JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Review

Cite This: J. Agric. Food Chem. 2019, 67, 2743−2753

pubs.acs.org/JAFC

# Review of the Sensory and Chemical Characteristics of Almond (*Prunus dulcis*) Flavor

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**ABSTRACT:** Understanding almond flavor, in terms of both sensory aspects and chemistry, is essential for processors to maintain almond quality and to correctly identify acceptable or unacceptable product. This overview of the sensory and chemical characteristics of almond flavor discusses raw and heat-processed almonds, the volatile compounds generated upon heating, the aroma qualities associated with various odorants, and the use of descriptive sensory analysis for sweet almonds. Flavor development and off-flavors in almonds due to rancidity is also explored. The review examines the existing methods used to assess common nonvolatile as well as volatile indicators of lipid oxidation in almonds and the correlation of these indicators with consumer acceptance. Recent research on the relationship among volatile profile, rancidity indicators, and consumer acceptance is presented.

**KEYWORDS:** *almond flavor, Prunus dulcis, aroma, off-flavors, rancidity, review*



## INTRODUCTION

Almond is a term applied to the seed of the almond tree ( *Prunus dulcis* (Mill.) D.A. Webb), a member of the genus *Prunus* L. within the Rosaceae family, native to south-central Asia and cultivated in Mediterranean-type climates, including California (United States), the Mediterranean, central Asia, and Australia.[1] Cultivated almonds have been designated with a variety of taxonomic synonyms, including *Amygdalus communis* L., *Amygdalus dulcis* Mill. and *Prunus amygdalus* Batsch, due to their cross fertility with other species such as peach.[2] In addition to commercially cultivated almonds, there are at least 30 species of wild almonds described which are generally more bitter than cultivated varieties.[3−5] The fruit of the almond tree is a drupe, composed of a fleshy hull surrounding a hard shell, which protects the edible seed or kernel. Kernels of the cultivated sweet almond consist mainly of lipids, protein, fiber, and high concentrations of vitamin E.[6]

Almond kernels contain varying amounts of amygdalin, a diglucoside that is broken down into hydrogen cyanide and benzaldehyde in response to crushing of the kernel and exposure to water or saliva. Almond phenotypes are characterized as sweet (nonbitter), semibitter, or bitter, depending on the concentration of amygdalin in the kernel.[7,8] Due to the high amygdalin content (>3%), bitter almonds are a significant source of benzaldehyde, which is an important flavoring substance also known as oil of almond or almond essence. However, most almond producers and processers focus on cultivated sweet almonds, and the popularity of sweet almonds in comparison with other nuts has soared in recent years. Almonds are the most widely produced tree nut in the world, reaching over 1.2 million metric tons during the 2017/2018 season.[9] The U.S. state of California is the major almond-growing region in the world, producing 81% of the world almond production, followed by Australia (7%), Spain (4%), Iran (1%), and Tunisia (1%).[6] In the United States, sweet almonds are the most highly consumed tree nut at 2.17 pounds (984 g) per capita per year, approximately 4 times the consumption rate of walnuts, the second most highly consumed tree nut.[9,10]

The eating quality of almonds is influenced by a number of factors, including the physiological development of the almond kernel in the field, the harvest and shelling conditions of the almond, and the processing and storage conditions. Almond kernels develop in the shell surrounded by a hull; as the kernels mature, the hull dries and splits open, allowing the in-shell nut to dry naturally before harvest. In California, almonds are harvested by mechanically shaking the trees to knock the ripened and split drupes to the ground, where they are allowed to dry for 8−10 days before being collected. The harvested almonds are then transported to huller−sheller facilities where the hulls are removed to produce in-shell almonds, or the hulls and shells are removed to produce almond kernels, by passing through a series of rollers.[11] Most almonds are shipped and sold after shelling, which allows the kernels with pest, mold, or mechanical damage to be sorted out and kernels to be graded by size. All California-grown almonds sold in North America (U.S., Canada, and Mexico) are required by law to be pasteurized, which can be accomplished through a surface treatment, such as steam processing or propylene oxide, which does not diminish the sensory attributes of the "raw" kernels, or through a heat treatment process such as blanching or roasting.[12] Almonds are often further heat treated (e.g., roasted) to develop flavor and modify texture.

## ALMOND FLAVOR

**Raw Almonds.** While it is important to ensure almonds are properly ripened, are free from insect, mold, and mechanical

Received: November 28, 2018
Revised: February 13, 2019
Accepted: February 14, 2019
Published: February 14, 2019




DOI: 10.1021/acs.jafc.8b06606
J. Agric. Food Chem. 2019, 67, 2743−2753

**Table 1. Volatile Compounds Identified in Raw Almond Samples and Reported by Two or More Studies of Almond Headspace Volatiles**

| compound group | name of compound | odor | ref |
|---|---|---|---|
| acid (organic) | acetic acid | vinegar-like[a] | 28, 30 |
| | hexanoic acid | sweaty, rancid[b] | 23, 28 |
| alcohol | 1-butanol | medicine, fruit, wine[b] | 23, 24, 28 |
| | 1-heptanol | herb[b] | 23, 29 |
| | 1-hexanol | resin, flower, green[b] | 23−25, 28, 29 |
| | 1-nonanol | aldehydic, waxy, citrus[b] | 23, 28, 29 |
| | 1-octanol | chemical, metal, burnt[b] | 23, 24, 28, 29 |
| | 1-pentanol | fruity[b] | 23, 25−28 |
| | 1,2-propanediol | not available | 23, 28 |
| | 2-ethyl-1-hexanol | sweet, floral, oily[b] | 25, 28 |
| | 2-heptanone | cheesy, banana, fruity[b] | 23, 25 |
| | 2-methyl-1-propanol | wine, whisky[b] | 23, 28, 29 |
| | 2-phenylethanol | floral, hyacinth/gardenia[b] | 25−29 |
| | 3-methyl-1-butanol | malty[a] | 23, 28, 29 |
| | 3-methyl-2-buten-1-ol | fruity, alcoholic, green[b] | 26−29 |
| | 3-methyl-3-buten-1-ol | not available | 26−29 |
| | benzyl alcohol | floral, phenolic[b] | 26−29 |
| aldehyde | benzaldehyde | sweet, marzipan[c] | 26−29 |
| | heptanal | rancid, pungent[b] | 23−25, 29 |
| | hexanal | green, grassy[a] | 23, 25−30 |
| | nonanal | citruslike, soapy[a] | 23, 24, 28−30 |
| | octanal | citruslike, green[a] | 23, 29, 30 |
| | pentanal | almond, malt, pungent[b] | 23, 25 |
| pyrazine | 2-methylpyrazine | roasted[b] | 23−25 |
| terpene | α-pinene | piny[b] | 23, 25 |
| | limonene | orange peel[b] | 23, 29 |
| lactone | butyrolactone | creamy, oily, fatty[b] | 23, 28 |
| alkane | toluene | painty[b] | 24, 26, 27, 29 |
| sulfur-containing | methional | cooked potato[c] | 24, 30 |

