.

In the PCA of individual samples, the first two dimensions account for 55% of the sensory variability in 2015 (Figure 1A) and 68% of the sensory variability in 2016 (Figure 1B). In both growing seasons, the PCA biplots show similar results in the first dimension (PC1), which is driven by texture attributes, with samples on the left side of the PCA biplots higher in hardness, fracturability, crunchiness, and astringency and samples on the right side higher in moistness, chewiness, and cohesiveness of mass (Figure 1).

In both 2015 and 2016, the Independence variety was higher in hardness, fracturability, crunchiness, and astringency (although there was only one sample in 2015), as were Sonora (higher in 2015 than in 2016), Padre (only in the 2015 growing season), and Wood Colony (higher in 2016 than in 2015, Figure 1). In both 2015 and 2016, Fritz and Monterey were higher in moistness, chewiness, and cohesiveness of mass, whereas Nonpareil and Aldrich were higher in these characteristics in 2016 than in 2015 (Figure 1). In 2015, the Monterey and Nonpareil samples showed high variation in PC1, with at least one sample significantly lower in moistness, chewiness, and cohesiveness of mass than the other samples of the same variety (Figure 1A).

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Figure 1. (A) Principal component analysis biplot of 2015 descriptive sensory analysis of 43 almond samples. (B) Principal-component-analysis biplot of 2016 descriptive sensory analysis of 40 almond samples. Lines connect samples from the same variety. A, aroma; F, flavor; T, texture.

There were more differences between the two growing seasons in the second dimension (PC2), which is driven by flavor attributes (Figure 1). In 2015, samples at the top of the PCA biplot were higher in total aroma intensity, total flavor intensity, hay aroma, and unripe/beany aroma, whereas samples at the bottom of the PCA biplot were lower in total aroma and flavor intensity (Figure 1A). In 2016, there was more differentiation of aroma and flavor attributes, with the top of the PCA biplot higher in total aroma intensity, woody flavor, hay aroma, and fruity/sour aroma and the bottom of the PCA biplot higher in total flavor intensity, marzipan/ benzaldehyde flavor, and to a lesser extent sweet aromatic flavor (Figure 1B). This opposing relationship of woody flavor and marzipan/benzaldehyde flavor is also observed in 2015 along PC1 (Figure 1A), suggesting that sweet almond varieties are primarily differentiated by either woody flavor or marzipan/benzaldehyde flavor.

Despite the different positions of Aldrich samples in the two PCA biplots, Aldrich had a relatively consistent sensory profile between the two years. Aldrich and Fritz samples were both higher in total flavor intensity and marzipan/benzaldehyde flavor in both growing seasons (Figure 1). This relationship

