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# Flavor and Acceptance of Roasted California Almonds During Accelerated Storage

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Supporting Information

**ABSTRACT:** Monitoring oxidative flavor changes in almonds is possible only if the chemical and sensory profile during roasting and storage is first established. Herein, almonds roasted at two different temperatures (115 and 152 °C) were stored at 39 °C for 0 to 12 months and were analyzed by headspace solid-phase microextraction gas chromatography−mass spectrometry, descriptive analysis, and consumer hedonic analysis. Volatile profiles, descriptive sensory profiles, and consumer hedonic scores were analyzed for predictive relationships. Descriptive attributes involving Roasted and Nutty as well as consumer liking were highest in fresh almonds, while flavors typically associated with oxidative rancidity such as Cardboard, Painty/Solvent, Soapy, and Total Oxidized increased during storage. Compounds most important for predicting rancidity-related attributes were lipid oxidation products, including pentanal, hexanal, heptanal, and octanal. Consumer liking was best predicted by similar compounds to those predicting Clean Nutty flavor, including Maillard reaction products such as 2- and 3-methylbutanal, 2-methylpyrazine, and 2,5-dimethylpyrazine.

**KEYWORDS:** *almond, Prunus dulcis, HS-SPME GC/MS, descriptive analysis, partial least-squares analysis*

## INTRODUCTION

As the most heavily produced and consumed tree nut worldwide,[1] sweet almonds (*Prunus dulcis*) represent a valuable agricultural commodity to California, which produces 80% of the world almond supply.[2] Almonds possess a number of beneficial nutritional and eating qualities, including high levels of monounsaturated fatty acids, vitamin E, fiber, and protein, as well as a relatively long shelf life.[3] Demand for almonds continues to grow worldwide,[4] and California almond products are increasingly shipped over longer distances and stored for extended periods of time under variable conditions, making it more important for producers and processors to monitor the flavor of almonds to ensure that the quality and value of exports and products are preserved.

To maintain the quality of almonds products, almond flavor must first be established and understood from a chemical and sensory standpoint. Flavor is perceived through a combined sensation of ortho- and retronasal detection of volatile compounds and stimulation of taste receptors in mouth during mastication.[5] Almond volatiles are derived from the raw almond and the various conditions that the almonds are exposed to, either directly or indirectly. During harvesting and shelling, almond nutmeats may be exposed to sunlight, heat, ambient humidity, metal ions, and atmospheric oxygen, all of which can elicit changes in almond volatiles by promoting oxidative degradation of almond lipids.[6] Further processing (e.g., roasting) can involve heating almonds to create flavor or texture changes. During roasting, food temperature can exceed 100 °C, promoting Maillard reactions that can result in the production of volatile heterocycles such as pyrazines, furans, pyrans, pyrroles, and pyridines, as well as some small Strecker aldehydes, ketones, and sulfides/thiols.[7−9] Secondary volatile products from oxidation of fatty acids may also be produced during roasting, and interactions and reactions of these compounds may further alter volatile profiles.[10] Measuring food volatiles can give insight into flavor and benchmarks for determining flavor change. Almond volatile profiles have been previously assessed in raw[8,11−14] and roasted almonds.[8,9,13−17]

Although measuring almond volatiles can offer understanding into the flavor changes occurring due to lipid oxidation and nonenzymatic browning, they may not necessarily correlate with flavor as it is perceived by humans. Therefore, descriptive analysis is frequently used to identify and measure specific flavor and texture attributes in food products using trained panelists. Descriptive analysis has been applied to almonds to study the variability in almond varieties grown in California,[18] the effects of irradiation on flavor,[19,20] the effects of almond coating on oxidative rancidity,[21] and the effects of toasting/roasting on flavor and texture.[22,23] Though descriptive analysis is useful for directly assessing human perception of food products, it is a time- and resource-intensive analysis and may

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not be practical for routine quality control. Combining descriptive analysis with volatile profile analysis may reveal volatile drivers of flavor attributes, which can then be used in place of descriptive analysis to indicate flavor changes in almonds. Of the aforementioned applications of descriptive analysis to almonds, only Larrauri et al.[21] measured volatile compounds in almond samples, though volatile measurements were limited to hexanal and nonanal.

Possibly even more important to almond processors than assessing almond flavor is measuring consumer acceptance of almonds and almond products. Though a number of studies have included some type of consumer evaluation of stored raw[24−28] and roasted[29−31] almonds, none of the existing studies include consumer liking, descriptive analysis, or volatile analysis of the same sample set. Measuring consumer acceptance in conjunction with descriptive analysis and headspace volatiles may identify the most important flavor attributes and volatile compounds driving consumer liking or disliking. However, as volatile compounds correlated with consumer liking are not necessarily responsible for certain sensory attributes (e.g., Clean Nutty flavor), addition or omission experiments still need to be conducted to prove causative relationships.

Herein, California Nonpareil almonds were dry-roasted at two different temperatures and stored under accelerated aging conditions for up to 12 months to assess changes typical to the entire shelf life of almonds.[32] Samples were assessed by descriptive analysis, volatile profiling by headspace solid-phase microextraction gas chromatography−mass spectrometry (HS-SPME-GC/MS), and consumer acceptance. The goals of this study were to identify changes in sensory attributes throughout accelerated storage, identify compounds related to sensory attributes, and assess which of these are most related to consumer liking. To our knowledge, this is the first study to combine general descriptive analysis, headspace volatile profiling, and consumer hedonic assessment in almonds.

## MATERIALS AND METHODS

**Chemicals and Reagents.** Stable isotope standards of octanal-$d_{16}$, 2-methylpyrazine-$d_6$, and *n*-hexyl-$d_{13}$ alcohol, representing three main categories of identified compounds (aldehydes, pyrazines, and alcohols), were purchased from C/D/N Isotopes Inc. (Pointe-Claire, QC, Canada). Authentic standards of 2-methylpropanal (97+%), butanal (97+%), 3-methylbutanal (97+%), hexanal (99%), heptanal (95%), (*E*)-2-hexanal (98%), octanal (99%), 1-chloro-2-propanol (70%), 2,5-dimethylpyrazine (98%), nonanal (95%), furfural (98+%), 2-acetylpyrrole (99%), 2-furanmethanol (99%), methyl acetate (99.9%), 2-pentanone (98+%), pentanal (99%), dimethyl disulfide (99+%), 2-methyl-1-propanol (99+%), 2-heptanone (98%), methyl hexanoate (99.8+%), 2-nonanone (99.5+%), decanal (95+%), 4-hydroxy-2,5-dimethylfuran-3-one (99+%), 1-nonanol (98+%), heptanoic acid (99+%), α-pinene (98%), and octanoic acid (99+%) were obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI, United States). Authentic standards of 2-butylfuran (98%), 2,3-butanediol (97+%), 2-methylpyrazine (99%), (*E*)-2-octenal (94%), acetic acid (99+%), benzaldehyde (99+%), 2-methylbutanal (95+%), 3-methyl-1-butanol (98+%), 1-pentanol (99+%), 2-octanone (99+%), 1-heptanol (99+%), 1-octen-3-ol (98+%), (*E*)-2-nonenal (95+%), 1-hexanol (99+%), 1-*H*-pyrrole (98%), 1-octanol (99+%), butanoic acid (99+%), 3-methylbutanoic acid (98+%), and nonanoic acid (99+%), were obtained from Sigma-Aldrich (St. Louis, MO, United States). Standards of hexanoic acid (98%), 1-butanol (99%), and ethyl 2-(methylthio)-acetate (95%) were obtained from Acros Organics (Thermo Fisher Scientific Inc., Waltham, MA, United States). Solvents, including HPLC/spectrophotometric ethanol and methanol, were purchased from Fisher Scientific Company (Fairlawn, NJ, United States) or Sigma-Aldrich Chemical Co. Standard of 2-(ethylthio)-ethanol (96%) was purchased from Alfa Aesar (Ward Hill, MA, United States), and 3-hydroxybutan-2-one was purchased from Supelco (Bellefonte, PA, United States).