[a]Aroma descriptor obtained from *Eur. Food Res. Techn.* **2008**, *228*, 265−273.[36] [b]Aroma descriptors obtained from http://www.thegoodscentscompany.com.[38] [c]Aroma descriptors obtained from *Food Chem.* **2017**, *217*, 244−253.[30]

damage, and are of a certain uniform size and weight, the final determiner of almond eating quality is flavor.[13] The term flavor describes the brain's integration and interpretation of sensations from taste receptors on the tongue and sensations from odor-active volatile compounds detected ortho- and retronasally during mastication.[14] This sensation is therefore influenced by three main constituents of flavor: nonvolatile components (taste), the compliment of odor-active volatiles compounds (aroma), and the mental interpretation specific to the taster (psychology).

The taste of sweet almonds is mainly influenced by the nonvolatile composition of the almond and almond texture, as these are directly assessed by taste and touch receptors on the tongue and in the mouth.[14] Composition studies indicate that all almond varieties cultivated globally are composed primarily of fat (44−61%), protein (16−23%), and dietary fiber (11−14%).[1] These macronutrients have not been shown to be detectable by recognized human taste receptors, though a recently discovered free fatty acid transporter expressed by taste cells suggests that humans may be able to detect free fatty acids in foods.[15] Almonds also contain a small amount of soluble sugars, including sucrose (3.95%), glucose (0.17%), and fructose (0.11%) as well as other monosaccharides (<0.1%) and sugar alcohols (trace levels).[6] Civille et al.[16] reported the primary descriptive taste dimensions of raw whole sweet almonds (with skin) to be sweetness and astringency, with little bitterness or sourness, and no saltiness observed by panelists. This is not surprising, as sweet almonds contain only trace amounts of salts and nonfatty acids,[6] which are unlikely to be detected at trace levels. Astringency in sweet almonds derives from the phenolic compounds in the skin. Flavanol monomers (i.e., (−)-epicatechin and (+)-catechin) as well as oligomers (i.e., proanthocyanidins or condensed tannins) up to seven units in length were identified as the most abundant type of flavonoids in almond skin[17] and have been shown to elicit astringent sensations in the mouth, with polymeric forms displaying increasing astringency with increasing degree of polymerization.[18]

The texture of almonds has been demonstrated to influence the perception of almonds and resulting affective or hedonic judgements of almond flavor.[19] The texture of raw almonds as it relates to almond variety was assessed by Civille et al.[16] using consensus scoring of raw almonds from seven almond varieties grown in California; along several of the 10 textural dimensions, the range of sample texture within one variety was large, one example being "crunch/snap" in Nonpareil variety almonds. Raw almond texture is likely affected by both the phenotypic characteristics of almonds, as determined by the tree variety, and the almond moisture content, but detailed information on the relationship of raw almond texture in relation to chemical composition is lacking. Some information is provided by the work of Vickers et al.,[19] who showed that increasing sample moisture content was related to increasing "moistness", "cohesiveness", and "fatty film" and to decreasing


DOI: 10.1021/acs.jafc.8b06606
J. Agric. Food Chem. 2019, 67, 2743−2753

**Table 2. Compounds in Toasted Almonds, Possibly Generated by Maillard Reactions or Sugar Pyrolysis during Heating, As Reported in One or More Studies**

| compound group | name of compound | ref |
|---|---|---|
| acid (organic) | acetic acid | 30, 35 |
| furan | 2,5-furandione | 36 |
| | 2-acetylfuran | 29 |
| | 2-methyl-4,5-dihydro-3(2*H*)-furanone | 36, 37 |
| | 2-pentylfuran | 23, 29, 35 |
| | 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (sotolone) | 30 |
| | 4-hydroxy-2,5-dimethylfuran-3(2*H*)-one (hdmf) | 30 |
| | 5-hydroxymethyl-2-furfural (hmf) | 24 |
| | 5-methylfurfural | 29, 36, 37 |
| | furfural | 23, 24, 29, 36, 37 |
| | furfuryl alcohol | 23, 29, 36, 37 |
| lactone | butyrolactone | 23, 24, 35 |
| ketone | 1-hydroxypropan-2-one | 23 |
| | 2,3-butanedione | 23, 30 |
| | 2,3-pentanedione | 30, 35 |
| | 3-hydroxybutan-2-one (acetoin) | 23, 24, 35, 36 |
| pyridine | 2-acetyl-3,4,5,6(or 1,4,5,6)-tetrahydropyridine | 30 |
| | 2-acetylpyridine | 29, 35 |
| pyrazine | 2,3,5-trimethylpyrazine | 23, 24, 29, 30, 35 |
| | 2,3-diethyl-5-methylpyrazine | 30, 37 |
| | 2,3-dimethyl-5(2-propenyl)-pyrazine | 37 |
| | 2,3-dimethyl-5-ethylpyrazine | 36, 37 |
| | 2,3-dimethylpyrazine | 23, 29, 35−37 |
| | 2,5-diethyl-3-methyl- + 2-methylpyrazine | 37 |
| | 2,5-diethylpyrazine | 36, 37 |
| | 2,5-dimethyl-3-ethenylpyrazine | 37 |
| | 2,5-dimethyl-3-ethylpyrazine | 36, 37 |
| | 2,5-dimethylpyrazine | 23, 25, 29, 35−37 |
| | 2,6-diethylpyrazine | 23, 29, 37 |
| | 2,6-dimethyl-3-ethylpyrazine | 36 |
| | 2-acetyl-3-methylpyrazine | 37 |
| | 2-ethyl-3,5-dimethylpyrazine | 30, 35 |
| | 2-ethyl-3-methylpyrazine | 36, 37 |
| | 2-ethyl-5-methylpyrazine | 29, 30, 35−37 |
| | 2-ethyl-6-methylpyrazine | 23, 35 |
| | 2-ethylpyrazine | 23, 25, 29, 35−37 |
| | 2-methyl-((*E*)-1-propenyl)pyrazine isomers | 37 |
| | 2-methyl-((*Z*)-1-propenyl)pyrazine | 37 |
| | 2-methyl-5-(1-propenyl)pyrazine | 36 |
| | 2-methylpyrazine | 23−25, 35−37 |
| | 3,5-dimethyl-2-ethylpyrazine | 37 |
| | 3-ethyl-2,5-dimethylpyrazine | 30, 35 |
| | acetylpyrazine | 36, 37 |
| | methyl-2-vinyl-5-pyrazine | 36 |
| pyrrole | 1-(2-furfuryl)-pyrrole | 36, 37 |
| | 1*H*-pyrrole | 36, 37 |
| | 1*H*-pyrrole-2-carboxaldehyde | 29 |
| | 2-acetylpyrrole | 23, 30, 36, 37 |
| | 2-methyl-1*H*-pyrrole | 36 |
| | 2-propionyl-1-pyrroline | 30 |
| Strecker aldehyde | 2-methylpropanal | 30, 35 |
| | 2-methylbutanal | 23, 29, 30, 35 |
| | 3-methylbutanal | 23, 29, 35 |
| sulfur-containing | 2-furfurylthiol | 30 |
| | dimethyl trisulfide | 30 |
| | methional | 24, 30, 36 |
| | methyl disulfide | 29 |
| | methylsulfanylmethane | 23 |