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Table 4. Contents ^a and (Significance (Fisher's LSD)	of Moisture, N	facro- and Mi	icronutrients, a	and Amygdali	n in 10 Almo	nd Varieties G	rown in 2016		
	Aldrich	Butte/Padre	Carmel	Fritz	Independence	Monterey	Nonpareil	Price	Sonora	Wood Colony	LSD
moisture (%)	4.7 ± 0.1	4.4 ± 0.1	4.1 ± 0.5	4.5 ± 0.2	3.4 ± 0.0	5.1 ± 0.1	4.0 ± 0.4	4.9 ± 0.5	4.5 ± 0.1	3.3 ± 0.2	0.4
protein (%)	23.2 ± 0.1	19.6 ± 0.6	20.6 ± 1.4	21.5 ± 0.5	25.8 ± 0.5	23.0 ± 0.1	20.9 ± 0.5	24.6 ± 1.7	22.8 ± 0.5	22.0 ± 0.4	1.2
dietary fiber (%)	16.8 ± 1.7	19.1 ± 1.3	18.9 ± 4.5	15.3 ± 2.9	19.1 ± 1.6	16.0 ± 1.6	19.4 ± 1.6	17.4 ± 1.2	19.7 ± 3.0	18.6 ± 2.3	NSD ^b
insoluble fiber (%)	15.5 ± 1.6	17.8 ± 1.3	17.6 ± 4.3	14.1 ± 2.6	17.6 ± 1.2	14.7 ± 1.4	17.7 ± 1.1	15.6 ± 1.2	17.9 ± 2.9	16.5 ± 2.0	NSD
soluble fiber (%)	1.3 ± 0.2	1.4 ± 0.3	1.3 ± 0.3	1.3 ± 0.3	1.5 ± 0.5	1.4 ± 0.6	1.8 ± 0.6	1.8 ± 0.6	1.7 ± 0.7	2.0 ± 0.7	NSD
ash (%)	2.7 ± 0.1	3.1 ± 0.1	2.8 ± 0.1	2.7 ± 0.2	2.9 ± 0.1	3.1 ± 0.1	2.8 ± 0.1	2.7 ± 0.1	2.7 ± 0.2	3.2 ± 0.1	0.2
sugars (%)	3.4 ± 0.5	4.8 ± 0.4	3.7 ± 0.8	3.4 ± 0.6	3.2 ± 0.2	5.1 ± 0.2	4.3 ± 0.4	3.8 ± 0.2	3.6 ± 0.3	4.0 ± 0.3	0.6
fat (%)	46.4 ± 0.7	48.0 ± 0.6	48.2 ± 1.2	49.4 ± 0.4	42.8 ± 1.4	44.7 ± 0.2	47.6 ± 1.2	44.4 ± 2.5	45.5 ± 0.6	48.0 ± 0.3	1.6
MUFA (%)	30.8 ± 0.5	28.5 ± 0.8	28.9 ± 1.0	30.7 ± 0.3	26.6 ± 0.7	26.9 ± 0.6	30.7 ± 1.1	27.7 ± 1.5	28.6 ± 0.2	32.5 ± 1.9	1.4
PUFA (%)	9.6 ± 0.2	12.8 ± 0.1	13.0 ± 0.6	12.5 ± 0.1	10.2 ± 0.4	11.6 ± 0.2	10.6 ± 0.5	11.0 ± 0.5	10.8 ± 0.3	8.4 ± 0.3	0.5
SAFA (%)	3.3 ± 0.0	3.8 ± 0.1	3.6 ± 0.1	3.4 ± 0.0	3.4 ± 0.1	3.7 ± 0.0	3.5 ± 0.1	3.2 ± 0.1	3.3 ± 0.1	3.3 ± 0.2	0.1
lpha-tocopherol (mg per 100 g)	23.5 ± 0.8	25.2 ± 1.6	25.9 ± 0.7	23.4 ± 1.4	16.6 ± 0.2	15.7 ± 0.4	23.1 ± 0.5	21.6 ± 0.8	27.1 ± 1.0	22.7 ± 0.3	1.3
calcium (mg per 100 g)	296.0 ± 18.7	319.8 ± 22.6	299.0 ± 56.1	312.3 ± 85.6	283.8 ± 11.9	224.5 ± 6.2	228.8 ± 10.3	231.0 ± 46.4	190.0 ± 11.5	349.8 ± 10.7	54.1
potassium (mg per 100 g)	627.8 ± 22.9	763.3 ± 53.3	654.3 ± 25.4	665.0 ± 25.8	760.5 ± 13.0	835.5 ± 15.9	738.0 ± 25.4	638.8 ± 39.7	752.3 ± 32.3	731.8 ± 9.3	42.0
phosphorus (mg per 100 g)	551.0 ± 9.9	506.0 ± 25.4	547.8 ± 18.4	514.8 ± 7.9	560.8 ± 8.8	552.0 ± 18.7	503.8 ± 31.5	545.5 ± 17.2	570.5 ± 16.8	612.3 ± 10.2	26.0
magnesium (mg per 100 g)	298.8 ± 5.0	265.5 ± 4.2	287.5 ± 19.8	285.0 ± 6.1	256.0 ± 6.7	300.8 ± 6.0	293.8 ± 5.4	303.8 ± 12.1	274.0 ± 11.2	290.3 ± 7.1	13.8
zinc (mg per 100 g)	3.2 ± 0.2	2.6 ± 0.1	2.7 ± 0.3	2.3 ± 0.1	3.0 ± 0.1	3.1 ± 0.1	3.3 ± 0.2	3.4 ± 0.6	3.2 ± 0.1	3.1 ± 0.1	0.3
iron (mg per 100 g)	4.9 ± 0.4	3.3 ± 0.4	4.0 ± 0.3	3.8 ± 0.5	5.3 ± 0.4	3.9 ± 0.1	4.5 ± 0.8	4.6 ± 0.9	4.0 ± 0.4	5.2 ± 0.2	0.7
copper (mg per 100 g)	0.9 ± 0.1	0.8 ± 0.0	1.1 ± 0.2	0.7 ± 0.1	0.7 ± 0.0	0.7 ± 0.0	1.0 ± 0.1	1.3 ± 0.1	1.0 ± 0.1	1.0 ± 0.0	0.1
manganese (mg per 100 g)	2.2 ± 0.1	2.7 ± 0.3	2.6 ± 0.3	2.0 ± 0.1	2.5 ± 0.1	2.6 ± 0.1	2.3 ± 0.3	2.3 ± 0.3	2.3 ± 0.3	2.6 ± 0.1	0.3
amygdalin (mg/kg)	27.2 ± 0.9	3.0 ± 0.4	9.8 ± 6.3	14.5 ± 3.0	0.4 ± 0.3	6.3 ± 3.1	2.0 ± 0.9	0.1 ± 0.0	0.9 ± 0.2	7.7 ± 0.7	3.5
^{<i>a</i>} Mean \pm one standard devia	ttion. ^b Not sign	ificantly different	among almond	varieties.							