**Accelerated Storage.** A 200 kg sample of dehulled, raw, 23/25 Nonpareil almond (*Prunus dulcis* "Nonpareil") kernels with skin (from the 2014 harvest year) were obtained from Blue Diamond Growers (Sacramento, CA). Almonds were dry roasted in a BCO-E1 electric convection (Bakers Pride, Allen, TX) under two different conditions: 115 ± 6 °C for 60 min and 152 ± 6 °C for 15 min to achieve a light degree of roast (LR) and dark degree of roast (DR), respectively. After, roasting almonds were cooled and vacuum-flushed with nitrogen in mylar foil laminated-type packages for transport to a controlled atmosphere chamber (KMF 240 Constant Climate Chamber by Binder Inc. Bohemia, NY). The batches of LR and DR almonds were then divided into 460 g lots and stored in open brown paper bags. Samples were stored at 15 ± 1% relative humidity and 39 ± 1 °C for intervals of 1−12 months to mimic accelerated storage conditions. Eight brown paper bags of LR and DR almonds each (previously designated to the current time point through random assignment) were withdrawn from the chamber every month, mixed thoroughly, and repackaged into polyethylene vacuum sealed packages, which were then stored at −80 °C (Revco Inc. Trumbull, CT) until further analyzed. For comparison, the control samples were repacked and stored at −80 °C immediately after roasting with no accelerated storage. HS-SPME-GC/MS of almond samples was performed within 2 weeks of sample storage at −80 °C. Descriptive and hedonic sensory analyses of almond samples were performed after all almond samples had completed accelerated aging after no more than 10 months of storage at 39 ± 1 °C.

## SENSORY ANALYSIS

**Sample Selection for Descriptive and Hedonic Analysis.** The fatiguing nature and breadth of the entire sample set necessitated the creation of a sample subset for sensory testing. To select samples for this subset, the entire sample set of 13 storage times for each roast level was evaluated in a benchtop tasting by 3 authors of the paper. A subset of 6 samples of each roast level (12 samples in total) was chosen by verbal consensus, consisting of 0 (control), 2, 4, 6, 8, and 10 month-old samples stored at accelerated temperatures. These storage times were chosen to best represent the sensory changes in the almond samples during storage while avoiding samples that were offensively oxidized.

**Quantitative Descriptive Analysis.** Ten panelists were recruited from a large group of experienced assessors, employed by Covance Laboratories, Inc. (Livermore, California) for sensory analysis. Panelists were trained during one 2-h session, in which they evaluated all 12 of the aforementioned samples and discussed product aroma, taste, and texture attributes. During this time, panelists also reviewed product attribute references, attribute term definitions, and evaluation methodology (attribute definitions given in Table 1S).

Panelists evaluated 9 samples in a 2-h period, including a 15 min break after the first 5 samples. Samples were evaluated 3 times (replicates) for a total of 30 observations of each sample. All samples were served in 5 oz soufflé cups with lids labeled with randomly generated 3-digit numbers. Each 3-digit coded sample was presented as a pair, with a labeled control sample. Panelists used a degree of difference scale to indicate how different each of the blinded samples were from the labeled control sample on an overall basis using a 15-point linescale anchored with 0 (no difference) to 15 (extremely different).

Samples were assessed monadically and sequentially in a balanced William's Latin Square design within each roast level. Panelists assessed all light roast samples before dark roast samples. Panelists were instructed to expectorate after tasting and score the intensity of each attribute. Panelists evaluated the samples in individually partitioned booths with controlled ventilation and lighting. Ambient purified drinking water, toothpicks, and unsalted crackers were provided for palate cleansing. Data were collected using Sensory Information Management System, Version 6.0, 2016.


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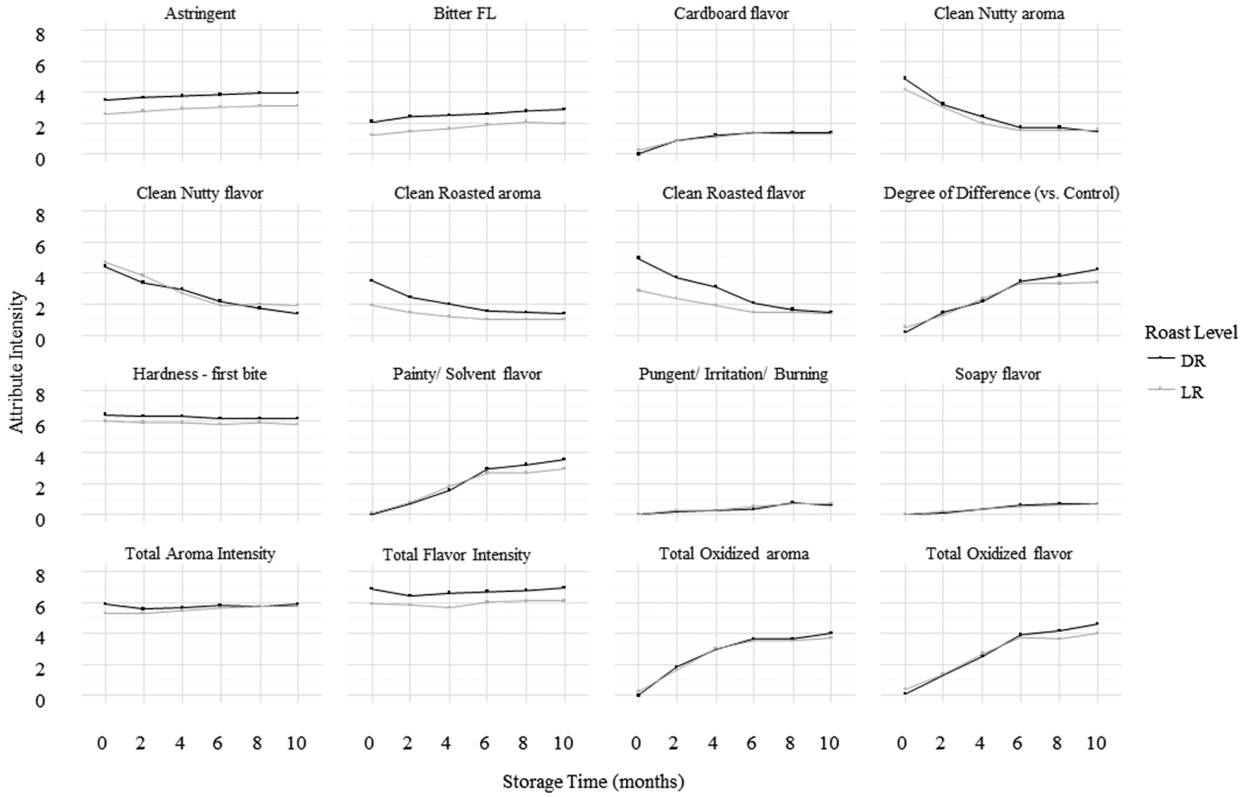


**Figure 1.** Descriptive attribute intensity over time in DR (black) and LR (gray) almonds. Average liking over storage time for each consumer group, along with percentage of consumers in each group. DR samples are depicted in black, and LR samples are depicted in gray.