"crispness", "number of pieces", and "crunchiness" after the first chew in whole raw, blanched, and dry roasted almonds. Results of the study confirmed the findings of Varela et al.[20] that consumers prefer drier, crisper, and crunchier almond texture.

As the main taste aspects of raw sweet almonds are limited to the sweet and astringency dimensions, and arguably the tactile dimensions of taste relating to almond texture, the greatest source of variability in almond flavor may be related to odor-active volatiles. Humans detect odor-active volatiles through g-protein coupled olfactory receptors expressed by olfactory nerve cells, of which several million are embedded in the olfactory mucosa located in the nasal passages.[14] Humans express about 350 of approximately 1000 volatile receptors coded into the mammalian genome, and each receptor can be activated by more than one type of compound or functional group.[21] In addition, each unique compound may activate multiple types of receptors, resulting in a highly complex activation pattern of olfactory nerves that may allow humans to distinguish several thousand types of odor-active compounds.[14] Furthermore, natural products may contain from a few to hundreds of odor-active compounds, further enhancing the variability of food solely in terms of aroma.[22]

Raw almond kernels contain fewer volatile organic compounds in comparison with dry-roasted kernels, as detected by gas chromatography.[23] Volatile compounds detected in raw almonds include C1−C9 alcohols,[23−29] C4−C10 aldehydes,[23−26,28−31] benzaldehyde,[4,23−29] organic acids,[23,28,30] and, in some cases, pyrazines,[23−25] terpenes,[23,29] and sulfur compounds.[23,24,30] Volatile compounds that were present in at least two studies of raw almonds are given in Table 1.

It is difficult to assess which compounds are important to raw almond aroma and which are not, as not all volatile compounds have odor and volatile compounds with odor may not have a significant effect on raw almond aroma, since the aroma effect will depend on the concentration and odor intensity of the volatile compound. Although the general classes of volatile compounds identified in raw almonds by various authors overlap, the relative compound abundances reported are highly variable.[23−31] For example, Agila and Barringer[24] found that the most abundant volatile compounds in raw almond samples were methanol and ethanol and hypothesized that these may be decomposition products of fatty acids, whereas all other groups reported that the most abundant compound in raw almonds was the odor-active compound benzaldehyde.[23,26,29,31] Benzaldehyde is considered


DOI: 10.1021/acs.jafc.8b06606
J. Agric. Food Chem. 2019, 67, 2743−2753

a key odorant in almonds having a bitter, almondlike odor and has a relatively low odor threshold (0.35 mg/L in water).[22] It is reported in superthreshold concentration in several studies, making this compound a main driver of raw almond flavor in these cases.[23,26,29,31] Levels of benzaldehyde are very low in raw sweet almonds in comparison with levels present in semibitter and bitter almonds, reflecting the relatively high levels of amygdalin in these almonds.[4,5]

Alcohols were most frequently reported in raw almonds;[20−26] however, their effect on almond aroma may be limited, as alcohols have comparatively high aroma thresholds[32] and may not be present in superthreshold levels in raw almonds. Aldehydes, apart from benzaldehyde, were also widely reported,[20−23,25−28] and these tend to have lower sensory thresholds in comparison to alcohols[29] and in some cases may contribute significantly to raw almond aroma. However, C5−C11 aldehydes are common secondary oxidation products of oleic and linoleic acid and are reported in highly variable concentrations among studies of raw almonds. This likely arises from varying conditions of sample age, storage, and degrees of lipid oxidation before analysis. Some of these compounds are odorants that may have a negative influence on almond aroma (e.g., hexenal, nonanal, octanal).

**Heat-Processed Almonds.** Almonds are generally roasted using either hot air or oil to generate roasted almond aroma. Roasted almonds, in contrast to raw almonds, are found to contain many more volatile organic compounds, as heating generates new volatile products through a number of reaction pathways, including lipid oxidation, sugar pyrolysis, and Maillard reactions. The last refers to a complex set of reaction pathways promoted by high-heat and low-moisture conditions. These reactions begin with the nucleophilic attack of a carbonyl carbon (mainly that of a reducing sugar) by a primary amine group (mainly that of an amino acid), which after a loss of water produces an imine (Schiff base).[33] The Schiff base can rearrange to form the Amadori rearrangement product (ARM), which refers to an interconversion of a 1,2-enol and 2,3-enol form of the original reducing sugar carbon skeleton.[34] Upon hydrolysis of the imine group, dehydrations, and cyclization, the 1,2-enol ARM can become hydroxymethylfurfural, 2-furfural, or a pyrrole, depending on the original reducing sugar and reaction conditions.[33] Loss of the original amino acid, rearrangement, dehydration, and cyclization of the 2,3-enol ARM leads to the formation of odor-active furaneol, 2-acetyl-3-hydroxyfuran (isomaltol), 2,3-butanedione, and hydroxypropanone among others.[33] A separate reaction pathway involving a Schiff base formed from condensation of an $\alpha$-dicarbonyl and an amino acid leads to the release of a Strecker aldehyde involving the original amino acid and an $\alpha$-amino ketone, which are the building blocks for pyrazine formation.[22] This reaction pathway leads to the generation of odor-active 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, and methional as well as a wide variety of alkylpyrazines.[33] The wide array of volatile products resulting from Maillard reactions is usually accompanied by nonvolatile melanoidins formed by further condensation of amines and ketones, which contribute to the characteristic brown color of roasted foods.