Figure 2. Principal-component-analysis (PCA) biplot of 2016 descriptive sensory analysis of 40 raw almond samples (circles, 10 almond varieties) from the 2016 growing season, with chemical data (vectors) overlaid.

was clearer in the 2016 biplot (Figure 1B), and the third dimension of the 2015 PCA biplot (8% of the sensory variance, data not shown). Aldrich was also higher in sweet taste and sweet aromatic flavor in both years (Figure 1), as well as higher in woody aroma in 2015 (driven by one sample, Figure 1A).

In both years, some Nonpareil samples were located at the top of the PCA biplots (Figure 1), being higher in total aroma intensity and hay aroma as well as woody aroma (2015, Figure 1A) and woody flavor (2016, Figure 1B); however, Nonpareil showed high variation in 2016 (Figure 1B). Sonora was located toward the top part of the PCA biplots in both years, being consistently higher in hay aroma (2015 and 2016, Figure 1), as well as in hay flavor (2015, Figure 1A). Carmel had a relatively intermediate (middling) aroma and flavor profile in both years (Figure 1), but was somewhat higher in total flavor intensity and sweet aromatic flavor in 2016 (Figure 1B).

Wood Colony also had a relatively intermediate aroma and flavor profile across both years, as did Price (Figure 1), with one sample in 2015, located toward the top of the PCA biplot, being higher in total aroma intensity, hay aroma, and woody aroma (Figure 1A). Of the remaining samples that were only measured in 2015, Butte and Mission had intermediate texture profiles and were both generally lower in total aroma and flavor intensity, except for one sample of Butte that was higher in marzipan/benzaldehyde flavor (Figure 1A).

Variability in the Sensory Profiles of Almond Varieties. In general, the Aldrich, Fritz, Wood Colony, and Price varieties had consistent sensory profiles in each growing season, as shown by the relatively close positions of the samples for each variety on the PCA biplots (Figure 1), whereas other varieties showed larger sensory variation within each year, such as Nonpareil (2015 and 2016), Monterey (2015), Carmel (2016), and Butte/Padre (2016). There tended to be more variability within varieties in the 2016 growing season (Figure 1B), which may be an element of sampling or external factors during the growing season. Interestingly, flavor was less differentiating of the samples and less consistent across the growing seasons compared with texture (Figure 1). This may indicate that flavor is influenced more by external factors, such as orchard practices or environmental factors, than by varietal composition.

Sensory differences among almond varieties tended to be greater than the variation within varieties. This was also shown for contents of tocopherol and other tocopherol homologues, where almond-oil cultivars were found to be significantly different from one another, despite there also being significant variability across the two growing years.^{14,15} López-Ortiz and coauthors¹⁴ hypothesized that the variability was due to climactic differences between the two growing seasons.