**Consumer Hedonic Analysis.** The method applied was identical to that of Franklin et al.[33] Briefly, 99 untrained consumers between the ages of 14 and 80, who were not pregnant and consumed almonds at least once a month, were recruited for hedonic analysis. Consumers were served samples of six or seven almonds at room temperature. Consumers were asked to taste two almonds at a time and indicate their liking of samples by marking a 9-pt hedonic scale. Consumers tasted samples in a random and counterbalanced order to minimize carry-over effects.

**Volatile Analysis.** HS-SPME-GC/MS detection of headspace volatiles was performed according to the procedure of Franklin et al.[33] Briefly, almonds were ground and sieved with a size 20 Tyler sieve (W.S. Tyler, Mentor, OH), and a 5 ± 0.02 g sample was weighed into a 20 mL glass headspace vials (Restek, Bellefonte, PA). Vials were capped and crimped with caps containing 3 mm-thick PTFE-lined silicone septa (Supelco, Bellefonte, PA) and allowed to equilibrate for at least 4 h. Sample handling and GC were performed using an Agilent 7890A (Santa Clara, CA) equipped with a CTC Combi/PAL autosampler (Zwingen, Switzerland). Samples were agitated at 500 rpm and pre-equilibrated at 40 °C for 45 min, after which they were extracted with a 1 cm 30/50um StableFlex divinylbenzene/carboxen/polydimethylsiloxane fiber at a depth of 29 mm for 45 min at 250 rpm. After extraction, the fiber was desorbed in a splitless injection at 250 °C for 0.9 min, at which time the split vent was opened at a 50:1 split for a total injection time of 10 min. The headspace volatiles were separated using a 30 m × 0.25 mm × 0.25 μm Agilent DB-Wax column (Santa Clara, CA) with a helium flow rate of 1.2 mL/min at 35 °C for 1 min then a ramp of 3 °C/min until 65 °C was attained, followed by a ramp of 6 °C/min to 180 °C, and finally 30 °C/min to 250 °C, which was held for 5 min. Quantitative data used for multivariate statistics consists of normalized headspace compound peak areas.

Mass spectrometric detection was performed by an Agilent 5975C inert XL EI/CI MSD (Santa Clara, CA) with a source temperature of 230 °C, quadrupole temperature of 150 °C, and electron energy of −70 eV. Volatile profiling was performed using a scan method in the range of 30−300 $m/z$. Tentative volatile identification in the resulting total ion chromatogram was performed using the NIST Mass Spectral Search Program (v. 2.2). Identifications were confirmed using retention index calculation and comparison with reference values (Kovat's Index), and retention time confirmation with standards when available. Integration was performed using Agilent MassHunter Quantitative Analysis software (v. B.07.00).

**Data Analysis.** Results from all measurements were analyzed using a two-way analysis of variance (ANOVA) with interactions and, when appropriate, a two-way multivariate analysis of variance (MANOVA) with interactions, testing roast level, and sample storage time as main effects. Where appropriate, a Bonferroni correction was made to the $p$-value to adjust for multiple iterations of ANOVA, and main effects were retested against significant interactions to confirm significance. When significant main effects were found, Tukey's honestly significant difference posthoc testing was performed to identify samples that significantly differed at 95% confidence level ($p < 0.05$).

Multivariate statistical analysis, including hierarchical clustering, partial least-squares (PLS) analysis, and variable sorting were performed on the centered and scaled data sets using the hclust function (R base), the rpe_pls function of the plsVarSel package,[34] and the plsr function of the pls package[35] in R, respectively.[36]

## RESULTS AND DISCUSSION

**Descriptive Analysis.** Descriptive analysis involving 16 attributes was performed on LR and DR almond samples stored at 39 °C for 0 (control), 2, 4, 6, 8, and 10 months. Almonds were not evaluated past 10 months as they were offensively rancid. The descriptive analysis mean data for the LR and DR almonds is presented in Supporting Information (see Table 2S). Eight out of 16 attributes were significantly different across roast level. Total Aroma Intensity, Clean Nutty Aroma, Clean Roasted Aroma, Hardness-first bite, Total Flavor Intensity,


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Clean Roasted Flavor, Bitter, and Astringent were significantly higher in the DR samples as compared to the LR samples.

All of the 16 descriptive attributes except Hardness-First Bite were significantly different across storage time. Most flavor attributes either increased or decreased with time (Figure 1). Intensity of Clean Nutty aroma and Clean Nutty flavor (correlation value with respect to time ($r_T$): −0.89 and −0.95, respectively) and Clean Roasted aroma and flavor ($r_T$: −0.71 and −0.80, respectively) decreased with storage in both LR and DR almonds (Figure 1). Attributes that increased in intensity over time were Total Oxidized aroma and Total Oxidized flavor ($r_T$: 0.91 and 0.95, respectively), as well as the oxidation-specific flavor attributes Cardboard ($r_T$ 0.86), Painty/Solvent ($r_T$ 0.96), and Soapy ($r_T$ 0.98). The mouthfeel attributes Pungent/Irritation/Burning ($r_T$ 0.94) and Astringent ($r_T$ 0.36) also increased over time, to a lesser extent (Figure 1). All attributes that were significantly different across time changed significantly in intensity from the control by 2 months of aging, with the exception of Hardness, Soapy, Pungent/Irritation/Burning, Total Aroma Intensity, and Total Flavor Intensity (all attribute intensities correlated significantly with time ($p < 0.05$) except Total Flavor Intensity) in LR samples, and Hardness and Astringent in DR samples.

These sensory attributes are characteristics in oxidized products and have been measured in other samples undergoing aging.[21,37,38] Larrauri et al. performed descriptive analysis on uncoated and coated almonds to test the effect of antioxidant-supplemented carboxymethylcellulose coating on the development of rancidity in roasted almonds stored in polypropylene at 40 °C.[21] Similar to our findings, they found that Cardboard and Oxidized flavor increased significantly over the 126-day storage period.[37] Grosso and Resurreccion used descriptive analysis, consumer hedonic analysis, and hexanal measurements to assess flavor changes in cracker-coated and roasted peanuts under accelerated aging conditions for 110 days.[37] Similar to our results, this group found that Astringency, Burning ("Tongue sting"), Painty, Oxidized, and Cardboard flavor attributes increased significantly in peanut samples over 66 days of storage, while "roasted" aroma ("Roasted peanuty") decreased significantly in the same interval.[12,26]

**Consumer Hedonic Analysis.** Hedonic ratings of LR and DR samples (Table 1) indicate that accelerated storage time had a significant effect on average consumer liking, while sample roast level did not. The average liking scores were highest at time 0 (7.2 and 7.4 for DR and LR, respectively) and decreased sequentially over time, reaching a low of 4.2 and 4.7 for DR and LR, respectively. A decrease in liking over accelerated storage was previously reported.[33] On average, consumers had a significant difference in liking between samples stored for 0, 2, 4, and 6 months, while there was no significant difference found between samples stored for 6, 8, and 10 months (Table 1). This initial period of significant change (0−4 months) and plateau (6−10 months) was similar to descriptive analysis results for LR almonds across Clean Nutty aroma and Clean Nutty flavor, Total Oxidized aroma and Total Oxidized flavor, and Painty/Solvent flavor. Similar trends were observed in DR almonds, though attribute intensities plateaued at 8 months. Results demonstrate that oxidation-related aromas and flavors increase and peak around 6−8 months of storage, while roasted and nutty flavors decrease and plateau around the same time, at which point consumer liking scores decrease to below 5.0 on average.