The volatile compounds resulting from Maillard reactions are well documented in heat-treated almonds. Frequently reported Maillard products in almonds include furfural, 2,5-dimethylpyrazine, 2-ethylpyrazine, 2-methylpyrazine, 2-acetylpyrrole, and 2- and 3-methylbutanal[5,23,25,29,30,35−37] (Table 2). Alkylpyrazines are frequently reported in food products subjected to high heat (greater than 100 °C), such as nuts, coffee, chocolate, and meat preparations, and individually display odor qualities pertaining to these food products, such as "nutty", "cocoa", "toasted", "hazelnut", "bread crust", "peanut", and "caramel" as well as "earthy" and "potato".[36] The odor thresholds reported for pyrazines generally decrease as the number of alkyl groups and the number of carbons in the alkyl groups increase, although the odor threshold is shown to be dependent on group position.[22] The odor thresholds for simple methylpyrazines are often higher than the concentrations reported in almonds, except in the case of 2-methylpyrazine (threshold: 0.06 mg/L in water) in almond varieties that included Butte/Padre, Comuna, and Marcona almonds.[23,36,37] Ethyl-substituted pyrazines were reported in superthreshold concentrations in the case of 2-ethyl-5-methylpyrazine (threshold 0.10 mg/L in water) and 2-ethyl-6-methylpyrazine (0.13 mg/L in water) in toasted Marcona and Comuna almonds.[36]

Furans, such as furfural and furfuryl alcohol, are also frequently reported in heat-treated almonds (Table 2) and have a sweet almond/bready and cooked sugar odor, respectively.[36] Though these compounds have a relatively high odor threshold (3 and 1.9 mg/L, respectively), furfural and furfuryl alcohol were reported in superthreshold levels in toasted Comuna almonds.[36] Strecker aldehydes 2- and 3-methylbutanal and methional have very low odor thresholds in oil (0.01, 0.0054, and 0.0002 mg/kg, respectively) and are frequently included in volatile assessments of roasted almonds, where they may provide chocolatey, malty, and cooked potato aromas to samples, respectively.[33,38] The compounds 2- and 3-methylbutanal were found in superthreshold concentrations in Butte/Padre,[23] Nonpareil,[30] and fried Spanish almonds,[29] while superthreshold concentrations of methional were reported in Nonpareil[30] and Marcona and Comuna[36] almonds.

**Sensory Analysis of Almonds.** Although measuring volatiles in almond headspace and comparing quantities with known sensory thresholds may give insight into the potential flavor profile of samples, the only way to assess flavor as it is perceived by human beings is to perform sensory analysis.[14] Descriptive sensory analysis is a method of revealing and quantifying individual sensory dimensions of a food product.[14] In this process, panelists openly discuss flavor dimensions of a given product or sample and gradually come to an agreement on product flavor dimensions and the terms used to describe them, allowing these terms to be relevant to and well understood by the panelists. This training process is further cemented by the creation of flavor, aroma, or texture standards to anchor the chosen descriptive terms and possibly train panelists in intensity. Civille et al. used a variation of this process that involved consensus scoring to create a comprehensive sensory lexicon for describing the appearance, aroma, flavor, and texture attributes of almonds.[16] Using a 9-member panel with extensive experience in descriptive analysis, they assessed the sensory attributes and differences among 7 varieties of raw California-grown almonds and developed a lexicon for 10 aroma attributes, 13 flavor attributes, 4 basic taste attributes, and 10 texture attributes. Aroma differences among raw almond varieties were minimal, and overall aroma intensity was low across almond samples. Flavor evaluations revealed that samples overall were mildly flavored (scores $\leq$5 on a 15-point scale) and that Butte and Nonpareil varieties were unique in having squash-like flavor, Nonpareil and


DOI: 10.1021/acs.jafc.8b06606
J. Agric. Food Chem. 2019, 67, 2743−2753

**Table 3. Almond Volatiles (Excluding Maillard Reaction Compounds) Shown To Increase in Concentration over Extended or Accelerated Storage, As Reported by One or More Studies**

| compound group | name of compound | ref |
|---|---|---|
| acid (organic) | 2-methyl-2-propenoic acid | 31 |
| | acetic acid | 50 |
| | heptanoic acid | 35. 50 |
| | hexanoic acid | 35. 50 |
| | nonanoic acid | 50 |
| | octanoic acid | 35. 50 |
| | pentanoic acid | 35. 50 |
| alcohol | 1-butanol | 35 |
| | 1-heptanol | 29, 35, 50 |
| | 1-hexanol | 27, 31 |
| | 1-nonanol | 50 |
| | 1-octanol | 27, 29, 31, 35, 50 |
| | 1-octen-3-ol | 29, 35, 50 |
| | 1-pentanol | 27, 29, 31, 35, 50 |
| | 3-methyl-1-butanol | 27, 31 |
| | 3-methyl-2-buten-1-ol | 27, 31 |
| | 3-methyl-3-buten-1-ol | 27, 31 |
| | benzyl alcohol | 27, 29, 31 |
| | benzene-ethanol | 27, 31 |
| aldehyde | (*E*)-2-decenal | 29, 50 |
| | (*E*)-2-heptenal | 29 |
| | (*Z*)-2-heptanal | 35 |
| | (*E*)-2-hexenal | 29, 35 |
| | (*E*)-2-nonenal | 29 |
| | (*Z*)-2-nonenal | 50 |
| | (*E*)-2-octenal | 29, 50 |
| | (*E,E*)- and (*E,Z*)-2,4-decadienal | 29 |
| | 2,4-nonadienal | 50 |
| | 2-undecenal | 50 |