Relationship of Sensory Attributes with Chemical Compounds and Physical Measures. Considering the 2016 analytical data, all measures were significantly different among the almond varieties, except for dietary fiber, insoluble fiber, soluble fiber, toluene, 3-methyl-2-butenal, 1,2-ethanediol, and 2-furanmethanol (Table 4).

All significant analytical measures (i.e., macro- and micronutrients, moisture content, amygdalin, and volatile compounds) were correlated with the 2016 sensory data and overlaid on the PCA biplot (Figure 2), to provide visual representation of the relationship between the two data sources. Analytical measures that are in proximity to sensory attributes in the PCA biplot are likely to be correlated with one another; however, there are multiple dimensions that explain the sensory variation. The first two dimensions are shown in



Figure 3. (A) Positive correlation of chewiness-texture intensity with moisture (%) of the 40 almond samples in the 2016 growing season (r = 0.87, df = 38, p < 0.0001). (B) Partial-least-squares (PLS) modeling of the relationship of chewiness texture with chemical measures.

Figure 2, which account for the majority of the sensory differences and relationships with the chemical compounds and physical measures.

Of the 72 chemical compounds and physical measures that were analyzed in the 40 almond samples, only moisture, amygdalin, and several volatile compounds were important in modeling the sensory profiles. This indicates that the majority of the analytical measures that were analyzed in this study were not important in differentiating the sensory profiles of the almond varieties tested, despite being significantly different among the almond varieties. It may be that these volatile compounds are below their aroma-detection thresholds or that these analytical measures are important in other almond varieties or different processes, such as in roasted, pasteurized, or aged almonds.

On the right side of the PCA biplot (Figure 2), moisture content is positively associated with the texture attributes: chewiness, moistness of mass, and cohesiveness of mass. The correlation (Figure 3A) and partial least squares (PLS) model (Figure 3B) of chewiness and moisture content confirm this relationship. Moisture content has a marked impact on fracturability (negative in nature), as can be seen by the size of the model parameter estimate in the PLS model in Figure 4B. This is primarily due to the wider range of intensity scores for fracturability than for chewiness. Fracturability (Figure 4A), hardness, and crunchiness are all negatively correlated with moisture content. Fracturability is also positively associated with several volatile compounds: acetoin, 1-butanol, 2butanone, and ethyl acetate (Figure 4B).

These findings are consistent with previous studies, where high humidity was shown to affect almond texture, including an increase in moistness of mass and cohesiveness of mass and a decrease in hardness, crispness, crunchiness, fracturability, persistence of crunch, and particulate mass.²⁰ High humidity also resulted in decreased consumer liking, as a direct result of these textural changes.^{20,22}

All samples in this study were handled and stored in the same conditions, so differences in moisture content are not likely to be due to humidity differences after harvesting. However, it may have been influenced by orchard-management practices. Slightly higher levels of moisture were found in almonds from nonirrigated trees, compared with those from

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Figure 4. (A) Negative correlation of fracturability-texture intensity with moisture (%) of the 40 almond samples in the 2016 growing season (r = -0.86, df = 38, p < 0.0001). (B) Partial-least-squares (PLS) modeling of the relationship of fracturability texture with chemical measures.

irrigated trees, and higher moisture levels were also found in almonds from trees treated with inorganic fertilizer, compared with those from trees treated with organic fertilizer.³² Early-harvested almonds were found to have higher moisture contents than late-harvested almonds,²³ likely because of not only the length of time on the tree but also the density and porosity of the almond shell.