Hierarchical clustering revealed three distinct clusters of like-minded consumers, representing 24, 55, and 21% of consumers (Table 2). Average liking of each cluster was found to be significantly different employing MANOVA, and average liking scores for each sample within each cluster were analyzed for the effects of roast level (LR vs DR) and time under accelerated storage. For clusters 1 and 2, only storage time had a significant effect, while scores for cluster 3 were significant for the interaction of storage time and roast. All of the clusters demonstrate a decrease in liking over the storage time of the roasted almonds (Figure 2).

For cluster 1 (24% consumers), average product scores were highest overall, with the only significant difference in liking found between the 0 month samples and samples stored for 6 months (Table 2, Figure 2). Cluster 2 (55% consumers) included the majority of consumers, who were on average more sensitive to differences in almonds due to storage, as liking scores decreased significantly after 2 months of accelerated storage. For cluster 3 (21% consumers), a significant decrease in liking for LR samples could be seen by 4 months of storage, but for DR samples, liking did not significantly decrease until 6 months of storage (Table 2).

**Partial Least Squares Multivariate Analysis.** The relationship between descriptive attributes, consumer preference, and headspace volatiles was evaluated using PLS analysis. PLS was chosen to inter-relate data sets because it is well-suited to situations with few observations and many correlated independent variables, as was the case with our data set.[39] In addition, our focus was on explaining the perceived sensory changes in almonds with changes in headspace volatiles, and PLS optimizes a solution to best explain the variation in both response $y$ variables (descriptive analysis attributes, consumer

**Table 1. Means of Consumer Hedonic Testing[a]**

| | time in accelerated storage (months) | | | | | |
|---|---|---|---|---|---|---|
| sample type | 0 | 2 | 4 | 6 | 8 | 10 |
| dark roast | 7.2 a | 6.8 b | 5.8 c | 4.7 d | 4.5 d | 4.2 d |
| light roast | 7.4 a | 6.6 b | 5.8 c | 4.9 d | 4.9 d | 4.7 d |

[a]Means followed by the same letter were not found significantly different by Tukey's HSD post-hoc testing ($p < 0.05$).

**Table 2. Mean Liking for Each Consumer Group[a]**

| | | | time in accelerated storage (months) | | | | | |
|---|---|---|---|---|---|---|---|---|
| grouping | number of consumers | roast level | 0 | 2 | 4 | 6 | 8 | 10 |
| cluster 1 | 24 | | 7.42 a | 7.08 a | 6.69 ab | 6.23 b | 6.73 ab | 6.79 ab |
| cluster 2 | 54 | | 6.95 a | 6.32 b | 5.17 c | 3.77 d | 3.77 d | 3.29 d |
| cluster 3 | 21 | light roast | 8.10 a | 7.62 ab | 5.81 cd | 6.57 bc | 5.67 cd | 5.10 d |
| | | dark roast | 7.90 a | 6.90 a | 6.95 a | 5.10 b | 3.81 c | 4.14 bc |

[a]Values in the same row followed by the same letter were not found to be significantly different by Tukey's HSD post-hoc testing ($p < 0.05$).



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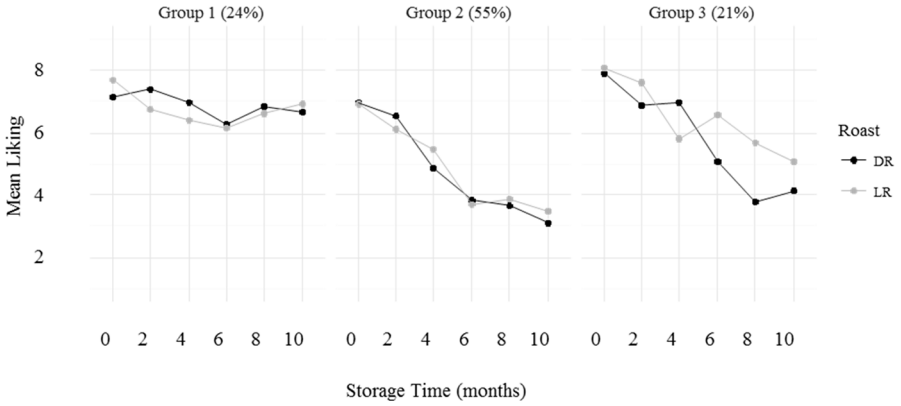


**Figure 2.** Mean liking for each consumer group. Values in the same row followed by the same letter were not found to be significantly different by Tukey's HSD posthoc testing ($p < 0.05$).

scores) by the variation in predictor $x$ variables (headspace volatiles). PLS2 indicates that the predicted matrix is multivariate, while PLS1 describes the modeling of one response variable with all predictor variables.[40]

**Variable Selection for Dimension Reduction of Headspace Volatile Data Set.** Ninety-two compounds were either tentatively identified or confirmed with standards in almond samples over the 12 months of accelerated storage[3,41] (Tables 3S and 4S). The highly dimensional headspace volatile data set (predictors) was filtered using PLS1 to make visual and conceptual interpretation easier and focus attention on only the headspace compounds most related to the descriptive attributes.[33,42]

The most important volatiles for each individual attribute were compiled and used as a selected variable data set for further analysis (indicated in bold typeface in Table 3). This filtered data set included five organic acids, eight alcohols, ten aldehydes, one ester, five ketones, two alkylfurans, two heterocycles, one lactone, three sulfur-containing compounds, and four pyrazines. Of these compounds, 30 were previously identified in studies assessing almond volatile compounds.[9,13,14,17,43]

Several of the filtered compounds likely originate from Maillard reactions and pyrolysis taking place in almonds during heat-treatment, including Strecker aldehydes 2-methylbutanal, 3-methylbutanal, and 2-methylpropanal, alkylpyrazines like 2,3,5-trimethylpyrazine, 2-methylpyrazine, 2,5- and 2,6-dimethylpyrazine, heterocycles like furfural and 1-*H*-pyrrole, and Maillard reaction products 2,3-pentanedione, acetoin, acetone, and dimethyl disulfide. Strecker aldehydes are released after the condensation of an amino acid and an $\alpha$-dicarbonyl during Maillard reactions, forming the precursors of alkylpyrazines.[7] Strecker aldehydes 2- and 3-methylbutanal have very low odor thresholds in oil (0.01 and 0.0054 mg/kg, respectively) and were previously found above threshold concentrations in heat-treated Butte/Padre,[14] Nonpareil,[43] and fried Spanish almonds.[7] Furans can be formed during roasting by pyrolysis of monosaccharides or Maillard reactions and generally contribute aromas like caramel, bread, sweet/fruity, and nutty,[44] while pyrroles contribute nutty, popcorn, and burnt aromas.[39] Alkylpyrazines are common Maillard reaction products that lend nutty, roasted, cocoa, and peanut aromas to foods.[9] In addition to furans and pyrroles, pyrazines are considered important flavor compounds to toasted almonds.[46] Dimethyl disulfide is a product of Maillard reactions involving methionine.[44,46] This compound can possess a garlic or cabbage aroma, but at low concentrations and in combination with other potent odorants, may add important savory or roasted notes.[41,47]