| compound group | name of compound | ref |
|---|---|---|
| aldehyde | benzaldehyde | 29, 35, 50 |
| | butanal | 29, 35 |
| | decanal | 26, 32, 50 |
| | heptanal | 27, 29, 31, 35, 50 |
| | hexanal | 27, 29, 31, 35, 50 |
| | nonanal | 27, 29, 35, 50 |
| | octanal | 27, 29, 31, 35, 50 |
| | pentanal | 29, 35, 50 |
| ketone | 2-butanone | 27, 29, 31 |
| | 2-decanone | 50 |
| | 2-heptanone | 29, 35, 50 |
| | 2-nonanone | 35, 50 |
| | 2-octanone | 29, 35, 50 |
| | 2-propanone | 27, 31 |
| | 3-octen-2-one | 29, 35, 50 |
| | (*E*)-3-nonen-2-one | 29 |
| | γ-oxepan-2-one | 50 |
| alkane | 1,3-dimethylbenzene | 50 |
| | styrene | 35 |
| | toluene | 27, 29, 31 |
| | pentane | 31 |
| | heptane | 27, 29, 35 |
| | octane | 29, 35 |
| other | 2-pentylfuran | 29, 35, 50 |
| | chloroform | 31 |
| | dimethoxymethane | 31 |
| | hexyl oxirane | 50 |
| | pentyl oxirane | 50 |
| | vinyl hexanoate | 50 |

Carmel varieties were distinguished by tea-like flavor, and that Butte and Carmel varieties were alone in having walnut-like flavor. Also, all samples displayed typical "almond nut meat" flavor in a similar score range, although Carmel had a higher score range of "sweet aromatics" and "benzaldehyde" in comparison to other varieties.

Toasted almonds (variety Desmayo Lagueta) were used by Guerrero et al.[39] to compare expert panelists with semitrained panelists using free choice profiling (FCP). FCP is a form of descriptive analysis in which panelists generate and employ their own descriptive terms. Semitrained panelists generated a wider variety of descriptive terms in comparison to the expert panel, including the aroma attributes milky, burnt, toasted, and smoky, the flavor attributes toasted flavor, bitterness, sweetness, astringency, woody flavor, and burnt flavor, and the texture attributes granular, oiliness, hardness, juiciness, and elasticity. More texture dimensions than flavor and odor attributes were employed to describe samples in the case of both expert and semitrained panelists, pointing to the importance of texture in the experience of tasting almonds. Sensory analysis of almond texture was evaluated by Varela et al.[20,40] in roasted almonds and by Vickers et al.[16] in slivered, sliced, whole blanched, natural whole, and dry roasted whole almonds. Through both a descriptive analysis of texture and consumer liking analysis of samples held at varying moisture levels, it was revealed that consumers distinguished samples more by texture liking than flavor liking, and samples with the least moisture and most crispiness and crunchiness were liked more.[19]

## OFF-FLAVORS IN ALMONDS DUE TO RANCIDITY

Although heat processing of almonds has a large effect on almond flavor and liking due to generation of a wide variety of Maillard volatile products, development of toasted flavor,[39] and crunchy texture,[19,20] the most significant changes in flavor may occur due to the oxidation of almond lipids.[38] Oxidative rancidity describes the occurrence of unpleasant off-flavors due to the oxidative degradation of unsaturated fatty acids in a food product.[42,43] A related process, hydrolytic rancidity, describes the hydrolysis of food triglycerides during cooking or storage, releasing free fatty acids which are more susceptible to lipid oxidation.[44]

Oxidation of unsaturated fatty acids occurs through a radical chain reaction, often conceptualized in three well-established phases. The initiation phase involves the abstraction of a hydrogen radical at the allylic carbon one position away from the double bond (C8 or C11 carbon in the case of oleic acid), except in the case of singlet oxygen, which directly attacks and forms a hydroperoxide at the vinyl carbon (C9 or C10 of oleic acid).[45] The radical generated from hydrogen abstraction is stabilized through resonance over three carbons, which lowers the energy of abstracting the original hydrogen radical.[46]

During the propagation phase, the radical generated may react with oxygen to form the fatty acid peroxyl radical, which can further abstract a nearby hydrogen to form a new fatty acid radical and a fatty acid hydroperoxide.[47] The hydroperoxide is subject to a variety of decomposition reactions, including metal-catalyzed hemolysis, thereby increasing the number of radicals in the system. The resulting fatty acid alkoxy radical


DOI: 10.1021/acs.jafc.8b06606
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can then undergo carbon−carbon cleavage, resulting in a wide variety of shorter-chained volatile aldehyde, alcohol, alkane, oxirane, and ketone secondary products that lend the characteristic aroma of rancidity to food products.[45,48]

The termination phase proceeds through the reaction of two radicals, which in the case of two fatty acid peroxyl radicals could lead to the generation of an aldehyde, alcohol, and singlet oxygen following decomposition of the tetroxide intermediate.[45] Low concentrations of secondary oxidation volatiles generated during certain cooking processes, such as deep frying, are considered positive additions to the overall flavor profile.[46] Oxidative rancidity describes the excessive accumulation of these volatiles, which alters the original natural flavor of the food product. These changes are considered by many to be negative flavor changes and are indicated by lower hedonic ratings of aged samples in comparison to fresh samples in studies of food products undergoing lipid oxidation.[27,31,49]

The high concentration of unsaturated fatty acids in almond lipids makes almonds susceptible to both hydrolytic and oxidative rancidity. Almonds are composed of oleic (18:1, 62−80%) linoleic acid (18:2, 10−18%), palmitic (16:0, 0.5−8%), and stearic (18:0, 1−3%) acids.[1]

The highest proportion of almond lipid is comprised of oleic acid, which may undergo addition of oxygen at any of four positions (carbon 8, 9, 10, or 11) due to resulting radical resonance or singlet oxygen attack. Decomposition of the resulting hydroperoxides leads to volatile products, many of which have been previously identified in almonds (Table 3), through $\beta$-scission of the carbon chain on either side of the peroxyl carbon.[45,48] Some examples include decomposition of an oleic acid C8 hydroperoxide resulting in decanal or 2-undecenal, a C9 hydroperoxide resulting in nonanal or 2-decenal, a C10 hydroperoxide resulting in octane, 1-octanol, or nonanal, and a C11 hydroperoxide resulting in heptane, 1-heptanol, or octanal, along with a nonvolatile acyl glyceride if the original fatty acid is esterified or C7−C10 organic acids if it is a free fatty acid.[45,48]