Samples in 2016 were harvested at similar times, from early August to late October; however, almond varieties differ in their maturing periods and harvesting dates. Independence, Sonora, and Wood Colony are early-maturing varieties with softer shells, generally harvested in August. These varieties tended to have lower moisture contents in the current study and were higher in hardness, fracturability, crunchiness, and astringency (Figures 2, 3A, and 4A), whereas Fritz and Monterey have harder shells and are late-maturing varieties, generally harvested from late September to October. These were higher in moisture content, moistness, chewiness, and cohesiveness of mass in the current study (Figures 2, 3A, and 4A). The late-maturing varieties may have higher moisture levels as they may take a longer time to dry on the orchard floor, and the hard shells may elongate the drying period. Contador and coauthors¹⁰ found that Nonpareil and Mission were lower in crunchiness, hardness, and crispness compared with the European cultivars Marcona, Supernova, Tuono, and Ferragnès. In this study, Nonpareil and Mission (2015 only) had intermediate texture profiles. These results are likely due to the context with which the samples were evaluated; however, clear texture differences were found among almond varieties,¹⁰ similar to the overall results of this study.

Marzipan/benzaldehyde flavor is positively associated with several volatile compounds, including benzaldehyde, amygdalin, benzyl alcohol, and phenylethyl alcohol, and negatively associated with hexanal and pentanal (Figure 5B). Although both Aldrich and Fritz samples are higher in total flavor intensity and marzipan/benzaldehyde flavor (Figure 1), the relationship of benzaldehyde and amygdalin with marzipan/ benzaldehyde flavor is primarily driven by Aldrich (Figure 5A).

This is consistent with Lee et al.,⁵ who found that Aldrich and Fritz had significantly higher levels of amygdalin among the sweet almond varieties. Amygdalin, benzaldehyde, and benzyl alcohol were previously related to marzipan flavor in sweet almonds, along with 2,3-butanediol.⁶ In this study, 2,3-

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Figure 5. (A) Positive correlation of marzipan/benzaldehyde-flavor intensity with benzaldehyde concentration of the 40 almond samples in the 2016 growing season (r = 0.92, df = 38, p < 0.0001). (B) Partial-least-squares (PLS) modeling of the relationship of marzipan/benzaldehyde flavor with chemical measures.

butanediol is not associated with marzipan/benzaldehyde flavor and is instead located on the right side of the PCA biplot (Figure 2), somewhat positively associated with fracturability (Figure 4B), and negatively associated with chewiness (Figure 3B), suggesting that it may be related to lower moisture content in the almonds tested. Phenylethyl alcohol, on the other hand, has aromas reminiscent of rose, honey, spice, and lilac.³³ This relationship may be more correlative than causal, as sweet aromatic flavor is somewhat correlated with marzipan/benzaldehyde flavor in 2016 (r = 0.70, df = 38), given their proximity on the PCA biplot (Figure 1B).

The amygdalin concentrations in this study are well below the reported average for sweet almond varieties,⁵ of which all samples in this study belong. There is very little variation in amygdalin concentrations within samples of the same variety in this study (standard deviations of less than 7 mg/kg, data not shown), whereas Lee et al.⁵ reported finding significant differences among growing regions for commercial varieties. This may be due to differences in sampling and longer storage times (sampled in the 2010 growing season and analyzed in 2012 after two years of storage in refrigerated conditions).⁵

More research is needed to confirm the results of this study, by investigating the relationships of the analytical measures with sensory attributes across multiple growing seasons and by including other almonds varieties. Investigating whether roasting negates these varietal differences may be useful, as well as whether orchard practices and environmental factors influence almond composition.

In summary, this study shows that although almond varieties differ in their sensory profiles, there are consistencies across growing seasons, particularly in texture. These sensory differences can be translated and presented to food manufacturers, retailers, and consumers to aid discussions around which almond varieties would best serve the purposes of the end-product. For example, almonds that are harder, more fracturable, and crunchy (Independence, Sonora, and Wood Colony) could be added as ingredients in cooking, as

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their texture profiles might complement other foods, whereas the moist, chewy almonds (Fritz and Monterey) may be better for almond milk given their high natural moisture content. Some varieties have distinct "almondlike" flavor profiles (more marzipan/benzaldehyde flavor in Aldrich and Fritz), which could be ideal for consumers who eat raw almonds or for use in aromatic, low-cooked foods (to preserve the flavor), such as baked goods.

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ABBREVIATIONS USED

HS-SPME GC/MS, headspace solid-phase microextractiongas chromatography-mass spectrometry; SAFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; ANOVA, analysis of variance; PCA, principle component analysis; PLS, partial least squares; VIP, variable importance in the projection

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