Many of the headspace volatiles observed are recognized secondary volatile products of lipid oxidation reactions. The high concentration of unsaturated fatty acids in almond lipids makes almonds susceptible to lipid oxidation. The highest proportion of almond lipids is comprised of oleic acid (~80%), which may undergo addition of oxygen at carbon 8, 9, 10, or 11.[41,48] Decomposition of the resulting hydroperoxides leads to volatile products like 1-heptanol, heptanal, heptanoic acid, nonanal, octanal, 1-octanol, and octanoic acid, which were included in the filtered data set. Linoleic acid makes up about 20% of almond lipids, and is a doubly unsaturated fatty acid, rendering it is C11 carbon more susceptible to hydrogen abstraction than the allylic carbons of oleic acid. Decomposition of linoleic acid hydroperoxide leads to several volatiles included in the filtered volatile data set, including hexanoic acid, 2-heptanone, gamma-hexalactone, 2-pentylfuran, 1-pentanol, hexanal, pentanal, 1-octen-3-ol, pentanoic acid, 2-heptenal, and 2-octenal.[41]

**PLS2 Analysis.** PLS2 analysis of the filtered headspace volatile data set was performed to give a visual overview of the relationship between consumer liking, descriptive analysis, and changes in the headspace volatiles (Figure 3). Dimension 1 explains 74% of predictor (volatile peak area) variance and 60% of response (descriptive attribute) variance, while dimension 2 explains 15% of predictor variance and 15% of response variance. Dimension 1 corresponds to increasing sample storage time. Dimension 1 explains a majority of the variance in both data sets, indicating that the effects of time under accelerated storage is responsible for most of the covariance between data sets.

Oxidative and rancidity-related descriptors were most positively correlated with dimension 1 and are associated with samples aged ≥6 months, while "clean" attributes, were associated with the control and 2-month samples, and negatively correlated with dimension 1 (Figure 3). Also negatively correlated with dimension 1 was liking of all consumer groups, of which average liking was almost perfectly correlated with Clean Nutty flavor and oppositely correlated with Total Oxidized flavor (Figure 3).

Dimension 2 somewhat corresponds with variance due to roast level of samples (Figure 3). Clustering of samples D6, L8, and L10 indicates a degree of similarity in these samples. Sensory attributes Total Flavor Intensity and Total Aroma


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**Table 3. Compounds Identified and Quantified in LR and DR Almond Headspace[a]**

| compound group | volatile compound | unknown KI | literature KI[b] (NIST) | quant. ion[c] |
|---|---|---|---|---|
| organic acid | 3-methylbutanoic acid[d] | 1681 | 1680 | 60.1 |
| | **acetic acid[di]** | 1427 | 1429 | 60.1 |
| | butanoic acid[d] | 1639 | 1650 | 60.1 |
| | **heptanoic acid[d]** | 1948 | 1954 | 60.1 |
| | **hexanoic acid[d]** | 1842 | 1849 | 60.1 |
| | nonanoic acid[d] | 2101 | 2144 | 60.1 |
| | **octanoic acid[d]** | 2040 | 2038 | 60.1 |
| | **pentanoic acid[e]** | 1744 | 1725 | 60.1 |
| low mol. wt. alcohol[f] | **3-methyl-1-butanol[d]** | 1212 | 1209 | 55.1 |
| | **1,2-propanediol[e]** | 1592 | 1599 | 45.1 |
| | 2-hydroxypropyl acetate[e] | 1571 | 1579 | 74.1 |
| | 1-butanol[d] | 1140 | 1145 | 56.1 |
| | 2,3-butanediol[d] | 1553 | 1542 | 45.1 |
| | 2-chloro-1-propanol[e] | 1364 | 1376 | 57.1 |
| | **1-chloro-2-propanol[di]** | 1317 | 1314 | 45.1 |
| | 2-methyl-1-propanol[di] | 1086 | 1092 | 84.1 |
| high mol. wt. alcohol[f] | **1-heptanol[d]** | 1442 | 1467 | 70.1 |
| | **1-hexanol[d]** | 1357 | 1355 | 56.1 |
| | 1-nonanol[d] | 1668 | 1661 | 56.1 |
| | **1-octanol[d]** | 1560 | 1553 | 69.1 |
| | **1-octen-3-ol[d]** | 1434 | 1430 | 57.1 |
| | **1-pentanol[d]** | 1261 | 1255 | 55.1 |
| | 2-furanmethanol[di] | 1661 | 1660 | 98.1 |
| | 3-heptanol[e] | 1307 | 1306 | 69.1 |
| low mol. wt. aldehyde[g] | **2-methylbutanal[di]** | 893 | 909 | 57.1 |
| | **2-methylpropanal[di]** | 821 | 819 | 72.1 |
| | **3-methylbutanal[di]** | 897 | 925 | 58.1 |
| | butanal[d] | 860 | 867 | 72.1 |
| high mol. wt. aldehyde[g] | (*E*,*E*)-2,4-decadienal[e] | 1808 | 1807 | 81.1 |
| | (*E*,*E*)-2,4-nonadienal[e] | 1702 | 1701 | 81.1 |
| | (*Z*)-2-decenal[e] | 1645 | 1644 | 70.1 |
| | **(*Z*)-2-heptenal[e]** | 1322 | 1319 | 83.1 |
| | (*E*)-2-hexenal[d] | 1213 | 1204 | 69.1 |
| | (*E*)-2-nonenal[d] | 1527 | 1530 | 83.1 |
| | **(*E*)-2-octenal[d]** | 1412 | 1412 | 70.1 |
| | (*E*)-2-undecenal[e] | 1754 | 1722 | 70.1 |
| | benzaldehyde[d] | 1507 | 1502 | 105 |
| | decanal[d] | 1488 | 1484 | 57.1 |
| | **heptanal[d]** | 1179 | 1174 | 70.1 |
| | **hexanal[di]** | 1074 | 1084 | 57.1 |
| | **nonanal[d]** | 1386 | 1380 | 57.1 |
| | **octanal[d]** | 1293 | 1280 | 84.1 |
| | **pentanal[d]** | 973 | 984 | 58.1 |
| ester | methyl acetate[di] | 829 | 828 | 74.1 |
| | **methyl hexanoate[d]** | 1184 | 1184 | 74.1 |
| low mol. wt. ketone[h] | **1-(acetyloxy)-2-propanone[ei]** | 1442 | 1469 | 74 |
| | **2,3-pentanedione[ei]** | 1051 | 1058 | 100.1 |
| | 2-pentanone[d] | 972 | 981 | 86.1 |
| | **3-hydroxybutan-2-one (acetoin)[di]** | 1283 | 1284 | 45.1 |
| | **acetone[ei]** | 822 | 819 | 58.1 |
| high mol. wt. ketone[h] | 2-decanone[e] | 1482 | 1482 | 58.1 |
| | **2-heptanone[d]** | 1176 | 1170 | 58.1 |
| | 2-nonanone[d] | 1382 | 1387 | 58.1 |
| | 2-octanone[d] | 1289 | 1297 | 58.1 |
| | 3-nonen-2-one[e] | 1501 | 1506 | 125.1 |
| | 3-octen-2-one[e] | 1395 | 1390 | 111.1 |
| alkane | styrene[i] | 1255 | 1261 | 104 |
| | toluene[i] | 1032 | 1042 | 91.1 |
| alkylfuran | 2-propylfuran[e] | 1028 | 1027 | 81.1 |
| | **2-butylfuran[d]** | 1122 | 1123 | 81.1 |
| | **2-pentylfuran[e]** | 1235 | 1231 | 81.1 |
| heterocycle | 2-acetylpyridine[ei] | 1598 | 1597 | 78.1 |
| | 2-acetylpyrrole[d] | 1949 | 1949 | 94.1 |
| | 4-hydroxy-2,5-dimethylfuran-3-one[d] | 1999 | 1997 | 128.1 |
| | **furan-2-carbaldehyde (furfural)[d]** | 1438 | 1455 | 96 |
| | **1-*H*-pyrrole[di]** | 1502 | 1498 | 67.1 |
| lactone | **gamma-hexalactone[e]** | 1698 | 1703 | 85.1 |
| | delta-hexalactone[e] | 1785 | 1770 | 70.1 |
| | gamma-octalactone[e] | 1901 | 1901 | 85.1 |
| | butyrolactone[ei] | 1619 | 1626 | 86.1 |
| | pantolactone[e] | 1998 | 1998 | 71.1 |
| sulfur-containing | **dimethyl disulfide[d]** | 1058 | 1077 | 94.1 |
| | methanethiol[e] | 665 | 692 | 48.1 |
| | 1-methylthio-2-propanone[e] | 1328 | 1293 | 104 |
| | **ethyl 2-(methylthio)-acetate[d]** | 1425 | 1450 | 62.1 |
| | **4-mercapto-4-methyl-2-pentanol[e]** | 1520 | 1535 | 75.1 |
| terpene | 3-carene[e] | 1133 | 1135 | 44 |
| | alpha-pinene[d] | 1019 | 1026 | 93.1 |
| | *o*-cymene[e] | 1271 | 1272 | 119.1 |
| pyrazine | 2-ethyl-6-methylpyrazine[ei] | 1378 | 1382 | 121.1 |
| | 2,3-dimethylpyrazine[ei] | 1332 | 1337 | 108.1 |
| | **2,5-dimethylpyrazine[d]** | 1322 | 1320 | 108.1 |
| | **2,6-dimethylpyrazine[ei]** | 1328 | 1325 | 108.1 |
| | 2-ethenyl-6-methylpyrazine[ei] | 1480 | 1488 | 120.1 |
| | 2-ethyl-3,5-dimethylpyrazine[e] | 1443 | 1444 | 135.1 |
| | 2-ethyl-5-methylpyrazine[e] | 1393 | 1397 | 121.1 |
| | 3-ethyl-2,5-dimethylpyrazine[e] | 1426 | 1430 | 135.1 |
| | 2-ethylpyrazine[ei] | 1332 | 1337 | 107.1 |
| | **2-methylpyrazine[d]** | 1266 | 1267 | 94.1 |
| | pyrazinamide[ei] | 1714 | 1740 | 80.1 |
| | pyrazine[ei] | 1206 | 1204 | 80.1 |
| | **2,3,5-trimethylpyrazine[e]** | 1393 | 1402 | 122.1 |