Linoleic acid has a lowered energy of hydrogen abstraction from the bis-allylic carbon 11, and therefor tends to produce a position 9 or 13 peroxyl or alkoxy radical, though position 10 and 12 peroxyl radicals can also be formed by other mechanisms.[45] Decomposition of linoleic acid hydroperoxide leads to several volatiles, including C9 hydroperoxide product 2,4-decadienal, C13 hydroperoxide products pentane, 1-pentanol, and hexanal, C10 hydroperoxide product 2-octene, and C12 hydroperoxide products hexanal and 2-heptenal,[45] which have been identified in almonds. Many other volatile products identified in almonds have been isolated in studies on oxidation of purified mixtures of single fatty acids, including the oleate product heptanal and linoleate products pentanal, heptanal, octanal, 1-octen-3-one, 2-nonenal, and 2,4-nonadienal.[46] These products may originate from a wide variety of decomposition reactions[48] or reaction of secondary products, such as 2,4-decadienal, which oxidizes to hexanal and other compounds.[46]

Many of these compounds have low odor thresholds, even in oily matrices, and make a substantial contribution to the odor of rancidity, even at low concentrations.[46] Particularly low retro- or orthonasal thresholds (r.t. and o.t., respectively) in oil have been identified for hexanal (r.t. 75 $\mu$g/kg), heptanal (r.t. 50 $\mu$g/kg), octanal (o.t. 55 $\mu$g/kg), (*E*)-2-octenal (r.t. 125 $\mu$g/kg), (*Z*)-2-nonenal (r.t. 0.6 $\mu$g/kg), (*E*)-2-decanal (r.t. 150 $\mu$g/kg), (*E,Z*)-2,4-decadienal (o.t. 10 $\mu$g/kg), and 1-octen-3-one (r.t. 0.3 $\mu$g/kg).[46] However, through extensive oxidation, even compounds with relatively high odor thresholds can exceed threshold concentration, and there is possibility of odor detection of compounds below their detection threshold due to an additive effect of multiple volatiles detected together.[22] The profile of volatiles originating in almonds due to oxidation has not been widely studied, though a limited number of studies involving volatile data of oxidized almonds exist.[5,27,29,31,35]

Mexis and co-workers evaluated volatiles in almonds, as well as other chemical markers of rancidity and hedonic scores of stored whole unpeeled almonds[27] and raw ground almonds,[31] under various packaging and storage conditions. In these studies, a variety of compounds were present in fresh samples and increased during storage, including hexanal, 2-propanone, 3-methyl-3-butenol, 3-methyl-2-butenol, benzene-ethanol, 1-pentanol, and benzene-methanol, whereas volatiles not present in fresh samples were detected as a result of storage, including confirmed lipid oxidation secondary products heptanal, heptane, octanal, 1-octanal, nonanal, and pentane and unconfirmed secondary or tertiary products 2-propanone, 2-butanone, 1-hexanol, and 2-propenoic acid.[27,31] As the samples were raw almonds, some of these volatile compounds may originate from enzymatic processes rather than purely lipid-hydroperoxide decomposition.

Almond lipids derived directly from nonenzymatic lipid hydroperoxide decomposition are more clearly identified in studies of roasted almonds, for which enzyme activity would not influence the volatile profile. Lee et al.[50] applied headspace solid-phase microextraction gas chromatography−mass spectrometry (HS-SPME GC/MS) to study the changes in headspace volatiles of almonds subject to two different roast conditions over the course of 24 weeks of storage at 25 or 35 °C and 65% relative humidity (RH). Analysis of almond volatile profiles revealed that 17 compounds originated from storage of the almonds, including ketones, aldehydes, alcohols, oxiranes, and short-chain acids. These compounds are given in Table 3 and include many compounds shown to originate from oxidation of oleic or linoleic acid. The results of this study indicated that some compounds originating during the storage of almonds showed significant increases in concentration before that of hexanal, the traditional marker of rancidity in foods; these compounds include 2-octanone, 3-octen-2-one, and acetic acid. These volatile compounds also were identified by Franklin et al.[35] using HS-SPME GC/MS in a subsequent study of oxidative changes in roasted almonds during accelerated storage.

Valdés et al.[29] used a variety of techniques, including HS-SPME GC/MS, primary oxidation product indicators, and thermal parameters, to track chemical changes in raw, fried, and roasted almonds during storage at room temperature and 100 °C. Only concentrations of volatiles for samples under accelerated storage were shown and, interestingly, typical oxidation products, such as hexanal, octanal, heptanal, 1-nonanol, and 1-heptanol, decreased in concentration over accelerated storage of raw almonds, while 1-octen-3-ol, nonanal, 2-pentylfuran, 2-octanone, and pentanal increased over storage at 100 °C. The inconsistency of these results in comparison with other studies is likely due to the accelerated storage temperature, which was much higher than temperatures recommended for realistic representation of room-temperature storage.[49] In roasted almonds, most lipid


DOI: 10.1021/acs.jafc.8b06606
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oxidation products showed peak concentrations at 3−5 days of storage at 100 °C and were detected at lower concentrations or not at all by 10 days of storage.[29] Volatiles found to increase during any part of accelerated storage are given in Table 3.

Franklin et al.[35] measured a variety of chemical markers, consumer hedonic response, and headspace volatiles using headspace solid phase microextraction (HS-SPME) and GC/MS in roasted almonds during 12 months of storage under conditions (39 °C, 15% RH) that promote rancidity development. HS-SPME GC/MS is an excellent method for evaluating volatile compounds in the headspace; however, investigators must remain aware of the various affinities for the fiber and competing equilibria of analytes among the sample, the headspace above the sample, and the fiber. Volatile products of oleic and linoleic acid decomposition were found to increase over the storage period. In addition, acetic, hexanoic, and pentanoic acids, organic acids previously identified as possible tertiary products of lipid oxidation,[5] were identified in the almond headspace. Regression of consumer liking to concentration of rancidity indicators revealed that heptanal, octanal, nonanal, 2-octenal, 2-heptanone, 2-pentylfuran, hexanal, and pentanal correlated strongly with negative consumer liking.