[a]Names with bold typeface were selected through regularized elimination procedures as particularly important to the prediction of descriptive attributes. All compounds were found to be significantly different with respect to time. [b]KI, Kovat's retention index based on 30m DB-Wax column; literature values obtained from NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/. [c]Quant. ion: extracted ion from total ion scan used for quantitation. [d]Compound identity confirmed with authentic standard. [e]Compound tentatively identified based on its MS fragmentation pattern and similarity of calculated Kovat's retention index with values from literature. [f]Low molecular weight or high molecular weight alcohol, indicating ≤4 carbons in length and >4 carbons in length, respectively. [g]Low molecular weight or high molecular weight aldehyde, indicating



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**Table 3. continued**

≤4 carbons in length and >4 carbons in length, respectively. [h]Low molecular weight or high molecular weight ketone, indicating ≤5 carbons in length and >5 carbons in length, respectively. [i]Compound not found to be significantly different across roast level at $p < 0.05$.

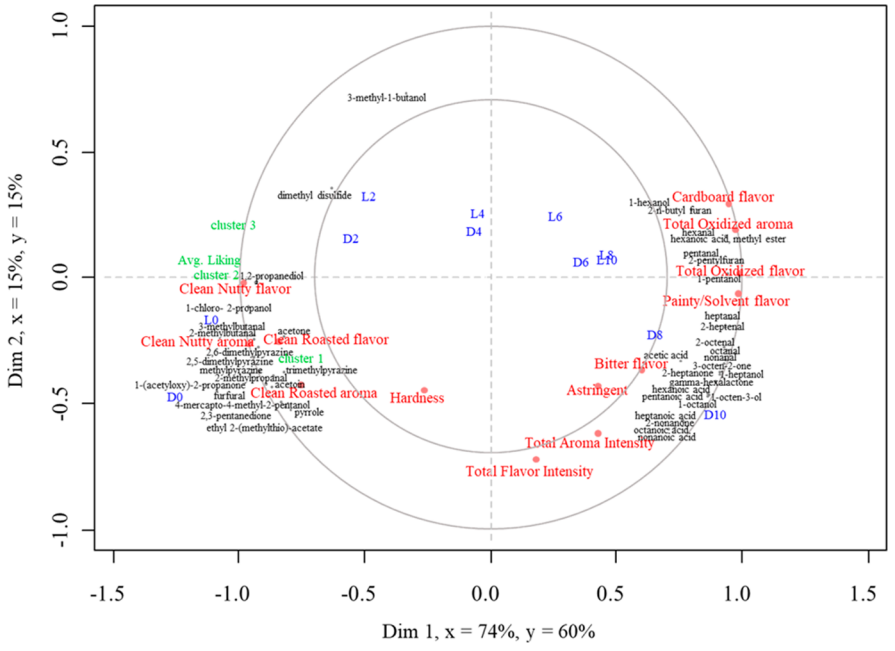


**Figure 3.** continued

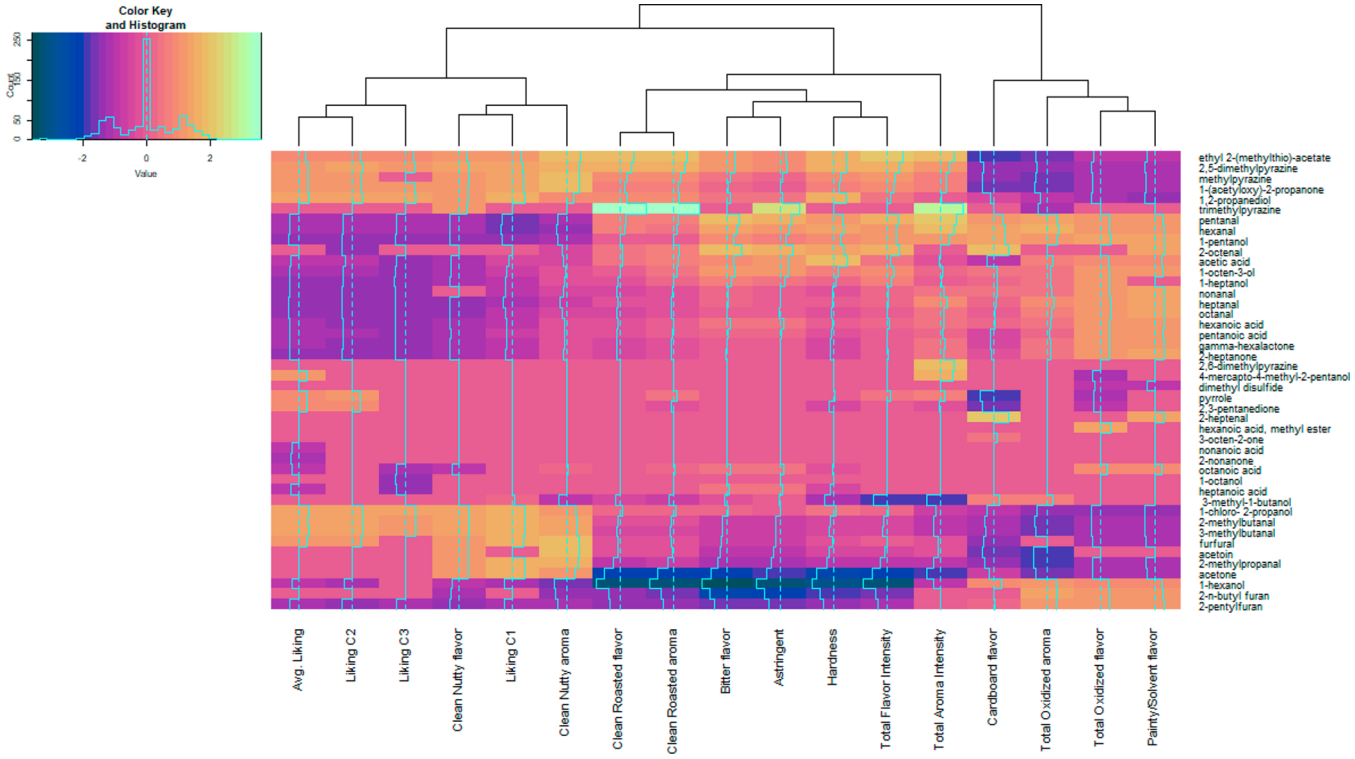


**Figure 4.** Heatmap indicating the relative importance of selected headspace compounds in explaining the variance of descriptive analysis attributes, as indicated by PLS1 model coefficient values (scaled to unit variance within heatmap columns). A value of 0 as indicated by mauve for the intersection of a compound and descriptive attribute means that this compound was not one of the filtered variables selected during variable elimination for this attribute and was therefore not important for predicting the given attribute.



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Intensity best correlate with dimension 2 (Figure 3). Clean Roasted aroma, Hardness, Astringent, and Bitter flavors are similarly correlated with dimension 2, though to a lesser extent, indicating that these attributes along with Total Flavor Intensity and Total Aroma Intensity were important to distinguishing DR samples from LR samples, especially in fresh samples and very oxidized samples (Figure 3).

Headspace volatile compounds separate into two main groups along dimension 1, corresponding to early and late storage times. The majority of compounds negatively correlated with dimension 1 and positively correlated with Clean Nutty and Clean Roasted attributes and consumer liking are compounds typically generated from Maillard reactions, including alkylpyrazines, Strecker aldehydes, acetoin, furfural, and 2,3-pentanedione.[8,9,14] Compounds most positively associated with dimension 1 and Total Oxidized, Cardboard, and Painty/Solvent attributes include volatiles typically generated during lipid oxidation, including 5 to 9-carbon aldehydes and organic acids, 5 to 8-carbon alcohols, 7- and 8-carbon ketones, and 2-pentylfuran.[41]

In addition to Total Flavor and Total Aroma Intensity, dimension 2 correlates most negatively with compounds present in highest amounts either at the beginning or end of the storage period in DR samples (Figure 3). Pyrazines, Strecker aldehydes, and other Maillard products are negatively correlated with both dimensions, similar to sample DR0 and Clean Roasted aroma and Flavor. On the opposite side of the plot, secondary oxidation compounds (e.g., 7-,8-, and 9-carbon aldehydes, alcohols, and ketones) and tertiary oxidation compounds (e.g., 5- to 9-carbon organic acids) are negatively associated with dimension 2 and positively associated with dimension 1, as are DR8 and DR10 samples, Total Aroma Intensity, Astringent and Bitter flavor (Figure 3). The plotted orientation of the aforementioned compounds with respect to dimension 2 and Total Flavor Intensity indicates that this attribute is related to both intensity in roast flavor of fresh DR samples and intensity of oxidation character in DR samples of the latest accelerated storage times.

**PLS1 Regression Coefficients for Individual Descriptors.** PLS1 models involving prediction of each attribute by a selection of the most relevant headspace compound predictors were assessed for PLS regression coefficient values at the minimum number of dimensions needed to substantially reduce the root mean squared error of prediction (RMSEP) of the model using cross validation. The regression coefficient values of the $x$ variables in a PLS1 model give an indication of their relative importance in predicting a $y$ variable and were used in this case to prioritize individual volatile compounds by their predictive importance for each descriptive attribute and identify volatiles potentially responsible for these attributes.[45] The regression coefficients of select headspace volatiles for each descriptive attribute are displayed in Figure 4, where regression values were scaled within each descriptive attribute column by the standard deviation (Figure 4). Values were not centered, however, so that a coefficient value of 0 (mauve in the heatmap, Figure 4) indicates a compound with no predictive importance to an attribute. The dendrogram depicted at the top of the heatmap indicates attributes and consumer clusters most similar to each other based on complete clustering and a Euclidean distance matrix.

The dendrogram identifies three main groups of predicted variables based on similarity in scaled regression coefficient values. These include a group containing all measures of consumer liking and Clean Nutty attributes, a group containing Clean Roasted attributes, Bitter flavor, Astringent, Hardness, Total Flavor Intensity, and Total Aroma Intensity, and a group containing Cardboard flavor, Total Oxidized attributes, and Painty/Solvent flavor (Figure 4). These groups are in good agreement with the plotted locations of descriptive attributes and consumer clusters with respect to dimension 1 in the PLS2 correlation loadings plot (Figure 3).

Clean Nutty flavor and Clean Nutty aroma were best predicted by a similar set of compounds to those best predicting consumer liking. Ethyl 2-(methylthio)-acetate and 2,5-dimethylpyrazine, 2-methylpyrazine, 1-(acetyloxy)-2-propanone, furfural, acetoin, and 2-methylpropanal were especially important to predicting Clean Nutty aroma (with positive coefficients) whereas Clean Nutty flavor was best predicted by 2,5-dimethylpyrazine, 2- and 3-methylbutanal, and 1-chloro-2-propanol, though the aforementioned Maillard products were also important to predicting this attribute. Maillard reaction products 2- and 3-methylbutanal, 2-methylpropanal, and furfural have malty/nutty, fruity/cocoa, fresh/floral, and sweet/almond/bread aromas, respectively (Table 3).[45] Civille et al.[18] identified some of the same aromas (fruity, sweet, nut) as part of a standard descriptive lexicon of almond flavor and therefore these compounds may contribute to the typical flavor of almonds. The close correlation of average consumer liking and liking of cluster 2 with Clean Nutty flavor (Figure 3) reveals a positive perception of these compounds and associated aromas within the almond flavor profile.

Consumer clusters were similar to Clean Nutty attributes in that they had positive predictive coefficients for a variety of Maillard compounds and negative coefficients for a wide variety of lipid oxidation compounds. In the PLS2 model, average consumer liking and liking of cluster 2 were correlated with Clean Nutty flavor (Figure 3), while liking of consumer cluster 1 is better correlated with Clean Nutty aroma and Clean Roasted Attributes.