## RANCIDITY IN ALMONDS

**Chemical Tests.** Due to the pronounced flavor changes and resulting threat that lipid oxidation poses to the quality and value of food products, several chemical methods have been established to assess the progress of lipid oxidation in foods with the goal of indicating product quality and shelf life.[51] These methods tend to quantify primary and secondary species generated during different phases of lipid oxidation. For instance, peroxide value (PV) quantifies the molar concentration of lipid peroxides (as mequiv [peroxide]/kg oil),[52] iodine value (IV) assesses the degree of lipid unsaturation,[53] *p*-anisidine value (AV) assesses the concentration of 2-alkenals,[54] while conjugated dienes or trienes assess the degree of double-bond rearrangement co-occurring with the peroxidation of linoleic or linolenic acid, respectively.[54] Free fatty acid value (FFA) does not assess primary lipid oxidation products but rather quantifies the degree to which hydrolysis has degraded triglycerides, a measure of hydrolytic rancidity.[55] These methods have the advantage of not requiring expensive analytical instruments and being widely used throughout the food industry, and there are often established *acceptable values* for these oxidation indicators specific to each food product and analysis. For instance, the established limits for PV and FFA in almonds are <5 mequiv/kg oil and <1.5% oleic, respectively.[56]

Several studies have applied these chemical tests for rancidity to examine the effect of either processing or storage conditions on the stability of almond lipids during storage.[29,52,54,57,58] For example, Lin et al.[53] used changes in the PV, FFA, IV, and lipase activity to compare the effect of various temperature (4.4−37.8 °C) and humidity (35−95% RH) conditions on the progress of oxidation in blanched and raw almonds, stored under conditions typical for almond transport. The PVs in raw almonds remained at a concentration below 3 mequiv/kg oil under all conditions tested for the entire storage period (250−500 days), while blanched almonds stored at 21 °C or higher exceeded these levels between 60 and 200 days of storage, depending on temperature and humidity conditions. Garcia-Pascual et al.[57] also examined PV levels, in addition to $\alpha$-tocopherol, moisture, and fat content and aflatoxin concentration, in four varieties of almonds to study the effect of temperature (8 vs 36 °C), processing (roasted vs raw), and packaging atmosphere ($N_2$ vs air) on lipid oxidation during 9 months of storage. The effect of packaging conditions on almonds also was examined by Severini et al.,[58] who hypothesized that addition of Maillard reaction volatile compounds (MRVc) generated during roasting to the packaging atmosphere would delay oxidative changes, thus prolonging shelf life. To analyze the difference in oxidative changes during storage in two varieties of either peeled or unpeeled almonds packaged under vacuum, with air, or with natural MRVc atmosphere, this group examined PV and oxidized triglycerides. Buransompob et al.[55] used PV in addition to FFA, thiobarbituric acid value (a method to detect malondialdehyde), and AV to examine the effect of short-time heat disinfestation treatments on lipid stability of almonds and walnuts during accelerated storage.

**Sensory and Chemical Characterization of Oxidative Changes.** Analysis methods such as PV, FFA, IV, and AV allow experimental treatments to be compared in their tendency to delay or accelerate the production of primary or secondary lipid oxidation products. However, analyzing chemical parameters alone will not determine sample shelf life. The shelf life of dry food products such as almonds, for which microbiological or structural changes are not a common problem, is dependent on the length of time the product retains sensory integrity.[59] The sensory integrity of almonds is related to the onset of rancidity, as defined by human perception of negative flavor changes. Sensory testing is the only analysis method that can detect and confirm these changes and thus what the proper shelf life is.[14]

To supplement the information provided by chemical oxidation analyses and better define sample shelf life, several groups have applied sensory testing in combination with chemical analysis to evaluate the effect of storage and packaging, or processing conditions on almond shelf life.[27,31,35,41,49,60−65] Most of these studies employed either triangle testing (a sensory test to determine whether a statistically significant sensory difference exists between samples) or some variation of hedonic analysis (in which panelists most frequently use an anchored or unanchored nine-point scale to rate overall liking or liking of a specific food attribute). These tests can be used to reveal when there is a significant sensory difference between samples and a control or when during storage there is a significant change in liking of samples, which might indicate the onset of rancidity.

One of the earliest studies applying this approach was undertaken by Harris et al.,[49] who applied triangle testing and consumer hedonic analysis in combination with FFA, IV, and headspace oxygen concentration to assess the effect of different storage temperatures (−17.8 and 37.8 °C) and confectionary treatments on the shelf life of diced almonds. More recent studies involving almond shelf life as indicated by hedonic analysis have focused mainly on the influence of packaging in extending shelf life. For instance, Senesi et al.[64] tested the effect of two types of packaging films, packaging atmosphere (vacuum vs $N_2$), and storage temperature (4 or 20 °C) on PV, FFA, fatty acid methyl ester composition (FAME), tocopherol concentration, water activity, color, and texture as well as hedonic ratings of peeled almonds during up to 546 days of storage. Similarly, the effect of two packaging types, atmosphere ($N_2$ vs oxygen absorber), lighting (fluorescent vs no light), and temperature conditions (4 or 20 °C) on PV,


DOI: 10.1021/acs.jafc.8b06606
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FAME, hexanal, and other headspace volatile concentrations and hedonic scores of raw ground and whole almonds during 12 months of storage were observed by Mexis and co-workers.[27,31] Raisi et al.[62] also examined the effect of packaging and storage conditions (unpackaged vs packaged under vacuum or 95% $CO_2$; 4 or 23 °C) on PV and conjugated trienes as well as consumer hedonic scores in whole and ground raw almonds. Similar shelf life studies of roasted almonds have been carried out, testing the effect of packaging material on PV, oxidized triglycerides, and preference scores of roasted peeled and unpeeled almonds stored in the dark for 8 months at 25 °C[65] and testing packaging atmosphere ($N_2$ vs air) on PV, conjugated dienes and trienes, FAME, and almond composition as well as hedonic scores of sample "quality" for peeled and roasted Guara variety almonds stored at 20 °C and 65−70% RH for 5 months.[41]

There is no widely agreed upon rule for determining which consumer hedonic rating indicates rancidity or the end of shelf life in almonds. However, some groups have the general rule that scores below a "neither like nor dislike" or neutral hedonic anchor indicate the end of product shelf life.[27,35] By this rule, previous studies on almond shelf life do not show uniformity in levels of oxidation indicators at the end of shelf life. For example, Mexis and Kontominas[27] found that, for raw, unpeeled almond samples stored in plastic under $N_2$ at 20 °C, the PV was between 6 and 7 mequiv/kg oil when the hedonic ratings decreased below a neutral point (8−10 months of storage). In contrast, Raisi et al.[62] found that, for ground and whole raw almond kernels stored in polypropylene packaging at 23 °C for 8−10 months, consumer ratings were below a neutral point and PVs were only 2.54−3.41 mequiv/kg oil. Furthermore, Senesi et al.[64] found that for peeled, raw almonds stored in clear plastic and metalized packaging at 20 °C under vacuum or nitrogen, sample PVs were only 0.84−1.32 mequiv/kg oil when consumer hedonic ratings decreased below a neutral score (5), while FFA values ranged from 4.09 to 6.70% oleic. The results were inconsistent with those of Harris et al.,[49] who found that FFA values were only 0.3−0.4% oleic when hedonic ratings were below 5 for samples of diced, roasted almonds stored at 37.8 °C for 3 months. Also, Franklin et al.[35] reported that average consumer hedonic ratings ($n$ = 99) of light and dark roasted almonds fell below the designated acceptable score of 5 ("neither like nor dislike") by 6 months of storage under accelerated conditions (39 °C, 15% RH), at which point the PVs were 2.84 ± 0.02 and 11.36 ± 0.23 mequiv/kg oil for the light and dark roasted almonds, respectively. Yet the corresponding FFA values for both types of almonds at 6 months storage were below 0.4% oleic. Furthermore, FFA values remained well below the industry rejection standard of <1.5% oleic throughout the 12-month storage study and thus are not a good marker of rancidity in roasted almonds stored in low-humidity environments.[35] These findings indicate that certain currently employed indicators of oxidation may not effectively correlate with consumer liking in almonds, and further work is needed to compare oxidative indicators in their ability to predict rancidity. For example, results of regression analysis by Franklin and co-workers between consumer liking and concentration of rancidity indicators revealed that selected headspace volatiles correlate better with consumer liking than do nonvolatile indicators such as PV and FFAs.[35,61]

Triangle testing and hedonic analysis can each provide answers about overall sensory differences or differences along a single, predetermined flavor dimension (i.e., bitterness, roasted flavor, rancid flavor), but these tests do not generally provide information on all of the sample flavor dimensions possibly detected during tasting.[14] This can present a problem when the experimenter assumes that a significant sensory difference in samples is due to rancid flavor, whereas the actual sample difference is due to another untested factor such as texture or appearance. Other problems can occur during difference and hedonic testing when an untrained panelist confuses one investigated flavor attribute for another (e.g., bitterness and astringency), or "dumps" their perception of an attribute not investigated (e.g., bitterness due to roasting) into their rating for an investigated attribute (rancidity flavor), which changes their final score of the investigated attribute. To avoid these issues, descriptive analysis may be employed.

By employing trained panelists and assessing the entire set of flavor and texture attributes perceived in a sample, descriptive analysis avoids the problems of attribute "dumping" or confusion. Dumping occurs when a sample differs in multiple attributes but the panelists are only asked to rate one attribute. In this situation, the panelist tends to subconsciously inflate or deflate the perceived intensity of the rated attribute to compensate for the other attributes differing in the sample.[66] In combination with hedonic or difference testing, descriptive analysis can answer the question of which specific sensory attribute is contributing to changes in sample liking and whether a sample is disliked due to rancidity or another unexpected change in flavor. Descriptive analysis has not been widely applied in studies of stored or oxidized almonds but was applied by Larrauri et al.[67] to study the effects of various carboxymethyl cellulose coatings on the oxidation and resulting flavor attributes of almonds during storage. Various chemical oxidation tests were employed in the study in combination with descriptive analysis, including PV, conjugated dienes, FAME, and headspace volatile analysis (only hexanal and nonanal are described). Oxidized and cardboard flavors were the only attributes found to significantly increase over storage, and the use of carboxymethyl cellulose coatings significantly reduced the increase of oxidized flavor in comparison with uncoated samples. This study provides insight into specific sensory changes in almonds during storage but does not provide enough information to explain all the flavor changes chemically, as most of the analyses involved primary products of lipid oxidation with no odor activity, and headspace volatile concentrations apart from hexanal and nonanal were not described.

Application of headspace volatile profiling, in which concentrations of all reliably detected headspace volatiles are analyzed, is limited for almonds undergoing lipid oxidation.[5,27,29,31,35] Headspace volatile profiling is often applied to food products in combination with descriptive analysis to provide insight into the possible volatile compounds responsible for flavor or aroma attributes. For example, this approach has been taken with wine,[68−70] dried whey protein concentrate,[71] peanuts,[72,73] and coffee.[74] As descriptive analysis requires specific tasting facilities, panel training, and standards, it is impractical to employ in routine quality assurance programs.[14] However, performing descriptive analysis in combination with headspace volatile analysis during storage of almond samples might provide volatile indicators of important flavor attributes, which are more easily assessed in routine testing of almonds than are sensory attributes. The simultaneous analysis of consumer hedonic ratings would


DOI: 10.1021/acs.jafc.8b06606
J. Agric. Food Chem. 2019, 67, 2743−2753

qualify chemical changes and descriptive attribute changes in almonds in terms of how much chemical change is necessary to elicit reduced consumer liking and which chemical or taste attributes are most related to changes in consumer ratings.

A recent study by our group combined general descriptive analysis, headspace volatile profiling, and consumer hedonic assessment to evaluate the flavor and acceptance of light or dark roasted Nonpareil almonds during accelerated storage at 39 °C for 0 to 12 months.[61] Predictive relationships were developed upon analysis of the descriptive sensory profiles, volatile profiles, and consumer hedonic scores. A number of volatile predictors of consumer liking also were identified, including the Maillard reaction products 2- and 3-methylbutanal and 2,5-dimethylpyrazine, which were predictors of the descriptive attributes "clean roasted" and "clean nutty". Lipid oxidation products, including pentanal, hexanal, heptanal, and octanal, were found to be most important for predicting rancidity-related attributes in the roasted almonds. Hexanal, the traditional rancidity marker in foods, was the most important predictor of "total oxidized" aroma. Interestingly, heptanal and octanal were better predictors of average consumer liking than hexanal and thus may be more reliable indicators of how consumers perceive rancidity in roasted and stored almonds.

Future studies should focus on identifying the optimal indicator of lipid oxidation to monitor quality in almonds reliably in a processing facility without reliance upon sophisticated equipment. This will be a compound that is easy to detect in the almond headspace, for which standards are widely available, and a compound for which there is a large change in concentration per unit change in degree of liking. This will allow for changes in concentration to be detected across a range of method precision and sensitivity and may be amenable to Enose or other portable detection devices. The ultimate goal will be to monitor quality in real time to allow for a more efficient use of almond product streams.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors wish to acknowledge and thank Sylvia Yada for her editorial assistance.

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