Liking of cluster 1 (24% consumers) and 2 (55% of consumers) and average liking was generally best predicted by 2,5-dimethylpyrazine, methylpyrazine, 2-methylbutanal, 3-methylbutanal, and furfural, as well as compounds associated with fresh roasted almonds such as 1,2-propanediol, and 1-chloro-2-propanal (Figure 3). However, 1,2-propanediol and 1-chloro-2-propanal are unlikely to play an important role in flavor perception due to the high flavor threshold for small alcohols.[43] Of the above predictors only 2-methylpyrazine, 2,5-dimethylpyrazine, and 2- and 3-methylbutanal were previously observed in almonds at concentrations above sensory threshold (threshold: 0.06 mg/Lin water,[9] 10 and 5.4 $\mu$g/kg[45] respectively).[9,13,14,17,43] Common to best positive predictors of liking for all consumer groups were 2- and 3-methylbutanal and 2,5-dimethylpyrazine (Figure 4), indicating that these compounds may serve well as analytical correlates or indicators of consumer liking.

Important predictors for consumer clusters with negative coefficient values include lipid oxidation products (i.e., pentanal, hexanal, 1-pentanol, acetic acid, 1-octen-3-ol, 1-heptanol, nonanal, heptanal, octanal, hexanoic acid, pentanoic acid, gamma-hexalactone, 2-heptanone, 1-hexanol, and 2-pentylfuran). The importance of these predictors to average liking scores was relatively uniform, though more negative values are given for 1-pentanol, octanal and heptanal than for other volatile predictors (indicated by the value trace line, light blue in Figure 4). These results are in good agreement with


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results of regression analysis between consumer liking and headspace volatile concentration of Franklin et al.,[33] which showed that heptanal, 1-pentanol, and octanal were among the best volatile correlates of consumer liking in roasted Nonpareil almonds.

Clean Roasted aroma and Clean Roasted flavor were set apart from other "clean" attributes by a very high positive coefficient value for trimethylpyrazine, as well as low but positive scaled coefficient values for pentanal, hexanal, 2-octenal, and acetic acid (Figure 4). Other important predictors of these attributes include ethyl 2-(methylthio)-acetate and 2,5-dimethylpyrazine. Trimethylpyrazine is a Maillard reaction product with cocoa/roasted peanut aroma that has been previously identified in heat-treated Butte/Padre,[14] and Nonpareil[43] almonds. The predictive importance to "Clean Roasted" attributes of trimethylpyrazine confirms the importance of alkylpyrazines to the flavor associated with roasting. Ethylpyrazine was reported to convey an "intense roasted" character during GC-olfactometry of peanut samples.[8,14,45] This group also found that intensity of "dark roasted" flavor decreased in peanut samples over 74 days of storage, in conjunction with decreases in the level of methylpyrazine, 2,5-dimethylpyrazine, 2,3-dimethylpyrazine, and 2-ethyl-5-methylpyrazine.[41,44,47]

Bitter flavor, Astringent, Hardness, Total Aroma Intensity, and Total Flavor Intensity are best predicted by a combination of compounds generated by roasting and most associated with fresh samples and lipid oxidation secondary volatiles, associated with samples of longer storage periods. These attributes also did not reflect the scaled coefficient patterns of any consumer cluster and indicates that flavor intensity was not as important as Clean Nutty attributes in consumer liking of almonds.

The last grouping of attributes includes Cardboard Flavor, Total Oxidized attributes, and Painty/Solvent Flavor. These attributes are well-predicted (with positive coefficients) by hexanal, pentanal, and 1-pentanol, as well as (with negative coefficients) by most of the compounds related to Maillard reactions and fresh samples. Painty/Solvent Flavor and Total Oxidized Flavor are the most similar based on scaled coefficient values (Figure 4).

Cardboard flavor is uniquely well-predicted by the unsaturated aldehydes 2-octenal and 2-heptenal. Previous studies on the source of cardboard off-flavor in peanuts[21] and whey protein isolate[38] have implicated a number of lipid oxidation products. Whitson, Miracle, and Drake[38] reported that pentanal and heptanal can each have a cardboard-like aroma, though a mixture of pentanal, heptanal, nonanal, 1-octene-3-one, and dimethyl trisulfide produced the most similar aroma to the real cardboard reference.

Total Oxidized aroma is best predicted by hexanal, pentanal,1-pentanol, 1-hexanol, 2-butylfuran, 2-pentylfuran, and heptanal. Total Oxidized flavor was best predicted by a wide variety of lipid oxidation compounds, with slightly more importance given for 1-pentanol and hexanoic acid. Hexanal is frequently identified in oxidized almonds and other foods and has a grassy, pungent, fatty aroma.[41,45] Hexanal was determined to be one of the most intense aroma compounds formed during oxidation of linoleic acid.[47] The peak area of hexanal exceeded that of all other headspace compounds in samples stored for 4 or more months (Tables S3 and S4 in the Supporting Information) and may have therefore been the principle compound responsible for Total Oxidized aroma. Pentylfuran is formed by oxidation of linoleic acid and can lend a beany, grassy, or rancid note to oil at concentrations of 5−20 ppm.[49] Lipid oxidation products 1-pentanol and 1-hexanol can have a fermented and grassy aroma, respectively, while hexanoic acid is often characterized by a sweaty or goat aroma (Table 3).

Painty/Solvent flavor was best predicted by saturated and unsaturated aldehydes (i.e., 2-octenal, nonanal, heptanal, octanal, and 2-heptenal). Saturated aldehydes are implicated in creating the "painty" flavor frequently perceived in products undergoing oxidative rancidity.[50] Lloyd et al.[50] reported identifying a good correlation between heptanal ($r$ = 0.95), nonanal ($r$ = 0.95), and octanal ($r$ = 0.87) and "painty" flavor in whole milk powder stored for up to a year at room temperature.

The purpose of this study was to highlight volatile compounds potentially responsible for specific attributes and consumer liking of almonds undergoing accelerated storage. Such volatiles could serve as chemical indicators of oxidative flavor changes and consumer acceptance in roasted and stored almonds. A number of volatile predictors of consumer liking were identified, including 2,5-dimethylpyrazine and 2- and 3-methylbutanal, which were predictors of "Clean Nutty" and "Clean Roasted" attributes. Additionally, a number of volatile correlates of rancid flavor attributes were identified, which may be used to indicate rancidity in roasted almonds, including hexanal, pentanal, 1-pentanol, 2-heptenal, 2-octenal, heptanal, octanal, nonanal, 2-heptanone, and 2-pentylfuran. Though hexanal had the most abundant peak area in almonds stored longer than four months and was the most important predictor of Total Oxidized aroma, heptanal and octanal were better predictors of average consumer liking and may be more reliable indicators of consumer perception of rancidity in roasted almonds. Further study involving addition or omission experiments are needed to form causative relationships between compounds and perceived flavors and acceptance.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.7b05295.

Table 1S, references and definitions of attributes used for training judges in descriptive analysis testing; Table 2S, mean intensity of descriptive attributes for LR and DR almond samples stored for 0 (control), 2, 4, 6, 8, and 10 months; Table 3S, peak area of all headspace compounds tentatively identified or confirmed with standards in DR almond headspace, sampled after 0−10 months of accelerated storage; Table 4S, peak area of all headspace compounds tentatively identified or confirmed with standards in LR almond headspace, sampled after 0−10 months of accelerated storage (PDF)

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